CEN's major programs up until the FCF began its operation in the 1960s. Other CEN work included a large glove-box installation to purify molten chloride salts for use in pyrometallurgical fuel reprocessing research and development (Fig. 2-7).

Herb Brown recalls that in the early years of Bldg. D-310 operation "the fan loft contained a large, high-horsepower, very noisy lobe blower that could be heard at a great distance from the building. Dr. Lawroski let it be known that as he arrived at Bldg. D-205 he could hear the blower running at Bldg. D-310. It was mutually agreed by all CEN people in 310 that the first one to arrive in the morning had it as his sworn duty to start the blower."

Over the years, the nature of the CEN programs changed in such a way that its occupancy of Bldg. D-310 diminished to the point where it became impractical for the Division to retain the primary responsibility for the building. It is now under the jurisdiction of the Reactor Engineering Division (RE). However, some CMT work is being done there, mainly on equipment development and testing in support of the ANL-W program on the electrochemical processing of EBR-II fuel.

DIVISION ORGANIZATION AND MANAGEMENT

The management style in CEN could probably be best described as basically corporate in nature with something of an academic flavor. Dr. Lawroski was a strong leader and was demanding of the Division personnel. At the same time, he had a good sense of humor and took good care of his employees. He insisted that the staff personnel continue to further their technical knowledge. As an example, when a division seminar was in progress, Vic Munnecke, the Assistant Director, would roam through the building and closely quiz anyone in his office or lab as to why he wasn't at the seminar. Most of the seminars were

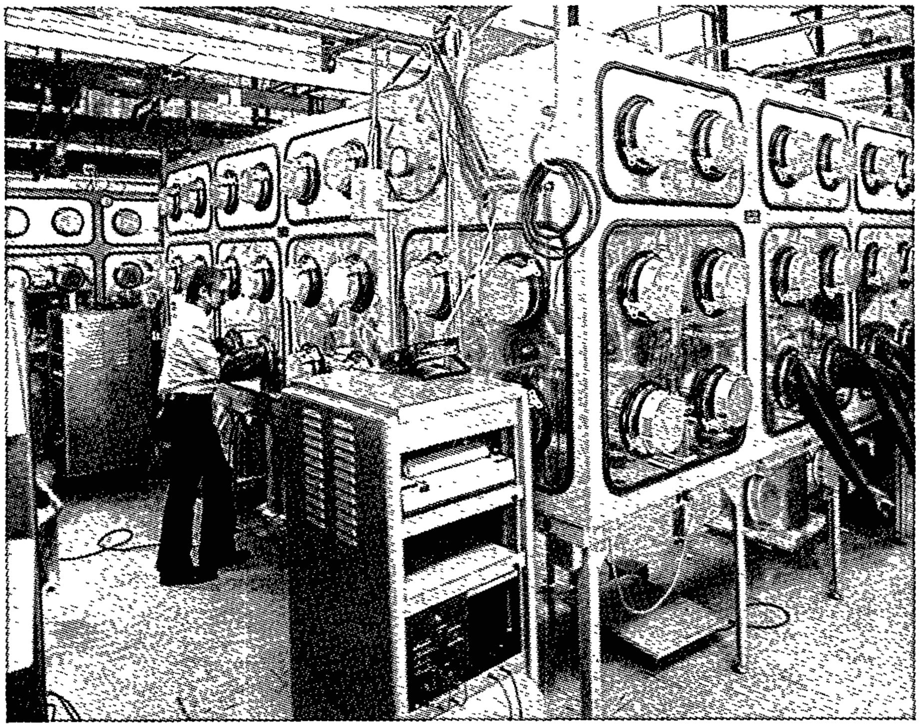


Fig. 2-7. Pyrochemical Facility in Building 310

given by staff members on their own work, and they were often challenged by one or two people in the audience who had made it a point to read up on the subject in advance and came in "loaded for bear." Hal Feder, in particular, often claimed that the speaker had overlooked some pertinent information that was in the literature, but he could never remember just where. After the initial irritation had worn off, this probably had a beneficial effect in causing the speaker to comb the literature on his subject more thoroughly.

The secretarial staff and the technicians were paid on an hourly basis and had to punch a time clock. (At one time, some people were playing "paycheck poker" games, which were based on the serial numbers of their checks; this was not encouraged by the Laboratory.) The technical staff were paid monthly and were not clocked, so a few began to trickle in a bit late in the morning. Dr. Lawroski solved this problem effectively by standing in the lobby in the morning and looking alternately at each late arrival and his wrist watch. He didn't have to say anything; they got the message. He also had an interesting habit of addressing individuals directly as "Mac," "Pal," or "Chum" when he was not pleased about something. There was some uncertainty as to just what these terms meant, which added to their effectiveness, but there seemed to be general agreement that "Chum" was the most ominous. When Dr. Lawroski was visiting a laboratory or was at a meeting and asked a question, the "askee" would have been well-advised to give the best straight answer he could. Any bluffing or double-talk was sure to result in further questions until he was in a very deep hole.

Dr. Lawroski made it a point to acquaint his more senior staff people with visitors and important people at meetings. This was beneficial to CEN's relationships with the AEC and other organizations. The AEC at that time seemed to trust the Laboratory management to handle the technical programs, and there was little or no micromanagement. The "189s" (budget justifications to the AEC) were simple one- or two-page documents which were all written by Vic Munnecke, the Assistant Division Director. Monitoring of the individual programs by the AEC generally consisted of a man from AEC Headquarters dropping in once a year or so for an informal chat and asking how things were going. One had more of a sense of support than any kind of a threat.

Early in the 1950s, the University of Chicago began holding annual reviews of the Division's performance during the preceding year. The people selected for these committees were well-known, highly regarded individuals from industry, academia, and other national laboratories, and included Henry Taube, who became a Nobel Laureate. Over the years these reviews have been generally commendatory and supportive of the Division's management and staff. There have been instances, however, where the recommendations of the Review Committees and the mandates of the AEC (or DOE) have been at odds, usually over the amount of basic research the Division should do in support of the applied programs. The annual Review Committee visits continue to require a lot of work in preparing the handouts of the slides and conducting dry runs of the talks, all of which leads to a last-minute mild state of panic both for the technical staff and the secretaries. A social evening during the review process has proved especially beneficial in allowing the Division staff members to talk with the Review Committee members on an individual basis. Poster sessions have also been used for the same purpose.

Group meetings and reports were weekly and Division meetings were held monthly on Friday afternoons in the early 1950s. With the lack of air conditioning, it was not unusual on a warm summer day to see somebody drop off to sleep during a Division seminar or meeting and suddenly "break his neck" waking up. Walt Rodger always wore dark glasses. Over the years, the group meetings became semimonthly, and then finally monthly, as they are now.

Individual secretaries were provided for the upper management and administrative personnel. Most of the secretaries were assigned to a section head and functioned as a "den mother," doing the typing and other work for all the people in that section. New arrivals in the Division soon learned who the upper management people were because they were always paged with the title "Dr." or "Mr." while the first and last names were used for everyone else.

When the Division moved to the DuPage site, Dr. Lawroski was the Division Director, Charlie Stevenson was the Associate Director, and Vic Munnecke was the Assistant Director. Walt Rodger was in charge of the engineering programs and Richard Vogel had the chemistry work. In 1954, Charlie departed to become the Technical Director of the Idaho Chemical Processing Plant (ICPP), at which time Rodger and Vogel became Associate Division Directors. In July 1958, Octave J. DuTemple, a chemical engineer in CEN, left the Division to become the Executive Director of the American Nuclear Society (ANS), which had about 3,000 members at the time. The society, which was formed in 1955 with Walter Zinn as President, had just moved from Oak Ridge to the John Crerar library in Chicago, and later established its current headquarters in LaGrange Park, Illinois.

Fig. 2-8. Walton Rodger

Dr. Rollin Taecker, a professor of Chemical Engineering from Kansas State University, took a sabbatical leave in 1953 working in CEN, and then returned to Argonne in 1955 to become the director of the International School of Nuclear Engineering (ISNE). The school, which opened on March 14, 1955, was an ANL organization fostered by the AEC to further the Eisenhower Atoms for Peace program, and it was headed up initially by Dr. Norman Hilberry. Its mission was to provide, in cooperation with universities, technical training in nuclear engineering for foreign and some American engineers and scientists. Several CEN staff personnel participated in the activities of the school by presenting lectures or seminars.

Among the temporary employees from academia, Dr. Joel Hildebrand, a Professor Emeritus from the University of California at Berkeley, who spent two months with CEN in 1953, was probably the most prestigious and also the most interesting. Although not a Nobel Prize winner, Professor Hildebrand received almost every other prize a chemist could. He liked to refer to Bob Steunenberg and others who had done their thesis work under his students as his "academic grandsons." One of the buildings at the University of California campus in Berkeley is named in honor of Hildebrand.

On February 20, 1957, Dr. Hilberry became the Laboratory Director, succeeding Dr. Zinn, who then became a vice president at Combustion Engineering, Inc. Hilberry was the person at the original test of CP-1 who had the assignment of standing on top of the pile with an axe to cut a rope suspending a "scram" safety rod that would drop into the assembly in case something went wrong. He was a highly competent scientist with a "down-home," easygoing manner and an impish sense of humor. One of his comments was that perhaps ANL should buy the Chicago Bears so as to gain full academic status. If you were at lunch at the cafeteria, he was likely to sit down and join your group for some conversation whether he knew you or not.

Dr. Lawroski's accomplishments and leadership received special recognition in 1959, when he was appointed Coordinator of Engineering Research and Development Programs at ANL. One important part of this position was to serve as Chairman of Argonne's Reactor Engineering Division Steering Committee. During the 1950s, he held many other positions of responsibility, both at ANL and nationally. He served on the ANL Scientific Personnel Committee, occupying the position of chairman for several years. He was a member of the Visiting Committee for the Nuclear Engineering Department and Reactor Division of Brookhaven National Laboratory. He was also Chairman of the American Standards Association Committee N5 and represented the Association Committee at the 1959 meeting of the International Organization for Standardization in Warsaw, Poland. He was a member of U.S. Fast Reactor Teams during which time he visited nuclear sites in the United Kingdom and in Europe. In 1956-57, he was Chairman of the Nuclear Technology Subdivision of the Industrial and Engineering Chemistry Division of the American Chemical Society. In the American Nuclear Society he served on the Board of Directors for a three-year term, was a member of the Executive Committee in 1958-59, and was Chairman of the Planning and Coordinating Committee during 1960-61. He also served on the Admissions Committee of the ANS. He was a member of the General Advisory Committee (GAC) for the AEC, and served later on the NRC Advisory Committee for Reactor Safeguards. After leaving the Division, Dr. Lawroski continued to garner many additional awards, and he was elected to the National Academy of Engineering in 1969.

Dr. Lawroski's brother, Harry, also a prominent figure in the nuclear business, was President of the American Nuclear Society in 1980-1981.

TECHNICAL PROGRAMS

Aqueous Processes

DETERMINATION OF BREEDING GAIN IN EBR-I

EBR-I, the first fast breeder reactor in the world, was built to demonstrate the feasibility of fast breeder reactors and the potential of the breeding concept. The CEN Division was concerned with two parts of the EBR-I program: first, the development of a chemical process for recovering enriched uranium from the reactor core; second, a determination of the conversion ratio (plutonium generated/U-235 consumed) of the reactor.

In giving ANL permission to design and construct EBR-I, the AEC stipulated that the enriched uranium in the core, which had been borrowed from the military stock, would have to be returned completely free of fission products and at a specific time. Development of a process to recover and decontaminate the enriched uranium in the EBR-I core began in 1949 in the West Stands at the University of Chicago and required about 60 man-years of effort. The result was a solvent-extraction process utilizing tributyl phosphate (TBP) diluted with carbon tetrachloride as the organic solvent. The process was then installed inside one of the 8- × 10-foot cells shielded by 18 inches of high-density concrete in Bldg. 205. A 40-foot-high, 1-in.-dia stainless steel column was used for the extraction-scrubbing step and a similar 35-foot-high column for uranium stripping. This plant was to have been ready for operation by the end of summer in 1951, but a decision was made by the AEC that the EBR-I core, other than samples removed for the work described below, would be reprocessed at the Idaho Chemical Processing Plant (ICPP).

The objective was to determine the conversion ratio (fissile material produced/ fissile material consumed) in the reactor. If the ratio is greater than unity, breeding has occurred and the difference is the "breeding gain." Samples of the core fuel rods and the blanket rods were selected in a manner that would allow calculations of the average core burnup and the plutonium content of the blanket. The samples were dissolved in nitric acid for analysis. Eighty-five core samples and 35 blanket samples were analyzed.

The U-235 burnup in the core samples was based on analyses of the dissolver solutions for cesium, whose fission yield had been well established. The dissolved blanket samples were analyzed for plutonium. Because some U-238 is fissioned at high neutron energies, a method was developed in cooperation with the Chemistry Division to distinguish between U-238 and U-235 fission by measuring the Ru-106/Cs-137 ratio.

The conversion ratio for this first core loading of EBR-I was found to be 1.00±0.04 atoms of plutonium for each atom of U-235 consumed, which is equivalent to a breeding gain of 0±0.04. This result showed clearly that plutonium breeding had reached the break-even point in EBR-I and that a significant breeding gain should be achievable with more advanced reactor designs and with plutonium as the fissile material.

Les Burris was the project leader for the process development work, and others who were involved in the engineering development included John Schraidt, John Natale, John Loeding, Virgil Trice, Ira Dillon, Norm Levitz, Les Coleman, Herb Brown, Don Hampson, Sy Vogler, and Bill Voss (from Central Shops). Milt Levenson was in charge of the design and start-up of the facility and made the calculations required to determine the conversion ratio. Wally Seefeldt directed the operations, which were carried out by Les Dorsey, Artie Freeman, and Bill Spicer. An enormous analytical effort on this project was carried out under the direction of Dick Vogel; some of the individuals contributing to this effort were Carl Crouthamel, Bob Schablaske, Chuck Seils, Myron Homa, and Jackie Williams. Tony Engelkemeier and Arthur Jaffey from the Chemistry Division, Ted Novey from High Energy Physics, and Dave Hess from Physics also participated in the program.

THE HALEX PROCESS

Because of the Cold War with the Soviet Union and the resultant arms race, the U.S. moved expeditiously in the late 1940s and early 1950s to expand its capabilities for the production of weapons-grade plutonium for nuclear weapons and tritium for thermonuclear weapons (the hydrogen bomb). To augment existing production capabilities at Hanford, the U.S. authorized construction of the Savannah River Plant (SRP) in South Carolina. Located within the large plant area were the production reactors, two large solvent-extraction plants for recovery and purification of uranium and plutonium, facilities for the recovery of deuterium and tritium, and research and development laboratories. E. I. du Pont de Nemours and Company operated the plant.

During construction of the plant, Du Pont operating personnel were assigned to various national laboratories for training. About 50 Du Pont trainees spent up to three years in the various divisions at ANL—in Chemical Engineering for solvent-extraction technology, in Reactor Engineering for reactor design and operation, in Chemistry for studies of organic solvents, and in Metallurgy for metallurgical studies of fuel fabrication and behavior in a reactor.

The Purex process, which uses tributyl phosphate (TBP) diluted with dodecane, was chosen for the uranium/plutonium recovery process. This process had been discovered in 1949 at Oak Ridge National Laboratory (ORNL). Early work on it was also conducted at the Knolls Atomic Power Laboratory (KAPL) in Schenectady, New York. It was subsequently installed in the processing plants at Hanford and Savannah River.

In the early stages of Purex process development, Du Pont became concerned about potential flammability of the dodecane solvent and sought a nonflammable alternative. Carbon tetrachloride was eventually selected, and the ANL Chemical Engineering Division was assigned the responsibility for demonstrating the Purex process, using carbon tetrachloride as the diluent. To distinguish this process from Purex, it was named "Halex."

Although carbon tetrachloride is not flammable, it raised other concerns. One was the extent of its radiolytic decomposition in high radiation fields to yield chloride ions. At concentrations above about 10 ppm, chloride embrittlement of stainless steel can occur. Another concern was the chemical toxicity of carbon tetrachloride, which requires precautions to prevent inhalation of vapors by workers. In the ANL studies, a thin (approximately 1-inch-thick) layer of water on top of the solvent in the feed tanks was used to limit vaporization of the carbon tetrachloride. The feed tanks were also vented to the Bldg. D-205 vent system. Finally, although not a concern, the high specific gravity of carbon tetrachloride (about 1.4) made the solvent the "heavy" phase, which is just the reverse of the situation in the Purex process where the organic solvent is the "light" phase. These concerns and the changes in the physical properties of the solvent warranted a pilot-plant demonstration under representative plant conditions.

To demonstrate the Halex process, a pilot-plant facility was installed behind 18-inch-thick concrete shielding walls in two adjacent 12-foot-high bays in the Bldg. D-205 G-Corridor (G-102 and G-118). The first cycle (IA) contactor banks were installed in G-118. A single set of extraction and stripping contactors was used alternately in G-102 for the second uranium and plutonium purification cycles. Fully irradiated Hanford fuel slugs were dissolved in one of the three dissolvers in J-117 to give a typical uranium feed solution.

Banks of mixer-settlers obtained from the Standard Oil Development Company were used as the contactors. These simulated the pump-mix mixer-settlers that had been selected by Du Pont for use at Savannah River, but they lacked the capability to pump the immiscible aqueous and organic solvent phases to the next stage. Therefore, each bank was tilted about 15 degrees to provide gravity flow of the immiscible fluids through the bank. The Standard Oil Development contactors were either 15- or 20-stage units, the former being used for the stripping operation and the latter for extraction-scrubbing and uranium-plutonium separation.

Many runs were made in the G-102/G-118 complex. The Halex process performed very well. Fission-product decontamination factors were equal to, if not higher, than those achieved with the Purex process. Complete separation of the uranium and plutonium was obtained in the IB unit, and high recoveries (>99%) of uranium and plutonium were achieved. The carbon tetrachloride proved to be highly resistant to radiolytic decomposition. Chloride ion concentrations in the high-level waste were 10 ppm or less. Despite the successful demonstration of the Halex process, Du Pont decided to go with the conventional Purex process, having become convinced that dodecane posed no significant fire hazard after all. Interestingly, carbon tetrachloride was used for many years at Hanford in the Recuplex process for recovering plutonium from scrap and recycle material.

Les Burris was the Project Leader for the Halex process demonstration. Major responsibilities for the design of the facility and its subsequent operation were borne by

John Loeding and Virgil Trice. The other participants in the program were mostly the same ones who had worked on the breeding gain effort. Again, much of the credit for the success of the Halex demonstration is due to the Analytical Chemistry Group, who, during the course of the program, analyzed the hundreds of samples required to evaluate the process performance.

AQUEOUS PROCESSING OF ALLOY FUELS

Several uranium alloy fuels for specialized reactor applications began to appear in the early 1950s. These were generally combinations of enriched uranium alloyed and/or clad with metals such as zirconium (or Zircaloy), aluminum or stainless steel, and they could not be dissolved readily by nitric acid, which was the standard procedure for metallic uranium fuel slugs. These fuels usually consisted of a small amount of highly enriched uranium in the other metal. Plutonium was not involved because the limited amount available at the time was needed for weapons.

Research and development work on the uranium-aluminum fuel resulted in a process in which mercury was used as a catalyst to dissolve the fuel in nitric acid. The zirconium-alloy fuels were more of a challenge, and this was addressed by CEN in a research effort that extended from about 1949 to 1954. This program was aimed at the fuels used in the Submarine Thermal Reactor (STR), which were of two types. One was 99.39% zirconium and 0.61% uranium; the other, in which Zircaloy was alloyed with the uranium, was 97.9% zirconium, 1.46% tin, and 0.64% uranium. Vic Munnecke and Elton Turk did the early work in this area in CEN. A general problem with nitric-acid based dissolutions was that explosions occurred under some conditions. An expanded effort was undertaken in which it was shown that the explosions could be avoided by the use of fluorides to complex the zirconium ions. Bob Larsen, Al Jonke, Harold Evans, Roberta Shor, Sy Vogler, and Elton Turk conducted these studies. Turk later transferred to the ICPP. The CEN work on processing methods for zirconium-alloy fuels was a major contribution to the technology, and it was used as the basis for scale-up studies, followed by plant-scale operation at ICPP, where it was used many years for the recovery of enriched uranium from naval fuels.

CONTACTOR DEVELOPMENT

In the late 1940s and early 1950s, the search for more selective solvents for recovery and purification of uranium was accompanied by increased efforts on the development of more efficient contactors. A major driving force was a need to reduce the height of the processing canyons, which had thick walls of concrete shielding, and their cost was essentially proportional to the height. More efficient low-height contactors became even more important when it was found that the height of an equivalent theoretical stage (HETS) was greater in the Purex process than in the Redox process, which required 40-ft-high towers packed with Raschig rings. The prospect of using 50-ft-high towers (or columns) for the Purex process was not appealing.

Hanford's solution was to use pulsed sieve-plate columns. On each pulse, the solvent (discontinuous) phase was driven through the next of an array of sieve plates, breaking the solvent into fine bubbles, and thereby increasing the surface area for mass transfer of uranium and plutonium. The pulsed columns worked very well and were used in the Hanford plant until it was shut down.

The people at Savannah River chose to use banks of mixer-settlers. Each stage in a bank consisted of a mixing region in which the two phases were vigorously agitated together and a settling region where they disengaged into two layers. The mixers provided sufficient pumping action to move the two immiscible phases into the next stage. As a result, a mixer-settler bank could be operated in a horizontal position, thereby reducing the required canyon height. Mixer-settlers have been in successful operation at Savannah River for over 30 years.

The small mixer-settler units used by CEN to demonstrate the Halex process were a close replica of the Savannah River units, but they were tilted slightly to induce gravity flow of the immiscible liquids through each bank. Argonne also built and demonstrated the Stacked Plate Contactor, a high-throughput contactor that had been designed by Merrill Fenske of Pennsylvania State University. Kegham Varteressian ("Varty") and George Bernstein conducted the ANL demonstration. A contactor had already been selected for the Savannah River plant, so further development of the Stacked Plate Contactor was not pursued.

One drawback of mixer-settlers is the large holdup of solvents in each stage. The long exposure of the solvent to the highly radioactive aqueous phase maximizes the opportunity for radiation damage to the solvent. This concern eventually led to the development of a centrifugal contactor capable of high throughput and low solvent hold-up, which was pioneered at Savannah River. The Savannah River work provided a basis for later intensive development work on centrifugal contactors at Argonne for application to high-burnup fast breeder reactor fuels.

Pyrometallurgical Processes

PYROMETALLURGICAL RESEARCH

By 1950, a strong interest had developed in the possible use of pyrometallurgical methods for reprocessing reactor fuels. Their potential advantages of compactness, simplicity, fewer criticality problems, and potentially low cost are discussed in the following section on process development. Exploratory and basic studies of pyrometallurgical separations were performed primarily in Hal Feder's group, which also had the responsibility for some other projects. The pyrometallurgical investigations at ANL were targeted almost entirely toward EBR-II and were therefore concerned mainly with recovery of enriched uranium metal from the core, where plutonium was of secondary interest, and recovery of plutonium from the metallic uranium blanket, which was a longer-range concern.

Feder, because of his excellent background in the nuclear area, knowledge of the pertinent literature, and understanding of thermodynamics and other theoretical principles, was a highly effective leader in this effort. (An area of special experience that he admits to, but never advertised widely, resulted from a stint in the Army where he was doing research on the use of banana peels as a lubricant for the ways used in launching ships.) A review article he wrote in the *Reactor Handbook* classifies pyrometallurgical separations into the following categories:

1. Fractional crystallization, with and without a liquid metal solvent
2. Fractional distillation
3. Liquid metal partition
4. Selective oxidation
5. Cyclic oxidation-reduction

Argonne was one of the leading laboratories in pyrometallurgical research at the time, but similar work was being done at several other sites, including Ames Laboratory, Atomics International, Brookhaven, the Canadian Atomic Energy Authority, Harwell in England, Los Alamos, and Oak Ridge. Los Alamos probably had the most comprehensive effort for two reasons, one being that their weapons production program used pyrometallurgical methods. The other reason was that they had been developing the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE), a reactor concept that utilized a molten Pu-9.5 at.% Fe alloy as the fuel. Among the methods that Los Alamos investigated for plutonium purification were liquation and filtration, oxide drossing, carbide slagging, halide slagging, halide conversion cycles, electrorefining, recrystallization from mercury, and liquid-liquid metal extraction. Brookhaven had proposed a liquid metal fuel reactor (LMFR) in which the fuel was molten bismuth containing 0.1-0.2% uranium, 250 ppm zirconium, and 350 ppm magnesium. The ternary eutectic salt 50 $MgCl_2$-30 NaCl-20 KCl (mol %) with a melting temperature of 376°C was used to extract fission products from the molten metal fuel. This salt composition was used in much of the work at ANL where it was referred to informally as "Brookhaven salt," much to the annoyance of Dr. Vogel. Oak Ridge conceived the Hermex process, in which metallic uranium was decontaminated by selective precipitation from mercury. Some of the other laboratories investigated potential fuel-reprocessing methods for thorium, as well as uranium and plutonium. Feder kept well abreast of these other programs and stayed in close touch with those doing the work. Because of the reputation he had developed in this field through these connections and his own program at ANL, he was often sought out as an authority to write review articles on the subject.

Members of Feder's group who were involved with the pyrometallurgical work in the early 1950s included Milt Ader, Karl Anderson, Paul Bergland, Norm Chellew, Guy Elliott, Don Fredrickson, Al Glassner, Irv Johnson, Al Martin, Marcel Nathans, Ralph Nuttall, Ken Rhode, Charlie Rosen, Ronald Uhle, Sy Vogler, Charlie Wach, and Bob Yonco. Jim Knighton, who was on loan from the American Smelting and Refining Company (ASARCO), later became an ANL staff member. Don Hampson and George Bennett contributed to the engineering aspects of this effort.

The earliest ANL studies were conducted on melt refining. Previous work had shown that many of the fission products can be removed from irradiated metallic uranium fuel simply by melting the fuel in an oxide ceramic crucible and holding it in the molten state for a few hours. The noble gases (Xe and Kr) and other volatile fission products were released or vaporized and the electropositive fission-product elements such as the rare earths and alkaline earths reacted with the crucible material to form non-volatile oxides. The noble metal fission products (Zr, Nb, Mo, Tc, Ru, Rh, Pd) remained in the molten uranium. Plutonium recovery was not a major concern in the recovery of EBR-II driver fuel, but some preliminary experiments showed that the plutonium/uranium ratio in the oxide product was about twice that in the metal phase. The following crucible materials were studied: alumina (Al_2O_3), magnesia (MgO), beryllia (BeO), thoria (ThO_2), and zirconia (ZrO_2). Both alumina and magnesia reacted stoichiometrically with the reactive fission-product metals (for example, $2\ Ce + Al_2O_3 \rightarrow Ce_2O_3 + 2\ Al$), and the reaction proceeded at a constant rate. The aluminum metal product from the reaction dissolved in the liquid uranium. With a magnesia crucible, metallic magnesium was vaporized. Beryllia, thoria, and zirconia, however, reacted to form suboxides in the crucible wall (identified by x-ray diffraction), and the rate increased with time. Little or no fission-product iodine was released. The molten uranium wet none of the crucible materials except Al_2O_3, which was wet only if the uranium contained dissolved molybdenum and ruthenium. The molten uranium in the various crucibles had a contact angle of 135° and its surface tension was 800 dyn/cm. Contamination of the uranium product by the crucible materials was in the order Al>Be>Th>Zr. Zirconia was chosen as the best crucible material for melt refining, and thermal shock problems were eliminated by stabilizing it with 5 wt% calcia (CaO).

Attention was given to possible methods for recovering bred plutonium from the EBR-II blanket material, using liquid magnesium as an extractant. Ralph Nuttall found that a surprisingly high plutonium recovery could be obtained by agitating hydrided-dehydrided U-1 wt% Pu in liquid magnesium. Some initial studies were conducted on the extraction of plutonium from molten uranium into a molten chloride salt (halide slagging).

The most extensive, systematic studies by this group in the 1950s were on the chemistry of liquid metal solvents, which had potential application both for EBR-II blanket processing and for the recovery of fuel values from melt refining residues. Solubilities of U, Pu, Th, and most of the important fission-product elements in liquid zinc were determined. Similar studies were done with liquid cadmium. Through a combination of temperature coefficients of solubilities, identifications of equilibrium solid phases, electrochemical and effusion measurements, coprecipitation experiments, and phase-diagram definitions, a large body of high-quality thermochemical data was generated. This work, which continued into the 1960s, was essential for much of CEN's ongoing pyrochemical process development work. In addition, it was a major contribution to the literature on the chemistry of liquid metals.

PYROMETALLURGICAL PROCESS DEVELOPMENT

Engineering development of pyrometallurgical processes for recovery of spent fuel discharged from fast breeder reactors was undertaken in the mid-1950s to meet the special needs of fast breeder reactor fuel cycles. These reactors, which use plutonium as a fuel, generate more plutonium than is consumed. As mentioned before, the amount of excess plutonium generated per cycle is called the "breeding gain." The doubling time is the time required to double the amount of fuel in the fuel cycle (that in the reactor plus that out of the reactor in storage, processing, and refabrication of fuel for return to the reactor). Minimizing the fuel in the out-of-reactor fuel-cycle operations reduces the doubling time needed to start a new reactor.

Metal fuels (uranium-plutonium alloys) provide the greatest breeding gain compared with other potential fast reactor fuels such as mixed uranium-plutonium carbides, nitrides, and oxides. Because of the successful experience with metal fuels in plutonium-production reactors and the developed technology for producing and fabricating uranium metal, metal fuels were the natural choice by ANL in its early development of fast breeder reactors.

For discharged fast breeder reactor fuels, solvent-extraction processes such as Redox and Purex were not attractive. These fuels required long storage (cooling) times of about two years before processing by solvent extraction to avoid excessive solvent degradation (radiation damage), which results in less effective decontamination of the uranium and plutonium products. Moreover, the complexity of the tail-end operations required to convert the uranium and plutonium in the dilute nitric acid product of the solvent-extraction process back to the metals increased the out-of-reactor plutonium inventory and the cost of the fuel cycle.

Another important factor in the design of processes for fast breeder reactor fuels is that high decontamination of the processed fuel is not required. The performance of fast reactors is affected very little by the presence of impurities, *e.g.*, residual fission products or alloying elements, in the fuel. In contrast, the performance of a slow (thermal) neutron reactor, *i.e.*, a light-water-cooled reactor, is seriously impaired by the presence of certain impurity elements in the fuel. Therefore, fuel-recovery processes for these reactors must provide very high fission-product decontamination.

While low decontamination is acceptable for the processing of discharged fast breeder reactor fuels, some removal of every fission product must be achieved to avoid unrestrained buildup of any individual fission-product elements as the fuel is recycled repeatedly. Low decontamination of processed fast reactor fuel is actually advantageous for another reason. The intrinsic high radiation levels in the processed fuel strongly discourage its clandestine diversion to weapons production or terroristic purposes.

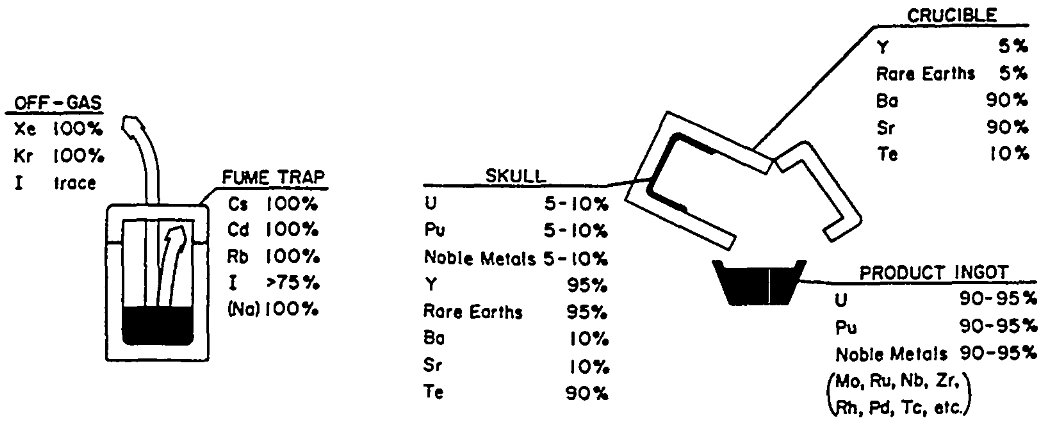
Pyrometallurgical processes appeared to be well suited to fast reactor fuels. Because organic materials are absent, they could accommodate the high radiation levels of short-cooled fuels. In addition, they offered the opportunity to avoid cumbersome product-conversion steps by keeping the fuel in the metallic state throughout the process. It should be noted here that, although plutonium was the fissionable material of interest, U-235 was employed in EBR-I core to provide sufficient reactivity to operate the reactor. Because significant amounts of U-235 were involved, the early process development was concentrated primarily on the recovery of U-235.

The first pyrometallurgical process that was investigated was zone melting, also called zone refining. In this process, a narrow molten zone, created by a movable heater, slowly traverses a long bar of metal. Impurities that favor the solidus in a phase diagram move counter to the direction of travel of the molten zone. Those that favor the liquidus move in the same direction as the molten zone. It is usually necessary to make a very large number of passes of the molten zone to achieve significant movement of the impurities to the ends of the bar where they can be removed by cropping off the end sections. Zone melting had been invented by William G. Pfann of Du Pont, who used it successfully to purify metals such as silicon and germanium for use in the electronics industry. The method was unsuccessful, however, for purifying uranium because the solidus/liquidus ratios of many fission products (especially the noble metals) at equilibrium were too close to unity to produce significant separation toward the ends of the bar at practical rates. The failure to separate fission products, the very long processing time under a high-purity inert atmosphere, and the requirement for a supplemental process to recover plutonium from the cropped ends forced abandonment of the process. This program did, however, result in a useful basic contribution to the mathematical modeling of zone melting. Les Burris, Ira Dillon, and Charles Stockman did this work.

Attention was then turned to a simple slagging-type process in which the fuel was melted in a calcia-stabilized zirconium oxide ($ZrO_2 + CaO$) crucible, held at a temperature of 1400°C for four hours and poured into a graphite product-receiver mold. The behavior of fission products during melt refining is shown in Fig. 2-9, and the melt-refining furnace in Fig. 2-10.

An appreciable fraction of most fission products is removed by the melt refining process, but noble metals (*e.g.*, ruthenium, rhodium, and palladium) and molybdenum are not removed. To prevent the buildup of these elements as the fuel is recycled through the reactor, a small fraction of the fuel, known as "dragout," is removed for separate reprocessing. The skull material remaining in the melt refining crucible, which constitutes 5 to 10% of the processed fuel, serves adequately as the dragout material. Details of the dragout process are presented later.

The melt-refining process was demonstrated at full scale (10 kg of U per batch) in prototypical plant equipment in Bldg. 205. Subsequently, it was installed in the EBR-II Fuel Cycle Facility at ANL-W, where it was used successfully for five years to recover and recycle fuel discharged from EBR-II.



At the high operating temperature of 1400ºC, strontium, barium, and rare earths, which form very stable oxides, are removed in a reaction layer on the wetted surface of the zirconia crucible. The noble gases (krypton and xenon) and some iodine are released when the fuel is melted. The volatile fission products (cesium and rubidium), and sodium, inserted into the fuel elements as a heat-transfer ligament, are volatilized. The noble metal fission products such as ruthenium, rhodium, palladium, and molybdenum are not removed. Their continuing buildup in the recycled fuel is prevented by removing a small fraction of the fuel, called "dragout" in each cycle for separate processing. The crucible skulls serve as the dragout stream.

Fig. 2-9. Fission-Product Removal by Melt Refining

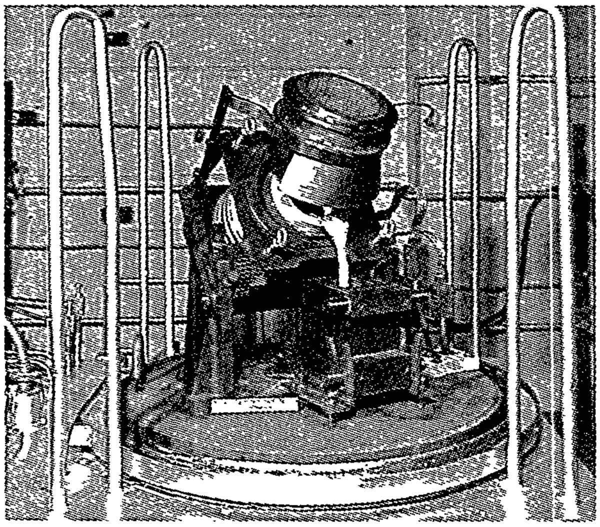


Fig. 2-10. Melt Refining Furnace

Two interesting synergistic developments occurred in the course of the research on melt refining. One was the injection casting method for producing fuel pins. It was an outgrowth of the method used for sampling molten uranium. Samples of the uranium were taken by drawing a small amount of the liquid into a 1/4-inch-diameter Vycor® (quartz) tube. Noticing the perfectly formed cylindrical segments of solidified uranium, Milt Levenson conceived the idea of using precision-bore Vycor tubes coated with a thoria (ThO_2) wash to cast fuel pins for EBR-II. So was born injection casting for EBR-II fuel. In the casting procedure, an array of open-ended Vycor tubes (closed at the top) suspended above a crucible of molten fuel alloy within an evacuated bell-jar furnace was plunged into the melt as the furnace was simultaneously pressurized. Molten fuel was forced up into the tubes to a height of 16 to 18 inches. After cooling, the perfectly formed fuel rods were recovered by crushing the Vycor. The rods were cropped to a 14-inch length, giving fuel pins, which were then clad with stainless steel and incorporated into fuel subassemblies for return to the

Fig. 2-11. Milton Levenson

reactor. The entire sequence of operations was performed in the EBR-II Fuel Cycle Facility.

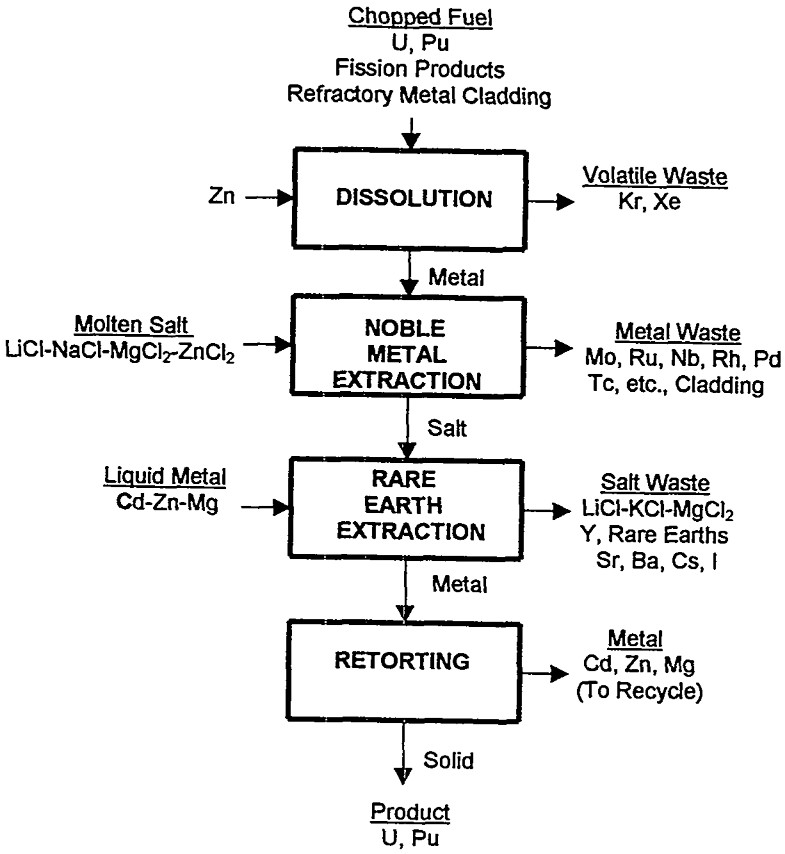
The second synergistic development was a reactor fuel alloy called "fissium." Fissium is the steady-state composition of fuel resulting from dragout (removal) of a small fraction of the fuel for separate processing to extract noble metal fission products and reclaim the uranium. The steady-state composition depends on the fraction of the fuel removed per cycle and the fuel burnup (assuming all the noble metals are completely removed from the dragout fraction). For a fuel burnup of 3 wt% of the uranium and a 7% dragout, the steady-state total concentration of noble metals is about 5 wt%. Fuel of this composition proved to have a remarkable resistance to radiation damage. Unlike uranium metal, which grows uniaxially (lengthwise) under irradiation, fissium undergoes a growth that is much smaller and equiaxial. The fissium fuel was found later to be capable of sustaining burnups in excess of 10 wt%.

After melt refining, between 5 and 10% of the charged fuel remained in the crucible as unpoured metal. Because the wetted surface had a cup-like shape, the unpoured material was called the "skull." It was decided that this material would constitute the dragout fraction. It was removed from the crucible by oxidizing the uranium to UO_2, which was dumped from the crucible as a powder.

Owing to their batch nature, pyrometallurgical processes were considered best suited to small, on-site processing plants serving one, or at most, a few reactors. The EBR-II Fuel Cycle Facility built adjacent to the EBR-II epitomized this concept. An early question was how to reclaim uranium from the skull material and maintain the concept of small, on-site plants. The large facilities required for solvent-extraction processes subverted the concept of compact, self-contained fuel cycles. Therefore, a pyrometallurgical process was sought for recovery of the skull material, and the idea of using liquid metal solvents and molten salts as processing media was advanced. The use of these media opened up a new frontier of process development and spawned research and development programs that have, with some interruptions, extended into the 1990s.

Solvent metals had to be able to dissolve uranium and to have sufficiently high vapor pressures at elevated temperatures to allow their ultimate removal by vaporization. The molten salts had to possess high chemical stabilities, reasonable liquid ranges at temperatures of process interest, and also sufficiently high vapor pressures at elevated temperatures for removal by vaporization. The most promising candidate metal solvents were zinc, cadmium, and magnesium. The molten salt systems of greatest interest were combinations of alkali and alkaline earth chlorides.

Several processes involving the use of liquid zinc as a solvent had been suggested and were generally referred to collectively as "pyrozinc processes." A typical pyrozinc process is illustrated in Fig. 2-12. These



The Pyrozinc process is appropriate for metallic reactor fuels. The fuel elements and their refractory metal cladding are chopped into short lengths and dissolved in molten zinc. Fission-product gases, Kr and Xe, are released in this step. The zinc solution, which contains U, Pu, and fission products, is then contacted with a molten salt such as $LiCl\text{-}KCl\text{-}MgCl_2$ containing $ZnCl_2$. The $ZnCl_2$ oxidizes the U, Pu, alkali metal, alkaline earth metal, and rare earth fission products to their chlorides, which are extracted into the salt phase. The liquid metal phase then contains the noble metal fission products (Mo, Ru, Nb, Rh, Pd, Tc) and the refractory cladding metals (typically V, Ti, Zr, W). This metal phase is discarded as a waste. The salt phase, which contains the chlorides of U, Pu, alkali metals, alkaline earth metals, and rare earths, is contacted with a liquid Cd-Zn-Mg alloy which reduces the U and Pu selectively to the metals, leaving the remaining fission-product elements in the salt phase, which is a waste stream. The purified U-Pu metal product is recovered by retorting off the Cd, Zn, and Mg solvent metals, which are recycled.

Fig. 2-12. Typical Pyrozinc Process

processes are predicated on the following observations:

1. The solubilities of nearly all common metals in zinc at 700-800°C are sufficiently high to dissolve reactor fuel elements in a single step.
2. Uranium oxides can be dissolved in zinc by the addition of magnesium, which reduces the oxides.
3. Uranium metal can be recovered from the zinc either by retorting or by the addition of magnesium to form a metallic uranium precipitate.
4. In a molten fluoride salt containing uranium chloride, uranium can be transferred electrolytically from a metal anode to a liquid zinc cathode.

One example of a pyrozinc process, the EBR-II "Skull Reclamation Process," utilized liquid zinc to leach the noble metal fission products from the skull oxides, and then a Zn-5 wt% Mg solvent with a $MgCl_2$-rich molten salt phase to reduce the UO_2 and dissolve the metallic uranium product. Selective precipitation of the uranium product was also used as a purification step. Further development work on the skull reclamation process, which continued into the 1960s, is discussed in the next chapter.

A simple, ingenious process was also developed for concentrating plutonium bred in the U-238 blanket of a fast breeder from less than 3 wt% to greater than 30 wt% in uranium. In this process, the blanket material was dissolved in a Zn-12 wt% Mg solvent at 800°C (the uranium solubility was about 20 wt%). Uranium, which is insoluble in liquid magnesium, was then selectively precipitated by the addition of magnesium, leaving the plutonium in solution. The solid and liquid fractions were then separated and processed to yield metallic uranium and plutonium products. While intended for installation at EBR-II, the blanket process was a casualty of the AEC decision to abandon metal fuels for fast reactors.

For the skull reclamation process, the requirement to reduce UO_2 to the metal resulted in a major research effort on reductions of UO_2, PuO_2, and even ThO_2 (of interest mainly from a basic research standpoint). Magnesium was selected as the reductant with zinc or cadmium as the solvent for the reduced metals. The molten salt phase was usually a LiCl-KCl-$MgCl_2$ mixture. (Multicomponent salts are required to provide a liquidus temperature low enough for process use.) The reduction is driven, in part, by the low chemical activities of uranium, plutonium, and thorium in the solvent metals. Plutonium dioxide proved to be the easiest oxide to reduce because PuO_2 forms an oxychloride that is soluble in the molten salt, thereby allowing its ready access to the magnesium reductant. Uranium dioxide was more difficult to reduce, but complete reductions were achieved under suitable conditions. Even ThO_2, which is the most stable of the three oxides, was reduced with particular salt compositions. The best and most used reductants were obtained with zinc as the liquid metal solvent. The ability to reduce UO_2 and PuO_2 turned out to be important in the development of processes for oxide fuels in the 1960s and, later, in the 1990s.

Milt Levenson and John Schraidt followed the engineering development program closely, but Les Burris was in charge of most of the work. Among the people working on the engineering research and development effort were Ray Beck, George Bennett, Tom Cannon, John DeKany, Les Dorsey, Jim Hesson, Terry Johnson, Ernie Johnston, Henry Lavendel, Paul Nelson, John Pavlik, Wilfred Pehl, Dean Pierce, Alfred Schneider, Irv Winsch, and Jerry Wolkoff.

THE EBR-II FUEL CYCLE FACILITY (FCF)

The successful operation of several experimental fast breeder reactors together with the promising results from the pyrometallurgical fuel reprocessing studies paved the way for a demonstration of an on-site, closed-cycle pyrometallurgical reprocessing facility coupled to the 62.5-MW(t) Experimental Breeder Reactor that was to be built by ANL at the National Reactor Testing Station (NRTS), now called INEEL (Idaho National Engineering and Environmental Laboratory). A closed-cycle process of this type offers a number of potential advantages over other methods for reprocessing the metallic fuel used in this type of fast breeder. Consolidation of all the reprocessing steps, including refabrication of the recycled fuel, into a closed, on-site operation should be cost-effective due to the low out-of-reactor fuel inventory, the simplicity of the reprocessing operations, and the low waste volume. Because fast breeders are less affected by fuel impurities than thermal reactors, only a modest fission-product decontamination factor of three or so is required.

The EBR-II Fuel Cycle Facility was a major project for CEN (Fig. 2-13). The magnitude of the project was too great for an adequate description here, but it has been covered in detail in a comprehensive book by Charlie Stevenson, entitled *The EBR-II Fuel Cycle Story*, which was published by the American Nuclear Society in 1987. The melt-refining process was chosen for this pilot-plant demonstration. As mentioned earlier, research studies were conducted on a number of potential process concepts in which the bulk of the spent fuel would remain in the metallic state throughout the process, thereby avoiding

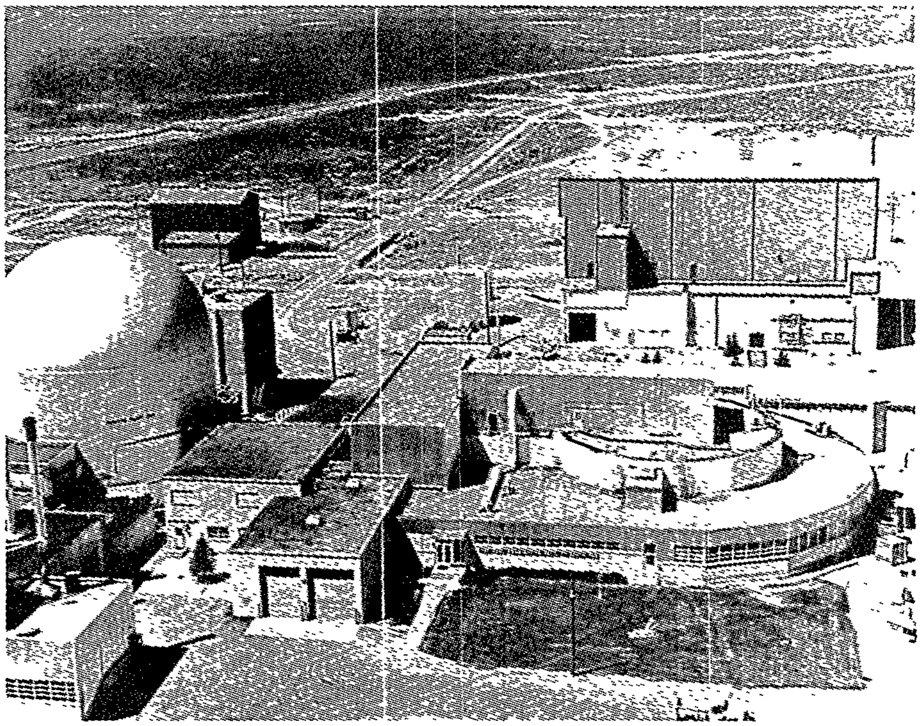


Fig. 2-13. Experimental Breeder Reactor-II with Adjoining Fuel Cycle Facility

chemical conversion steps, which tend to be complex and costly. The melt refining process appeared to be the most promising approach, based on the earlier research and development work on various pyrometallurgical processes.

Detailed designs of EBR-II and the Fuel Cycle Facility were initiated in 1957, construction began that same year, and the facility was completed in 1962. The first fuel was processed in 1964. Although the design of the Fuel Cycle Facility was spearheaded by the ANL Chemical Engineering Division, it was a major interdivisional cooperative effort involving the Reactor Engineering, Metallurgy, and other divisions. Within CEN, the principal engineers handling the project were Milt Levenson, John Schraidt, George Bernstein, Johan Graae, Les Coleman, and Don Hampson. Many others, including Tom Eckels, Dick Malecha, Phil Fineman, Al Chilenskas, and Jim Hesson were also involved. In fact, it seemed as if almost everybody in the Division sooner or later played some role in the project. There was a great deal of traveling between Chicago and Idaho during this period, and several CEN personnel spent months or even a year or more in residence at the site.

As shown in Fig. 2-14, the plant consisted of two large shielded cells and associated equipment. The overall building dimensions were 135 by 170 ft. The rectangular cell on the left was a rather conventional shielded "cave" with an air atmosphere, and it was equipped with the usual windows, manipulators, cranes, *etc.* This cell was used for partial disassembly of the fuel subassemblies and assembly of new ones, as well as the canning of scrap and equipment maintenance.

The second cell was circular and had a high-purity argon atmosphere to permit the handling of pyrophoric materials such as uranium, plutonium and sodium without other special precautions. The cell was an annular structure 72 ft in diameter. The process equipment was contained within the shielded annulus, the operations being conducted by personnel in the area outside the annulus through the use of shielding windows, manipulators and cranes. A shielded control

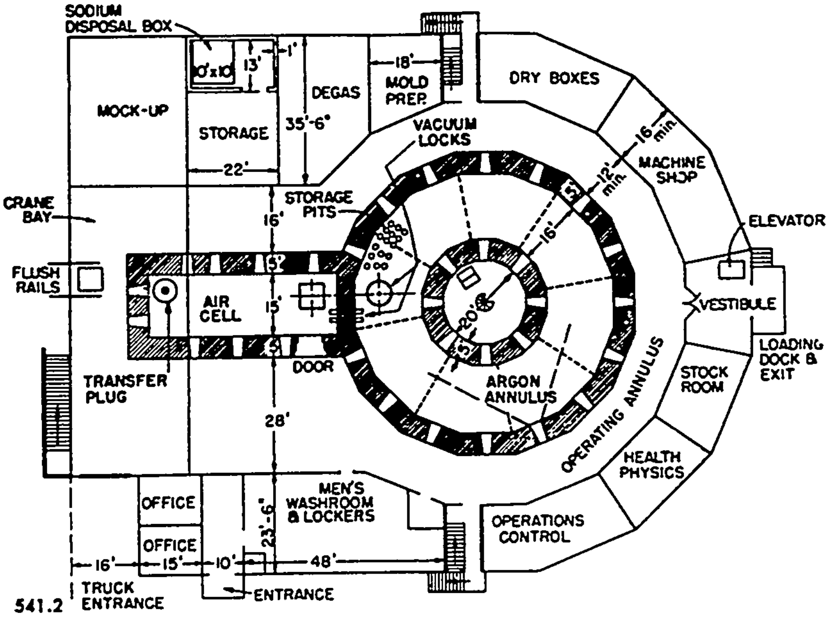


Fig. 2-14. EBR-II Fuel Cycle Facility

room at the center of the annulus permitted observation of the cell from the inside. A subcell was used for various service activities.

The rather unorthodox circular cell design (attributed to Johan Graae) was based on several considerations, the principal one being that by mounting the manipulator and crane bridges to swing around a central pivot, all locations in the cell could be reached by any of these units without their interfering seriously with one another. The design also worked well for the process train where the discharged fuel came in through the transfer lock from the air cell, progressed through the various processing steps as it went around the circle, and left the cell through the same transfer lock ready for reassembly and insertion into the reactor.

A large development effort was required for this facility because of its unique features, some of which are illustrated by the sectional view in Fig. 2-15. Such simple equipment components as graphite bearings in motors had to be modified because the graphite behaved more like an abrasive than a lubricant in the ultra-dry atmosphere. Mineral insulation was used in electrical cables to avoid radiation damage. The shielding windows consisted of six thick layers of radiation-resistant (nonbrowning) glass, which were optically coupled by oil laminations between the layers. Since the inner layers were still expected to darken under the anticipated radiation levels of 106 R/h, they were designed for periodic replacement, and heavy steel shutters on the inside were used to protect the glass when the windows were not in use. High-intensity lighting was required due to attenuation of light by the windows. This was accomplished with 1-kW mercury-vapor lamps (72 in the argon cell and 24 in the air cell). The inside of the annulus was lined with galvanized steel, which was shot-peened to minimize diffusion of gases through the cell walls. A special purification system was needed to maintain the argon atmosphere at a water concentration below 5 ppm, with the oxygen below 100 ppm and the nitrogen at 5 vol% or less. (These stringently low levels were relaxed somewhat later when it was found that they caused metallic sodium to stick to metal surfaces.) These were just a few of the typical problems that required extensive design and development work.

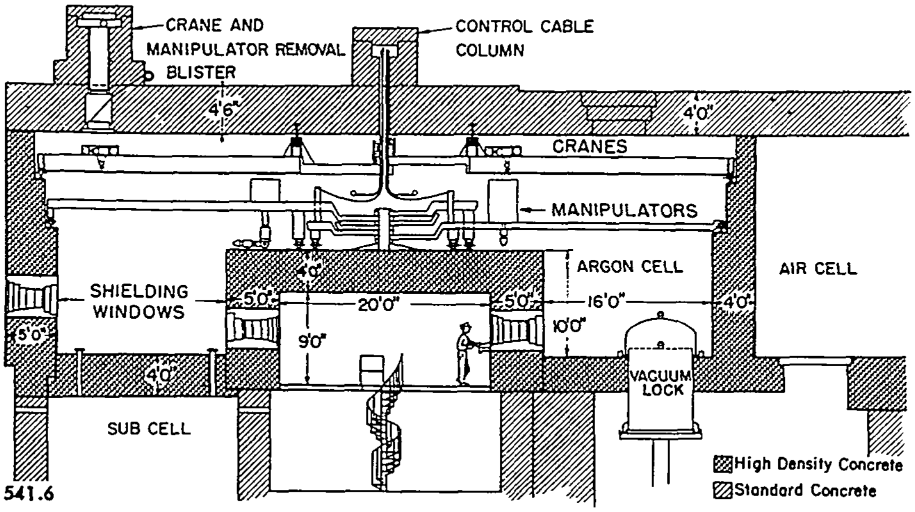


Fig. 2-15. EBR-II Fuel Cycle Facility (Sectional View)

Because fuel processing in the Fuel Cycle Facility did not begin until 1964, this subject is deferred to the next chapter.

Fluoride Volatility Processes

Brief reference was made in the previous chapter to some preliminary studies that were conducted on fluoride volatility processes for the recovery of uranium from spent reactor fuels. This work was expanded into a major CEN program in the 1950s, and several new staff personnel who had previous experience in fluorine chemistry (Glenn Schnizlein, Bob Steunenberg, Larry Stein, and Roger Jarry) were added to the staff. Also, Joe Katz, Herb Hyman, and Irv Sheft of the Chemistry Division (CHM) continued to participate in the program, mainly in an advisory capacity, for several years.

When Schnizlein arrived on the scene, one couldn't help being impressed by his height—6 ft 8 in. One day in the laboratory, he demonstrated that with just a little stretching he could achieve a seven-foot reach between his fingertips. He also had a craggy Lincolnesque visage, and, later in life, he appeared in many parades and other public events around DuPage County in a top hat and tails as Abraham Lincoln, along with his wife, Lois, as Mary Todd.

Jack Fischer, who joined the volatility group soon after arriving at ANL, was another one of the more memorable CEN staff personalities. He was a highly competent physical chemist and turned out a lot of excellent work, but frequently had an abrasive manner. Although the technicians or assistants who worked for him didn't particularly appreciate that trait, they saw a certain humor in the situation. He had a short fuse, and one day when a driver sat in a car blocking the crosswalk in front of the building, Jack, not saying a word, opened the back door, slid across the seat, exited from the other back door, and proceeded on his way, leaving both doors open, much to the amusement of bystanders. On another occasion, during an American Chemical Society meeting in Minneapolis, he curbed a city bus that had cut him off in the traffic, leaving the bus driver dumfounded. In spite of his idiosyncrasies, Jack had many good friends in the Division, and, unlike many people with his personality traits, he could often laugh at himself.

The major emphasis of the fluoride volatility program at that time was on the recovery of enriched uranium from metallic fuels, using a strong fluorinating agent to convert the uranium to UF_6, which is a volatile compound. The need to recover plutonium, as well as uranium, was recognized, but it was not a top priority. A major advantage claimed for the process was that the UF_6 product could be returned directly to a diffusion plant for reenrichment, thereby avoiding a series of chemical conversion steps that are required by solvent extraction or other aqueous processes. By the same token, UF_6 is easily reduced to UF_4, which is the usual precursor for the metal-production process where uranium metal is the desired product.

The choice of a fluorinating agent involved several considerations. Elemental fluorine gas converts metallic uranium to the hexafluoride, but the highly exothermic reaction and the absence of a condensed phase to remove the heat make temperature control difficult. The following halogen fluorides in Table 2-3 were considered for the fluorination step.

Table 2-3. Fluorinating Agents

Fluorinating Agent	Boiling Point, °C
Chlorine monofluoride (ClF)	-101
Chlorine trifluoride (ClF_3)	12
Bromine trifluoride (BrF_3)	126
Bromine pentafluoride (BrF_5)	41

The bromine fluorides were selected for the work at CEN because they are liquids at convenient working temperatures. Soon after work on the fluoride volatility process was started at ANL, similar programs were initiated at Brookhaven (BNL) and Oak Ridge (ORNL). The Brookhaven people, like those at ANL, selected the bromine fluorides as the fluorinating agents, while the Oak Ridge workers preferred the chlorine fluorides.

Although the reactions of liquid halogen fluorides with uranium are somewhat less energetic thermochemically than those of fluorine, they, being condensed phases, pack a very large amount of fluorinating power into a small volume. Like fluorine, they must be handled in materials such as nickel, Monel, and fluorinated plastics such as Teflon® (polytetrafluoroethylene) or Fluorothene®, also known as Kel-F (primarily polychlorotrifluoroethylene). Fluorothene and Kel-F were especially useful in laboratory experiments because they are somewhat transparent and were frequently used as cold traps and sight glasses. In corrosion studies, nickel, Monel, and K-Monel showed excellent resistance to BrF_3 attack. Inconel and Duranickel were also satisfactory. Stainless steel, low-carbon steel, and aluminum were used in some less critical applications. All metals that withstand fluorine attack do so by forming a protective layer of fluoride on their surfaces. The unavailability of suitable valves for fluorine and halogen fluorides was a problem in the early stages of the program; this difficulty was overcome by contracting with Hoke Incorporated to manufacture valves made of nickel with Teflon® gaskets, which were purchased in large quantities. Some of those special valves may still be in use in Bldg. D-205. Several other special types of apparatus, including pressure gauges with Monel Bourdon tubes, differential pressure transmitters, and thermal flowmeters were procured or developed for the fluoride volatility work.

Elemental fluorine is normally received in full-size cylinders containing the compressed gas at 400 psi. With the proper equipment and know-how, high-pressure fluorine can be handled safely, but it demands a great deal of respect. Opening the valve on those cylinders was always a tricky operation, because the valve tended to stick and could not be throttled easily. The result was a sudden burst of 400-psi fluorine, which can burn its way through many metals and most other materials. Old-timers from university and industrial laboratories had a practice of keeping their bare hand on the valve bonnet, so if anything went awry they could detect the heat immediately and shut it off. That was not an acceptable practice at ANL, where the cylinder was enclosed in a heavy steel box, and the valve was operated remotely by a steel rod that extended through the top of the box and terminated with a T-shaped handle. On occasion, when a cylinder was opened a lead gasket between the cylinder outlet and a fluorine supply line would fail, releasing the entire contents of the cylinder. The nickel tubing used to pipe high-pressure fluorine required careful handling. A spot of grease or oil could react with the fluorine, creating a small hot spot that caused the tubing itself to burn in the fluorine, producing flame and molten metal droplets. The people building the fluoride volatility pilot plant discovered that even sharp bends in the tubing can cause a fire. Hal Feder was always greatly concerned about any release of fluorine, and he could detect its pungent, chlorine-like odor long before anybody else could. Bob Steunenberg once unintentionally discovered that a release of just a few milliliters of fluorine gas in a hood in G-134 would bring Hal roaring out of his office "I smell fluorine!" at the end of A-Wing within five minutes or so.

The halogen fluorides are also hazardous materials—they react explosively with organics and many other materials. On a couple of occasions in G-134 a very small amount of BrF_3 was pumped accidentally into a rubber vacuum-pump line, and when it contacted the rubber hose it detonated with a sound like a shotgun blast. When the original BrF_3 fluoride volatility pilot plant was being built in G-134, a tradesman would occasionally drop a pipe or other large object on the floor behind someone working with halogen fluorides in a Blickman hood, shattering his nerves. Metal equipment used to contain fluorine and/or the halogen fluorides was degreased meticulously, dried, and prefluorinated carefully both for safety reasons and for prevention of volatile fluoride loss by reduction on the container walls.

Safety was a major concern because exposure to the bromine fluorides, as well as fluorine and bromine themselves, can result in very serious burns. Early in the program, members of the engineering and research groups were sent into Chicago and fitted with leather jackets and pants as protective clothing. These were used together with gauntlet leather gloves and face shields during much of the work. At the time, the medical profession had only limited experience in handling burns from fluorine, hydrogen fluoride, and the halogen fluorides because they had not yet been used widely in industry. After much discussion, a decision was made that a saturated magnesium sulfate ($MgSO_4$) solution was the best first aid measure, and large bottles of this solution were located in the areas where these materials were in use.

When Martin Steindler first joined the Division and was being shown around the laboratories, a few people in their protective garb were on their hands and knees on the floor in Laboratory G-134 pounding on small samples of frozen BrF_3 to see if they would detonate. That science-fiction-like scene may be the reason he went to work in Hal Feder's group in another program initially, but he eventually became the head honcho and leading expert in the CEN fluoride volatility research. Notwithstanding the large number of people in this program at ANL and the wide variety of operations, nobody was ever injured by these materials.

The basic reaction for the fluorination of uranium by BrF_3 is

$$2\ BrF_3 + U \rightarrow UF_6 + Br_2$$

Nearly all the fission products are also converted to the fluorides. Most of them form solid, non-volatile fluorides, some form very volatile fluorides, and two or three form fluorides having vapor pressures not far different from that of UF_6, which can then be separated from them by fractional distillation. (Because UF_6 has a triple point of 64°C at 1137 torr, a small pressure is required to maintain it in the liquid state.) The principal fission-product species that may be present after the fluorination are shown in Table 2-4.

The only fission-product fluorides having vapor pressures close to that of UF_6 are those of As, I, Mo, Tc, and Te. The vapor pressure of PuF_6 (b.p., 62°C at 1 atm) is near that of UF_6, which has a sublimation point of 56.5°C at 1 atm. The free energy relationships, however, are such that BrF_3 converts the uranium to UF_6 and the plutonium to PuF_4, which remains with the non-volatile fluorides.

The primary fluorination reaction of uranium with BrF_3 is complicated by the fact that bromine product reacts with the BrF_3 to form BrF, which exists as a gas in a mobile equilibrium with the BrF_3-Br_2 mixture:

$$BrF_3 + Br_2 \leftrightarrow 3\ BrF$$

At the time this work was being done, little was known about BrF, the only evidence for its existence being some rather obscure spectroscopic data in the literature. Pressure measurements and spectrophotometric studies of BrF_3-Br_2 mixtures by Bob Steunenberg and George Redding in CEN showed that the above reaction occurs, and that the equilibrium reaction produces sufficient BrF to be of

Table 2-4. Volatilities of Fission-Product Fluorides

Non-volatile Fluorides			Volatile Fluorides (b.p., °C)			
AgF	CsF	SnF_2	AsF_3	63	RuF_5	313
BaF_2	LaF_3	SnF_4	AsF_5	-53	SbF_3	319
CdF_2	$(RE)F_3$[a]	SrF_2	IF_5	100	SbF_5	150
CeF_3	RhF_3	YF_3	IF_7	4[b]	TeF_4	284
CeF_4		ZrF_4	MoF_6	35	Te_2F_{10}	59
			NbF_5	229	TeF_6	-39[b]
			TcF_6	55		

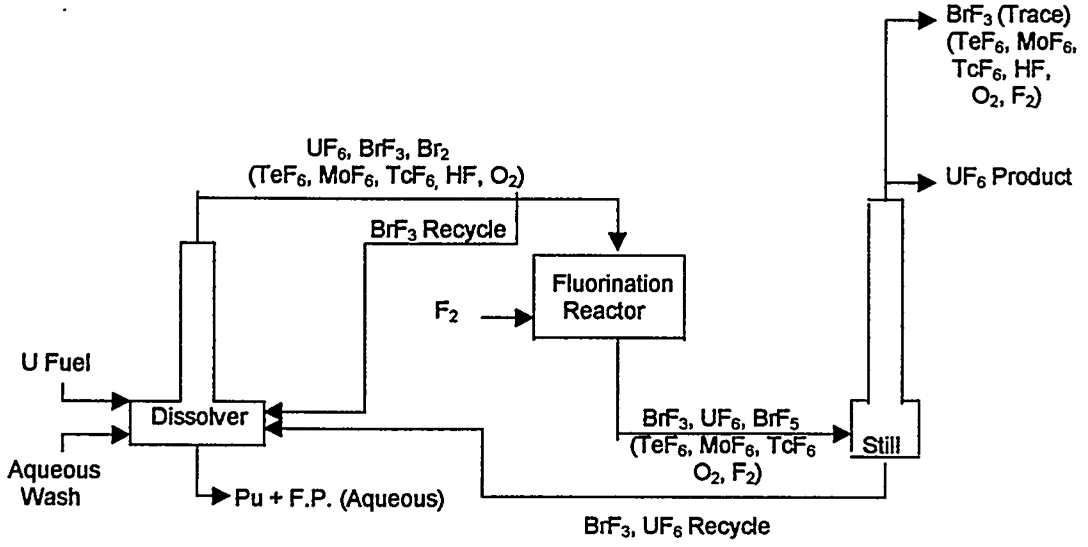
[a] Rare earth fluoride.

[b] Sublimation point.

concern in a process. Larry Stein in the Chemistry Division (CHM) later refined these results with further experimental studies. Although the generation of BrF was of concern, this reaction can be suppressed by the addition of fluorine or BrF_5, and a step of this type was incorporated into some of the fluoride volatility process flowsheets.

The first version of the fluoride volatility process to be investigated at ANL was designed for metallic fuels and utilized BrF_3 as the fluorinating agent. The basic process was fairly simple, as illustrated in Fig. 2-16. The metallic fuel slugs were dissolved in BrF_3, the volatile UF_6 product and fission-product fluorides were collected by condensation, and then separated by fractional distillation. The non-volatile fission products and the PuF_4 remained in the dissolver vessel as solids. Two options were invoked for recovery of the plutonium. One was to fluorinate the dissolver residue with elemental fluorine and collect the volatilized PuF_6. The other option was to dissolve the residue in a small amount of aqueous solution for recovery in an existing solvent-extraction plant.

This version of the volatility process was investigated both in the laboratory and in pilot-plant studies. The actual process was considerably more complex than shown in Fig. 2-16 because of numerous recycle and refluorination steps. Pilot-plant runs with irradiated fuel slugs gave an excellent fission-product decontamination factor greater than 10^8. No effort was made to recover the plutonium, since the main objective was to recover the enriched uranium. These results showed that the fluoride volatility process had the potential for excellent recovery and decontamination of enriched uranium from metallic fuels. At ORNL, E. L. Nicholson published a study indicating that fluoride volatility processes might have a significant economic advantage over aqueous processes, but that they were not accepted as a main-line process for two major reasons: (1) Large-scale Purex plants already in operation could do the same job, and also had the built-in facilities for plutonium recovery. (2) It was beginning to become apparent that civilian power reactors would use oxide, rather than metal fuels.



This simplified flow diagram shows a fluoride volatility process for recovering decontaminated uranium as the hexafluoride from irradiated uranium metal fuel. The fuel slugs are declad mechanically or chemically and dissolved in BrF_3, which comes from a recycle stream. This stream also contains UF_6, which increases the dissolution rate of the uranium. The main products from the dissolver are UF_6, BrF_3, Br_2, and BrF. The TeF_6 is a fission-product fluoride; HF and O_2 may be present as trace impurities. A fractionating column on the dissolver permits recovery of some of the BrF_3 for direct recycle. The other fraction from this column is treated with F_2 to reconvert the Br_2 and BrF to BrF_3 and a small amount of BrF_5. The resulting mixture enters a fractional distillation column, which separates the UF_6 product from the more volatile impurities and the BrF_3, which is recycled to the dissolver with some of the UF_6. During the dissolution, plutonium is converted to solid PuF_4, which remains in the dissolver with the non-volatile fission-product-fluoride waste. The plutonium is recovered by an aqueous wash for recovery and purification in a solvent-extraction plant. Later versions of this process included treatment of this residue with F_2 to recover the plutonium as volatile PuF_6.

Fig. 2-16. Bromine Trifluoride Process

Enthusiasm for processes involving the dissolution of metallic uranium in BrF_3 was also dampened somewhat by an ingenious set of experiments conducted by Larry Stein, prior to his transfer to the Chemistry Division. The highly exothermic nature of the reaction was recognized, and many studies had shown that the reaction was smooth and controllable as long as the metal was covered by liquid BrF_3 to conduct heat away from the reaction site. Larry set up an apparatus in which color motion pictures were taken of a metallic uranium sample exposed only to the interhalogen vapor. The metallic uranium sample became incandescent, and, except for the red bromine fumes, looked very much like a pat of butter melting in a microwave oven. Larry repeated these experiments with other halogen fluorides and obtained similar results.

Brookhaven National Laboratory (BNL) had a program, smaller but similar to the one at ANL, in which metallic uranium slugs were dissolved in BrF_3 and the UF_6 product was purified by distillation. An explosion occurred in their pilot-plant unit, blowing out a wall and throwing a panel board against one of the workers, who was injured. Several people from the volatility program at ANL aided in an investigation, and the general conclusion was that a uranium slug had hung up on a slug "feeler." The phenomenon that Stein had observed then occurred, dropping molten uranium into the liquid BrF_3, causing the explosion and fire.

On one occasion, a decision was made at ANL to conduct a mock incident drill in the fluoride volatility pilot plant in Laboratory H-126. To make it as realistic as possible, the ANL emergency units, including Health Services, were given very limited, if any, advance notice of the drill, and only a half dozen or so people in CEN were informed of it. Bob Kessie was to play the role of a victim who needed to be rescued from one of the upper levels of H-126, and a couple of smoke bombs were activated to add realism. The high-bay area was filled with smoke, which nearly eliminated the light and visibility. The "Dial 13" system was activated.

Fire trucks arrived and the building was evacuated. The ANL physician from Health Services arrived *via* a high-speed ambulance ride and was said to have been in a state of near shock. Meanwhile, Kessie, who is very near-sighted, was wearing a gas mask with non-prescription lenses, and, not being able to see a thing, came close to falling over the railing. The CEN Fire Brigade was having similar problems. After a while, the building ventilation system cleared the smoke and things returned to normal except for some frayed tempers. The drill actually proved to have been quite useful in that it revealed a number of improvements that were needed both in the CEN emergency planning and in the operation of the ANL site-wide emergency communications procedures.

In spite of the lack of an immediate application, the work on fluoride volatility processes for metallic fuels generated a large body of useful information on the basic chemistry and the technology of dry processes using fluorine. Some of the individuals who worked on the chemistry of the process included Jim Bingle, Ron Breyne, Octave DuTemple, Jack Fischer, Lee Gaumer, Bob Hildebrandt, Herb Hyman, Milt Levenson, Bob Liimatainen, Ray Long (Ph.D. student), Walt Ludewig, Bill Mecham, Glenn Schnizlein, Paul Seufzer, Irv Sheft, Bill Shinn, Dave Steidl, Larry Stein, Verne Trevorrow, Homer Tyler, and Warren Wade. The Group Leader was first Joe Katz, followed by Dr. Vogel, and then Bob Steunenberg. The pilot-plant personnel included Lee Gaumer, Jeff Goring (Union Carbide Corp.), Bob Kessie, Bob Liimatainen, Walt Rodger, Wally Seefeldt, and Jonathan Thigpen. Milt Levenson was the first Group Leader, followed by Bill Mecham.

In the mid-1950s, work was started on the recovery of plutonium by fluorination of the dissolver residues and other materials to produce PuF_6. Although this compound was known to exist and some information was available on its properties, it was clear that a significant research effort would be required to obtain the definitive data needed to consider its use in a practical process. Research on PuF_6 was a challenging task because of its marginal stability with respect to the reaction

$$PuF_6 \leftrightarrow PuF_4 + F_2$$

Plutonium hexafluoride (PuF_6) is very readily reduced and can be handled only in scrupulously clean, prefluorinated metals such as nickel. When PuF_6 is stored in a vessel, this disproportionation reaction is enhanced by the alpha activity of the plutonium. Previous research on the properties of PuF_6 had been conducted by Art Tevebaugh and others at Ames Laboratory and by John Malm and Bernie Weinstock of the ANL Chemistry Division. Al Florin at Los Alamos was the first investigator to carry out a systematic research study on the subject. The CEN researchers concentrated more on the process-oriented problems. Martin Steindler and Dave Steidl performed a careful investigation of the fluorination rates of PuF_4 by fluorine and continued on with a variety of studies. Max Adams looked at the thermal stability of the material and methods for performing quantitative transfers. Sy Vogler also contributed to this work. These efforts expanded into several other studies, including the fluorination of oxides, which laid the groundwork for fluoride volatility processes aimed at oxide reactor fuels.

Also, in the mid-1950s, an interest developed in the use of molten fluoride salts as media for processing various kinds of enriched uranium alloy and oxide fuels in which plutonium was not produced in sufficient amounts to warrant its recovery. These fuels generally consisted of U-Al and U-Zr alloys, UO_2 clad with stainless steel, and molten fluoride salts containing the lower-valent uranium fluorides. In one such process, U-Zr alloy fuel elements were immersed in a NaF-ZrF_4 melt at 600°C. Anhydrous HF was then bubbled through the melt, converting both the uranium and the zirconium to the soluble tetrafluorides. Fluorine was passed through the melt to convert the uranium to UF_6, which was vaporized and collected. This product could then be decontaminated by distillation or by selective sorption-desorption cycles using solid NaF beds. Argonne and ORNL both worked on this process concept, with ANL using the distillation step while ORNL preferred the sorption-desorption approach. Both fluorine and the halogen fluorides were investigated as fluorinating agents. Various melt compositions were also studied.

As might be expected, severe corrosion problems arose in the molten salt processes. Graphite and a number of fluorine-resistant metals were used as the container material, and some work was done at ANL on a "frozen wall" approach. In pilot-plant experiments at ANL, two different dissolvers were used. The first, Mark I, was made of A-nickel, and the second, Mark II, was low-carbon nickel. These runs included only the dissolution and fluorination steps, since the decontamination of UF_6 by distillation had been demonstrated earlier. The pilot plant was operated with 200 lb of NaF-ZrF_4 molten salt at 600°C; the fuel charged to the system was 14 lb of Zr-1 wt% U alloy. In six hours, 90% of the metal had dissolved. After three more hours of HF sparging, the dissolution was complete, and 99.5% of the uranium was recovered after 1.3 h of fluorination with BrF_5. The personnel most involved with the molten salt laboratory and pilot-plant work were Jack Fischer, Jeff Goring, Bob Kessie, Bob Liimatainen, Bill Mecham, Walt Rodger, and Sy Vogler. Wally Seefeldt did an outstanding job of coping with the materials problems posed by this process. Bob Steunenberg was the Group Leader, and, as with the other development programs, Dr. Lawroski and Dr. Vogel kept in close touch with this project and made many useful suggestions.

Work on fluoride volatility processes extended on into the 1960s; this continuing effort is covered in the next chapter.

Feed Materials Processing

CONVERSION OF URANYL NITRATE SOLUTION TO URANIUM OXIDE

One of the steps in the nuclear fuel cycle entails the conversion of uranium nitrate solutions from solvent-extraction purification processes to solid uranium trioxide (UO_3). In the past, this conversion had involved a labor-intensive batch process in which molten uranyl nitrate hexahydrate [$UO_2(NO_3)_2 \cdot 6H_2O$)] was heated in agitated pots. A continuous process employing a fluidized bed was developed and demonstrated on a pilot-plant scale by a group at CEN. The uranium nitrate solution was sprayed into a bed of UO_3 that was agitated by air flow and maintained at a temperature of 300-350°C. Under these conditions, the liquid feed dispersed itself over the particle surfaces and decomposed to the UO_3 product, which was withdrawn from the bottom of the bed to maintain a constant bed level. The off-gases were passed through filters or cyclone separators to recover entrained uranium oxide particles. The equipment used for this work was similar to that described later in a discussion of waste calcination in fluidized beds.

The feasibility of the process was demonstrated by a large number of development runs in which several thousand pounds of UO_3 was produced in a 6-in.-diameter stainless steel calciner. The capacity of the equipment was about 100 lb/h. During the runs, many useful data were collected on the effects of operating variables. This work was followed by scale-up studies at the Mallinkrodt Chemical Works. The principal investigators in the program at CEN were Dr. Lawroski, Al Jonke, John Loeding, Ed Petkus, and Rollin Taecker.

PRODUCTION OF REFINED URANIUM HEXAFLUORIDE

At the suggestion of Dr. Lawroski, a group of CEN staff members began to look into the possibility of eliminating some of the purification steps required to convert uranium ore concentrates into refined UF_6 suitable for direct introduction into the diffusion plants for uranium isotope separation. The compositions and physical properties of the ore concentrates varied from plant to plant, depending on the type of uranium ore and the technology used to recover the uranium values. Two general types of concentration processes were in use at the time: acid leach and carbonate leach. In some cases a prior salt roast was used to convert the uranium to a soluble form. The ore concentrates were produced by precipitating diuranate from the leach liquors with ammonium or sodium hydroxide. The precipitates were then filtered, dried, and calcined. The concentrates consisted primarily of uranium oxides or diuranates (*e.g.*, $Na_2U_2O_7$), assaying at least 70% as U_3O_8 in most cases. The major impurities were oxides of the gangue elements, *e.g.*, V, P, Mo, S, Fe, Na, Cu, Ni, Pb, Bi, Sb, As, Sb, Ca, Si, Al, Cr, Mg, and Mn.

In the existing feed materials plants, various purification methods such as solvent extraction, ion exchange, and selective precipitation were used to produce refined uranium oxides. These oxides were then reduced to UO_2 with hydrogen (or cracked ammonia), converted to UF_4 with anhydrous HF, and then treated with elemental fluorine to produce UF_6. The overall fluorination sequence is:

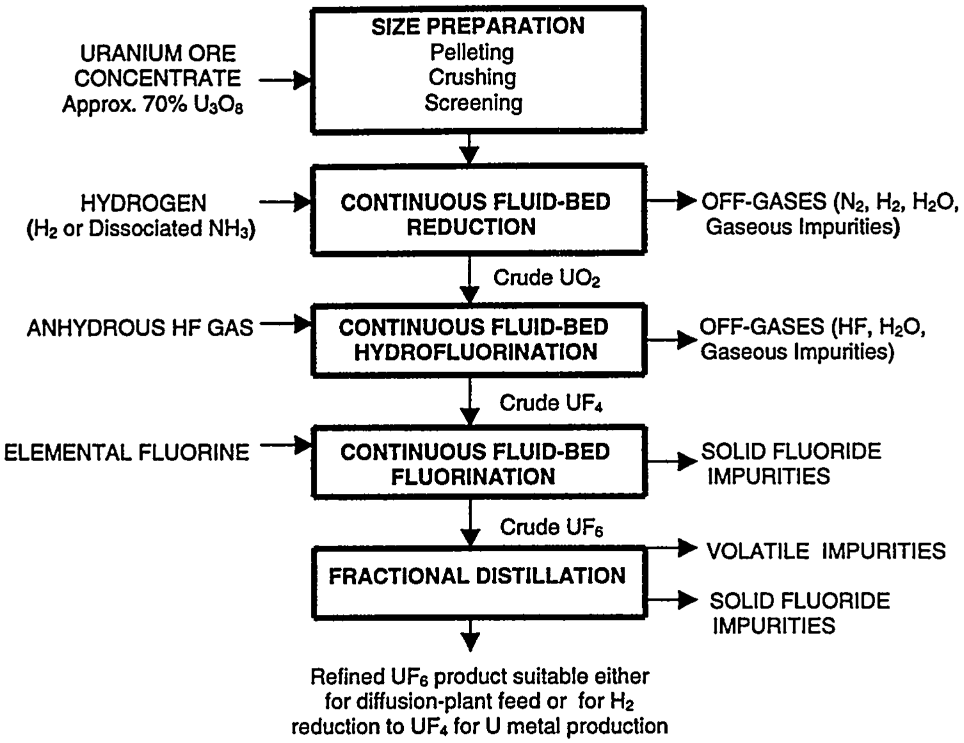
$$UO_3 + H_2 \rightarrow UO_2 + H_2O \text{ or } U_3O_8 + 2\ H_2 \rightarrow UO_2 + 2\ H_2O$$

$$UO_2 + 4\ HF \rightarrow UF_4 + 2\ H_2O$$

$$UF_4 + F_2 \rightarrow UF_6$$

Some of the uranium oxides in the first two reactions may be in the form of uranates. Several types of solid-gas contacting equipment, such as vibrating-tray reactors, horizontal screw-feed reactors, and fluidized beds were being used by the processing plants for these operations.

The process proposed by CEN, illustrated in Fig. 2-17, eliminated the chemical purification steps and introduced the ore concentrate directly into the hydrogen reduction, hydrofluorination, and fluorination sequence, using continuous fluidized-bed contactors for all the steps. These steps removed most of the gangue elements, and any remaining impurities were eliminated by fractional distillation of the UF_6 product. This process did, however, require a preliminary size preparation step to produce a material



The physical and chemical characteristics of the uranium ore concentrates can vary considerably, depending on the source of the ore and the concentration process. The uranium may be present in the form of uranic oxide (UO_3), urano-uranic oxide (U_3O_8), or diuranates such as $Na_2U_2O_7$, and normally assays at 70 wt% or more as U_3O_8. To convert the material to a particle-size range suitable for use in fluidized beds, coarse material is crushed or ground, and fine material is pelletized or briquetted. Hydrogen or cracked ammonia is used to convert the uranium oxides to UO_2 in a fluidized bed, and then anhydrous hydrogen fluoride (HF) is passed through the bed to convert the UO_2 to UF_4. These two steps remove some troublesome impurities such as silicon, boron, and sulfates, which appear in the off-gases. The crude UF_4 is treated with elemental fluorine to convert it to volatile UF_6, which is collected from the off-gas. Most of the gangue-element fluorides are non-volatile and remain in the bed. Any volatile fluoride impurities are then removed from the uranium by fractional distillation. The reduction step was operated at about 575°C and the fluorination step around 450°C.

Fig. 2-17. Production of Refined Uranium Hexafluoride from Ore Concentrates suitable for fluidization. The sizing procedures depended on the nature of the particular ore concentrate, but they included combinations of crushing, screening, briquetting, and pelleting.

Initial studies of the conversion of uranium oxides to UF_4 were conducted by Norm Levitz, Al Jonke, Al Litty (General Chemical Co.), and Ed Petkus, using single-stage fluid beds 3 and 6 in. in diameter, and additional demonstrations of the process were made in a pilot plant consisting of a 5-in.-diameter, four-stage stainless steel reduction reactor connected in series with a 6-in.-diameter, five-stage Monel hydrofluorination reactor. The two reactors operated at 575°C and 450°C, respectively. These and other similar tests were, in general, very satisfactory, and showed that the rapid reactions in the fluid beds would permit the use of single-stage beds.

John Vogel, Bob Steunenberg, and Oscar Sandus worked on the fluorination of UF_4 to UF_6. Although plant-scale tower fluorinators were in general use for this conversion, it was doubtful whether they would be suitable for the impure UF_4 because the tower reactors use a high-temperature fluorine flame reaction that would most likely result in product sintering and caking.

Initial studies used a 1-in.-diameter Monel reactor with a bed temperature of about 450°C. Different concentrations of nitrogen were used to dilute the fluorine, and CaF_2 was added to maintain the bed of solids as the UF_4 was consumed. A pilot-plant fluorinator consisting of a Monel 2.5-in. reactor topped by a 6-in. disengaging section was operated in conjunction with a condenser that was 10 ft tall and 3 in. in diameter. The fluorinator was operated at temperatures of 350-500°C and gas velocities of about 0.5 ft/sec. The results of the tests were considered to be satisfactory, and the only significant impurities in the UF_6 were vanadium and molybdenum. These two impurities were not unexpected because they form the volatile compounds VOF_3, VF_5, and MoF_6, which have vapor pressures that would cause them to condense with the UF_6. They can, fortunately, be separated from the UF_6 by fractional distillation.

The UF_6 distillation studies were performed by Bill Mecham, Bob Liimatainen, Bob Kessie, and Verne Trevorrow. Very little information on the vapor pressures of VOF_3 and VF_5 and no vapor-liquid equilibrium data on the systems VOF_5-UF_6, VF_5-UF_6, and MoF_6-UF_6 were available in the literature. The vapor-pressure data were generated by CEN. Workers at the Allied Chemical and Dye Corporation, who were interested in using the process, obtained vapor-liquid equilibrium data. The solubility of VOF_3 in UF_6 was found to be low, indicating that periodic removal of the VOF_3 from the UF_6 condenser might be necessary. Preliminary pilot-plant experiments were conducted with a 2-in.-diameter, 16-ft-long distillation column. The nickel column consisted of a still pot, tower, condenser, overhead receiver, and charging and sampling facilities. The runs involved approximately 100-pound charges of UF_6 spiked with the molybdenum and vanadium impurities. Overall results from the UF_6 distillation studies indicated that it would be a practical process operation.

The ANL results were augmented by work performed under the direction of Sy Smiley at the Oak Ridge Diffusion Plant (Y-12) on the fluorination of crude UF_4 and on UF_6 distillation.

A number of additional CEN people were involved in this project, including Dr. Lawroski, Dr. Vogel, and Dr. Rodger, who provided technical guidance, Wally Seefeldt, who investigated the corrosion aspects of the process, and the Analytical Chemistry Laboratory. This turned out to be a highly successful program. The process was placed in a full-scale plant operation at Metropolis, Illinois, by Allied Chemical, which has been a major UF_6 production facility for about 40 years.

Although this particular program was aimed at the recovery of UF_6 from ore concentrates, the technology involved in any one or more of the individual process steps is directly applicable to various conversions of high-purity materials that might be needed in other types of fuel-cycle operations that require chemical conversions.

Waste Treatment

INCINERATION OF RADIOACTIVE SOLID WASTES

One of the first major projects to be undertaken by CEN after the move to Site D was a pilot-plant demonstration of an incinerator for the disposal of low-level combustible radioactive waste materials generated at the Laboratory. These wastes consisted of materials such as paper, clothing, wood, filters, rubber gloves, *etc.* that had been discarded as DAW (dry active waste). The activity level in this material was typically in the range of 30-50 mR/hr.

This operation, which was conducted in Bldg. D-310 during the period of 1950-1953, had three objectives:

1. To design and construct an incinerator that would handle the combustible waste generated at ANL
2. To obtain operating data that would point to design modifications for increased efficiency
3. To provide a prototype for any future incinerator projects

The entire installation was heavily instrumented because it had the dual purpose of generating pilot-plant data and serving as a routine production facility.

A. D. Little of Cambridge, MA, was contracted to provide the basic design of this pilot plant. The primary unit was the incinerator furnace, which was made of Type 330 stainless steel, and consisted of a cylindrical section 5 ft in diameter and about 10 ft high atop a 4-ft-long conical bottom that tapered to a diameter of 8 in. at the bottom. The furnace contained a cast iron grate system, and its top was equipped with a waste-charging system of interlocking doors. The combustion system consisted of three gas burners at the periphery of the furnace, and primary air was blown through four 4-in.-diameter ducts located 4 in. below the grate. Secondary air was introduced through four 1-in. tangential pipes 16 in. above the grate to generate turbulence for good mixing. The cone at the bottom contained water to collect the fly ash and terminated in a valve to release the wet material into collection bags.

The upper portion and top of the furnace were jacketed with a carbon steel shell to provide an annulus that served as a boiler for heat removal; the resulting steam was condensed in three cooling units in the fan loft. The steam-condensing capacity of these cooling units was the limiting factor on the throughput of the furnace. The operating temperatures of the furnace ranged between 850 and 1450°F, with an average of about 1150°F.

An extensive off-gas treatment system was used to prevent the escape of any radioactive particulates to the environment. This system included a Schreiber-Bartolucci vane plate washer to remove large particles, and a Pease-Anthony venturi followed by a Peabody scrubber. An AEC filter was used for final cleanup.

The installation operated for 20 months, incinerating 16,000 ft^3 of waste with a volume reduction of 95%. The normal throughput was 17 ft^3/hr. In one test, the operation was run continuously for 120 hr. The decontamination factor for the exhaust gas was 3×10^7, which resulted in an activity level lower than that of the outside ambient air. The reduction in volume decreased the cost of storing the solid waste by about 50%.

During the development and operation, a few problems such as plugging and caking were encountered, but these were not major and were corrected. As might be expected, corrosion was identified as a long-range problem that would require attention; some of this was attributed to the sulfate in the large amount of paper that was burned.

Don Hampson, Ed Hyken, and Walt Rodger had the major responsibility for this work. Herb Brown, O. Levison, Wilfred Pehl, and Don Hulet were the principal operators of the equipment; C. Bullinger provided design assistance and John Schilb was responsible for the analytical work.

This program was successful in meeting its three objectives; a report (ANL-5067) was issued in 1953; and the installation was dismantled in the mid-1950s to make room for other projects.

FLUIDIZED BED CALCINATION OF AQUEOUS WASTES

In a report issued by the AEC in 1957 (WASH-742), the inventory of high-level liquid wastes in tankage in the U.S. was stated to be greater than 60 million gallons, and another 10 million gallons was expected within the next two years. Most of this waste was from the Hanford plutonium production plants, and this method of storage was to have been a temporary stopgap measure. As we all know, these liquid wastes are still a problem and a subject of national embarrassment.

In the mid-1950s, the staff at CEN came up with the idea of using the Division's expertise in fluidized bed technology to investigate calcination as a method to convert the liquid wastes into a more innocuous solid material. This was a joint undertaking between CEN at ANL-E and the Phillips Petroleum Company at the Idaho site. The personnel involved in this program were Walt Rodger, Al Jonke, John Loeding, Bob Larsen, and Dr. Lawroski at ANL, and E. S. Grimmett, J. I. Stevens, and Charlie Stevenson at Phillips.

At the Idaho Chemical Processing Plant (ICPP), highly enriched uranium fuels were reprocessed to recover the fissionable material, with the principal high activity waste coming from the processing of MTR- (Materials Test Reactor-) type U-Al alloy fuels. The resulting acidic $Al(NO_3)_3$ solution was being stored underground in stainless steel tanks. Parallel efforts were conducted at the two sites, using fluidized bed calciners. The fluidized bed material was Al_2O_3 particles, although almost any inexpensive, inert solid could be used, as, for example, for a Purex waste, where little solid material would be generated during the calcination.

Four pilot-plant units were built and operated, two at ANL and two at Phillips. All were of a similar design, in which the fluidized bed was supported on a porous plate that also served as a gas distributor. Preheated air was directed upward through the bed, causing it to behave much like a vigorously boiling liquid. This mixing action provides excellent gas-solid contact and heat transfer to the vessel wall. The bed was maintained at temperatures in the general range of 400 to 500°C either by heating the vessel wall or by heat-transfer tubes within the bed. The liquid waste solution was injected into the bed by several spray nozzles around the periphery of the calciner in a horizontal plane near the bottom of the unit. As the liquid droplets contacted the bed particles, they were flash dried and deposited as the oxides. The strongly agitated bed provided sufficient attrition of the solid particles to produce new nuclei so as to prevent a continuing increase in the overall particle size. The product was withdrawn continuously from the bottom or from an overflow pipe. The calciner off-gases, which consisted mostly of water vapor and nitrogen oxides, were passed through high-efficiency filters or liquid scrubbers to remove entrained radioactive oxide dust. Special provisions were required to remove fission-product ruthenium, which forms volatile compounds under these conditions.

After some preliminary experiments with a 3-in.-diameter stainless steel unit, two 6-in. calciners were operated at ANL, one for inactive studies and the other for hot runs behind shielding. External electrical heaters maintained the bed temperature in both units, and two filters that could be blown back alternately were used for the off-gases. At Phillips, a 6-in. calciner, of a generally similar design as the ANL units, was used to process up to seven liters of $Al(NO_3)_3$ solution per hour, and a larger unit with a cross-sectional area of 4 ft^2 was designed to process up to 100 liters per hour.

The hot runs at ANL showed that all the fission products except ruthenium remained in the solid bed. Various measures for suppressing or handling the ruthenium activity, including the addition of CO to the fluidizing air, were investigated.

Operation of the larger pilot-plant unit at ICPP was so successful that the unit began to be used routinely as a plant for liquid waste disposal in 1963, and this operation continued until 1981 when a newer calciner came on line. During that 18-year period, this facility processed more than 4 million gallons of liquid waste into about 77,000 ft^3 of granular solids, thereby decreasing the waste volume by a factor of 7 to 10. This was the first facility in the world to convert radioactive liquid wastes into solids on a plant scale, and the achievement was recognized at a ceremony on March 17, 1994. The facility, currently operated by the Lockheed Idaho Technologies Co., was named by the American Nuclear Society as a National Historical Landmark. The early development of this process was one of the major achievements of CEN.

ION-EXCHANGE STUDIES

Operation of a research and development laboratory which handles a wide variety of radioactive materials inevitably produces large volumes of low-level aqueous waste. In Bldg. D-205, the drains from all the laboratory sinks empty into 1,500-gal retention tanks where the wastewater can be monitored to make certain that unacceptable levels of radioactivity are not sent to the ANL wastewater treatment plant. If the levels exceed the standard for normal disposal, the water is sent to a special treatment facility for cleanup. Safety rules forbid the dumping of radioactive material into laboratory sinks, so this is a backup precaution.

The removal of low levels of radioactive species from wastewater is, however, a more general problem, which was addressed by Gladys Swope and her co-workers in a study of cation-exchange methods. This study was aimed primarily at mixed fission-product activities in tap water. The exchange media were of the styrene-base sulfonic acid type, which are commonly used for water softening.

The results showed, in general, that 75-80% of the beta-gamma activity was removed up to the point of hardness (calcium and magnesium) breakthrough, which was about 260,000 gal per cubic foot of resin. Flow rates up to 10 gal/min per cubic foot of resin were achieved without loss of performance. As might be expected, strontium-90 was removed up to the point of calcium/magnesium breakthrough. Prior to breakthrough, the principal limitation on performance was due to cesium and ruthenium leakage; these activities were the limiting factor on the efficiency of the ion-exchange approach. Total rare earths were removed both before and after hardness breakthrough. The overall conclusion was that water containing low levels of fission-product activity requiring removal factors of 80% or less could be processed economically.

The disposal of radioactive liquid wastes became a routine operation in the 1950s and extended well into the 1960s. Some of the people involved in this work, which was also under Swope's direction, were Joe Harast, Bruce Kullen, Ken Brewer, Ruth Juvinall, and Carl Ryberg. Several different types of operations were performed, depending on the nature of the particular waste: evaporation and concentration, filtration, cation exchange, absorption in Vermiculite®, and neutralization. The quantities of liquid waste were typically in the range of about 30,000-40,000 gallons per month.

Extensive support from the Analytical Laboratory was required both for the research studies and for the routine waste-processing operation. Doug Krause was in charge of the analytical work at that time, and the analyses were performed by Ruth Juvinall and Arden Schilb. Elton Turk provided technical advice.

When Gladys Swope left ANL later on, she established a consulting business in the Chicago area on water treatment.

GAMMA IRRADIATION FACILITY

Scientists and engineers in the early 1950s felt that there must be some practical uses for the highly radioactive fission products that were being produced in reactors and came up with a variety of suggestions. One of these was irradiation with gamma rays to preserve food, since gammas kill bacteria, but induce no activity into the irradiated material. To pursue this and other studies of the effect of gamma radiation on materials in general, the Argonne High Level Gamma Irradiation Facility was constructed as an underground annex on the south side of Building D-310 (Fig. 2-18). The facility was a water-filled canal 28-ft long, 14-ft wide, and 24-ft deep, in which spent fuel rods from the Materials Test Reactor (MTR) and CP-5 were contained in racks at the bottom. The level of the water, which served both as shielding and as a coolant, varied from 16 to 20 ft. The water was demineralized and circulated constantly through an ion exchanger at 800 gallons per hour at a temperature of 76°F. The facility was designed under the direction of Phil Fineman, and it went into operation on August 5, 1955.

There were three fuel-rod racks. One consisted of a honeycomb of 12 fuel rods with six 4.25-in.-diameter sample ports where flux intensities as high as 3.5×10^6 rad were achieved. The second one could accommodate a sample as large as 20 in. in diameter and 30 in. high. It was surrounded by eight fuel rods at least 150 days old, so the flux was much lower—about 15,000 rad/h. The third rack had the same size sample ports as the first one (4.25 × 28 in.) with four fuel rods that had been cooled even longer. The gamma dose intensity in this unit was about 200,000 rad/h. Provisions were made to rotate the samples in the first two racks. The oxidation rate of ferrous sulfate ($FeSO_4$) solution in dilute sulfuric acid was used to determine the radiation doses at various locations.

This facility was popular with visitors. When the room lights were turned off, the blue glow from the Cherenkov radiation was impressive. On display were also several food samples that had been irradiated and kept for several months, including some bananas that looked almost as good as new. These food-irradiation studies were supported by the Army Corps of Engineers and the Quartermaster Food and Container Institute for the Armed Forces. Some CEN personnel used this facility for research. Alfred Schneider used it for his Ph.D. thesis, and Martin Steindler and Dave Steidl carried on gamma decomposition studies on PuF_6. A few glass items that had been colored by the gamma radiation were given out

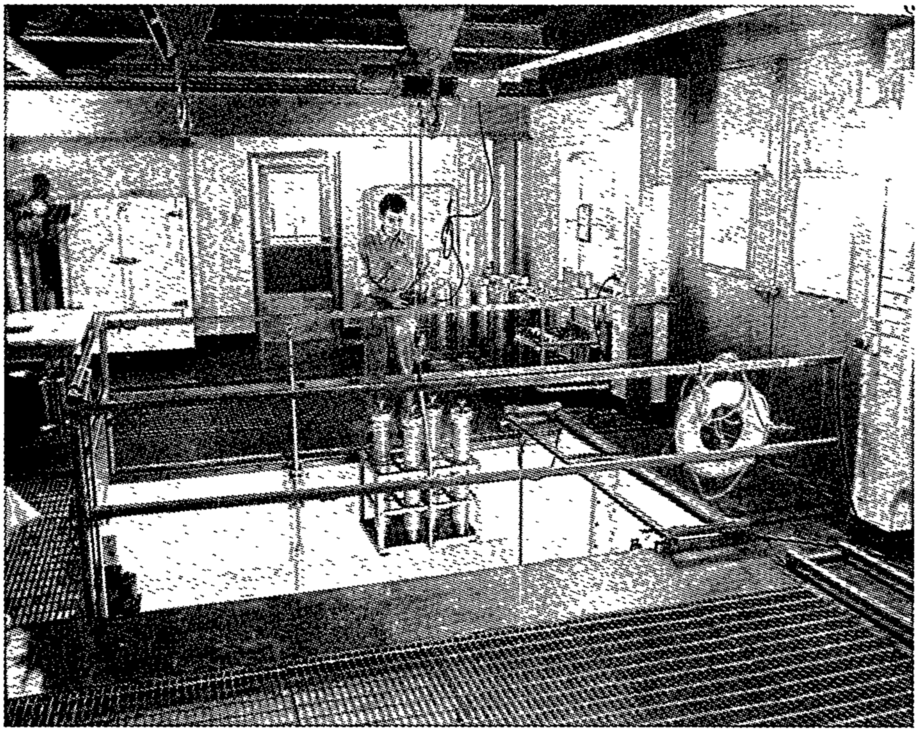


Fig. 2-18. Gamma Irradiation Facility in Building 310

as souvenirs after a Geiger counter was used to show the visitors that the glass was not radioactive.

Gladys Swope was also the principal operator of this facility under the direction of Walt Rodger. Gladys was a rather assertive individual, and she seemed to believe that she was immune to radiation. At one time, she objected to the rule that she must wear a dosimeter and film badge, but apparently decided that it wouldn't do any harm and would keep her supervisors happy. In that connection, one time she called her boss, Walt Rodger, on the phone and put him on hold when he answered; he wasn't a bit happy. Even today, that's not considered to be good protocol and Walt was livid.

THE "HOT ROCK"

Another approach to the use of fission-product radiation was investigated by mixing the radioactive fission products into concrete, which was cast in the form of a small, hollow cylinder. The concrete cylinder was surrounded by lead and concrete shielding, and the hollow core was designed to accept samples for irradiation testing. This device, which was fabricated by John Loeding, Ira Dillon, Ed Petkus, George Yasui, and Walt Rodger under the direction of Dr. Lawroski, was sent to the Massachusetts Institute of Technology for studies of food irradiation.

The possibility of using mixed fission-product activity for large-scale applications such as sewage treatment and heat sources has, in general, been unsuccessful for several reasons. Two major problems are the shielding requirements and the rapid decay rate of fission products at cooling times sufficiently short to provide the high energy output that is needed. Small amounts of a few specific isotopes, however, can be recovered and used for various purposes.

Fluidized Bed Technology

Fluidized beds were used extensively in the research and development programs in CEN. This technology was not new. It had been used widely in the petroleum industry and elsewhere, but CEN was a pioneer in adapting it to a wide variety of new applications in the nuclear fuel cycle. The diversity of these applications is illustrated by the following list of processes that were investigated in the 1950s:

1. Calcination of radioactive waste solutions to produce a much smaller volume of less innocuous solid waste for storage or further treatment
2. Denitration of uranium solutions to form solid uranium oxide
3. Conversion of U_3O_8 to UO_2
4. Conversion of UO_2 to UF_4
5. Conversion of UF_4 to UF_6
6. Combinations of the above steps to convert uranium ore concentrates to refined UF_6

Later on, in the 1960s, fluidization methods were used for even more applications, including direct fluorination of oxide reactor fuels, preparation of uranium carbide and nitride fuels, processing of uranium-zirconium alloy fuels, and control of sulfur emissions in the burning of coal by limestone additions.

A fluidized bed is a bed of granular solids through which an evenly distributed stream of gas is passed at a velocity sufficient to cause partial suspension of the particles. Such a bed takes on the general appearance of a vigorously boiling liquid. The free movement of the particles results in their continuous agitation and mixing. This movement, along with the large surface area of the particles, creates a highly favorable condition for gas-solid reactions.

Fluidized beds have several favorable features that are particularly useful for processing radioactive materials, where remote operations are required. Plant operations are simplified by the fact that the fluidized solids can be handled much like a liquid. The bed requires no internal mechanical moving parts, temperatures tend to be uniform, and heat transfer to the vessel walls is excellent due to the high thermal conductivity of the bed. Reaction rates are high because of the continuous mixing and the large gas-solid surface areas.

The disadvantages relate mostly to the particular application. The solid particles cannot be too fine or too coarse. Sizing operations on the starting material such as pelleting, briquetting, or crushing may be required. Caking can occur as a result of sintering or other types of agglomeration. Attrition or chemical conversion may produce fines that plug the off-gas filters. (Alternating blowback between two or more filters and the bed has been used to handle plugging in some instances.) Finally, as in any process equipment, corrosion and erosion are sources of potential problems.

Although most of the work with fluidized beds in CEN was related to one specific process or another, systematic engineering research studies were also conducted to investigate the basic characteristics of these systems. Bed size and geometry were important not only to the operating characteristics, but also to nuclear criticality considerations in some systems. Other factors such as gas dispersion techniques and flow rates, particle-size distribution, densities, methods of introducing liquids, and heating and cooling methods are important in establishing optimum equipment designs and operating conditions. When one considers the complexity of the factors that can arise in a fluidized bed operation, it is a tribute to the workers that CEN was so successful in applying this technology to such a wide variety of applications. Basic studies of fluidized beds continued into the 1960s.

Reactor Safety

Two programs designed to provide basic information on the safety aspects of various operations employed in nuclear technology were initiated by CEN in the mid-1950s. The first was aimed at fire and explosion hazards resulting from ignition of metals such as uranium, zirconium, plutonium, and thorium in air or oxygen atmospheres. The other program was directed toward reactions of metallic nuclear fuels with water that could occur in reactors as a result of nuclear transients or loss of cooling.

METAL-AIR REACTIONS

The initial studies were made with uranium and zirconium. Both the ignition behavior and the subsequent burning characteristics were investigated. Metal powders, turnings, foils, wires, and small solid bodies were ignited in air and oxygen atmospheres. Turnings were of special interest because fires had occurred frequently in machining operations. Although high specific area was established as a major factor in lowering the ignition temperature and increasing the burning propagation rate of uranium and zirconium, other variables that were studied included purity of the metal, alloying additives, surface and gas contaminants, and surface etching. During these studies, a complementary investigation was conducted on the fundamental kinetics of oxidation.

In 1958, a report (ANL-5974) was issued on the ignition behavior and kinetics of oxidation of uranium, zirconium, plutonium, thorium, and the binary alloys of each. Subsequent work was geared more toward the burning process after ignition had occurred. Electron-diffraction studies were performed on partially burned specimens to reveal the nature of the oxide layers on the metal surfaces.

Ignition and burning-propagation-rate experiments were performed with foils of binary plutonium alloys containing 2 at.% Al, Fe, C, Ni, Mn, and Cr. Manganese lowered the ignition temperature and aluminum raised it.

Dr. Vogel and Glenn Schnizlein were the principal investigators in this program; other workers included Jim Bingle, Don Fischer, Len Leibowitz, Larry Mishler, Phil Pizzolato, and Marv Tetenbaum.

METAL-WATER REACTIONS

A condenser-discharge technique was used to obtain fundamental reaction-rate data under conditions that could be expected to prevail during a serious accident in a nuclear reactor. Either a nuclear runaway or a loss of coolant in a water-cooled nuclear reactor could result in contact of very hot fuel and cladding metals with water or steam. In the condenser-discharge experiments, metal wires were quickly melted and dispersed in a water-filled cell by a surge current from a bank of capacitors. A surprisingly large amount of information can be obtained by this relatively simple technique. The energy input to the wire was used to calculate the initial metal temperature; the transient pressure indicated the reaction rate; the quantity of evolved hydrogen gave the extent of the reaction; and the particle size of the residue revealed the surface area exposed to the reaction. An analysis of the data based on known laws of metal oxidation and a simple heat-transfer model produced rate constants that could then be used for a detailed analysis of any other particular system. It is interesting to note that these calculations were made in cooperation with the Applied Mathematics Division (AMD) using an analog computer program. Capacitor-discharge experiments were conducted with uranium and zirconium, and the reaction rates in both cases showed parabolic behavior. At higher temperatures (2600-2700°C), where zirconium oxide reaches its melting point, the reaction became explosive.

A pressure-pulse method involving momentary contact of water vapor with molten metal in a crucible was also being developed to investigate metal-water reactions. Reliable techniques for using this method were still being developed at the end of the 1950s.

In-pile experiments were conducted to investigate metal-water reactions initiated either by a nuclear reactor transient or by a loss-of-coolant incident in the presence of an intense neutron and gamma radiation field. The initial work was done by inserting an autoclave containing the samples into the CP-5 reactor; subsequent tests were conducted in the TREAT (Transient Reactor Test) facility. Data were obtained on unclad uranium metal pins, Zircaloy-2-clad metal core pins, and oxide and cermet core pins jacketed with aluminum, stainless steel, and Zircaloy-2. The amount of metal reacted was obtained from hydrogen analyses, using a mass spectrometer, and the effects of the transients were evaluated by direct physical examination supplemented by metallographic methods.

The principal investigators in the metal-water program were Walt Rodger and Lou Baker. Bob Liimatainen, Don Mason, Peter Martin, and Ray Warchal did the condenser-discharge work, and Professor Martin Kilpatrick of the Illinois Institute of Technology served as a consultant. Dick Ivins, Marshall Deerwester, Bob Liimatainen, and Frank Testa were involved in the in-pile work.

Calorimetry

The calorimetry program in CEN began in about 1957 as a part of the pyrometallurgical research group under Hal Feder. At that time, the U.S. Bureau of Standards in Washington, the U.S. Bureau of Mines at Bartlesville, Oklahoma, and various universities were doing most of the calorimetric work in the U.S. It seemed a bit odd that an organization such as CEN would enter that field, but there was a good reason for it. Combustion calorimetry up to that time had normally been done with oxygen, and the realization struck that the use of fluorine, a much more powerful oxidizing agent, could extend the combustion method to include many materials that could not be burned satisfactorily with oxygen. Fluorine will normally convert all the elements in a substance to fluorides of their highest valence states in a clean reaction. Many of the materials that were investigated in this program, such as zirconium, were important in nuclear technology. Fluorine-combustion calorimetry was an attractive prospect, but it offered some difficult challenges in the handling of fluorine for this particular application. Nearly all the necessary technology and "know how" to meet these challenges were already available from the CEN fluoride volatility program.

The Division was fortunate in being able to hire Ward Hubbard to lead the effort. Ward, who was employed by the Bureau of Mines at the Bartlesville Petroleum Research Center at the time, was already a nationally recognized calorimetry expert when he came to Argonne. This expertise, coupled with the CEN fluorine technology, was ideal for this program. Ward was also one of the certifiable characters in the Division; he was always up to something. One of his first outside interests was learning to fly. Once he got his license, he liked to take the secretaries for rides, some of whom thought it had been a death-defying experience. Later on, he graduated to gliders and became quite successful in national competitions of high-performance sailplanes. Another personal quirk of Ward's had to do with food. Several people in the Division had gardens with the usual over-production of zucchini squash. Ward was always willing to take it off their hands, and nobody could figure out what anyone could do with that amount of squash. He also seemed to be the principal instigator of an ongoing weight-losing competition that went on for several years and involved various people, including John Ackerman and Paul Cunningham. The weighings were conducted on the platform scale at the end of H-Wing. It was rumored that the grand prize was to be a bottle of high-quality scotch, but nobody ever qualified for it. Jerry Johnson claims that Ward kept a personal weight-loss chart in which the first derivative of the curve was always zero.

The first calorimetry laboratory was set up in J-137. Provisions were made for both fluorine and oxygen combustions. The oxygen calorimeter was a platinum-lined, rotating unit so the products could be collected in a solution. The fluorine bomb was made of nickel. Members of the group at that time included Don Fredrickson, Elliot Greenberg, Ralph Nuttall (probably the quietest person ever to have inhabited Bldg. 205), Ed Rudzitis, Jack Settle, and Steve Wise. Larry Stein, who had transferred from CEN to the Chemistry Division in the mid-1950s, served as an advisor for the fluorine work.

Some of the early work involved calorimetric combustions of molybdenum in fluorine to form MoF_6. Sixteen combustions of oxygen with MoS_2 and equivalent mixtures of molybdenum and sulfur were used to obtain the enthalpy (heat) of formation of MoS_2. The heats of combustion of TiS_2 in oxygen and the heats of formation of ZrF_4 and BF_3 were measured by fluorination of the elements. In the 1960s, the scope of the calorimetry program expanded to include a wide variety of materials.

The Analytical Chemistry Laboratory

Throughout the history of the Chemical Engineering/Technology Division, one of the most vital parts of the organization has been the Analytical Chemistry Laboratory. Nearly every programmatic effort over the years has relied on their services in one way or another, and their contributions have not always been fully recognized in publications by the other groups, probably because analytical work often tended to be regarded only as a service. The group has sometimes been referred to as the "routine analytical laboratory," but many of the samples they have analyzed have been anything but routine due to interferences, matrix components that were difficult to dissolve, and other complications. Procedures often had to be modified or new ones developed to meet the particular need.

Doug Krause was the Group Leader when the Division moved to Bldg. D-205, and the people who were in the group during the 1950s are listed in Table 2-5. This unofficial list is based on the collective memories of a number of people, some technical reports, and various items in the *Argonne News* at the time, so it may not be complete. In addition, some individuals were occasionally assigned to other groups.

Alberta Hoover was the "dishwasher," situated in Laboratory A-101. Some of the individuals developed specialties; for example, Bob Schablaske became an X-ray specialist, and Myron Homa began to concentrate on gas chromatographic analyses.

The Analytical Chemistry Laboratory occupied almost all the laboratory space and all the office space in B-Wing, except the two rooms at the end, which were used for research by Carl Crouthamel and his group. Some of the offices were converted to laboratories for instruments such as the X-ray equipment. Because some of the samples to be analyzed were too "hot" to be handled in open laboratories, a "Junior Cave" was installed in G-102 where work could be done behind shielding. Bill Sovereign and John McCown and, later, Ray Popek were the principal operators of the Junior Cave. (The term "Junior Cave" could lead to confusion in that it was applied both to the facility in Bldg. D-205 to distinguish it from the Senior Cave in K-Wing, and to a remotely operated analytical setup used much for the same purpose at the Idaho site in connection with EBR-II).

Table 2-5. Analytical Chemistry Group in the 1950s

David Anthers
Steve Banacek
Jim Bingle
Lee Deutsch
Antoinette Engelkemeier
Alice Essling
Douglas Fairgrieve
Florence Ferry
Stan Flikkema
Irene Fox
Carol Garsky
Ruth Hanna
Beatrice Hjelti
Marilyn Hlavnicka
Jodie Hoekstra
Myron Homa
Miriam Jurlow
Ruth Juvinall
Gwen Kesser
Doug Krause
Eugene Kucera
Gene McCloud (Kucera)
John McCown
Ray Popek
Betty Reilly (Peterson)
Mary Robinson
Laury Ross
George Sato
Bob Schablaske
Arden Schilb
John Schilb
Chuck Seils
Bill Sovereign
Bob Sweezer
Jackie Williams

The Analytical Group in the 1950s had a wide range of capabilities, particularly considering the state of the technology at the time. Much of the work involved radiation counting, using Geiger counters or a single-channel gamma analyzer for specific isotopes. X-ray diffraction and fluorescence were valuable tools for compound identification and semi-quantitative determinations of elements. Standard gravimetric and volumetric methods (often EDTA titrations) were used extensively. A Beckman Model B colorimeter and a Beckman Model DU spectrophotometer were available for quantitative determinations of certain elements. The gas chromatograph was used for a variety of analyses, including glove-box atmospheres.

Because most of the research and development programs in the Division were concerned with the processing of spent reactor fuels, a large fraction of the analytical work involved the actinide elements, particularly uranium and plutonium, and a wide spectrum of fission-product isotopes. Due to the wide scope of the work, a great deal of effort was required to prepare and maintain standard solutions and to calibrate the equipment.

The standard procedure was for the person submitting the sample to fill out a card to indicate what analyses he or she wanted, the expected concentration range, and any other elements or matrix materials that might be present. A big problem for the researchers in many cases was the difficulty in obtaining representative samples, which was their own responsibility, and they occasionally blamed the analytical lab for unexpected results caused by their inadequate sampling procedures. On one occasion, Jim Knighton received a result that was nearly exactly one-half the value he expected. His group leader suggested that he talk with the analyst about it, and they did, indeed, find that a factor of two error had been made in taking an aliquot—a very rare occurrence. From that time on, however, Jim repeatedly tried to figure out how an incorrect aliquot could account for every obviously bad data point, and it was hard to convince him that they just don't take weird aliquots such as, for example, 5/8ths.

In 1954, Bob Larsen became the Group Leader of the Analytical Laboratory. He had joined Argonne in 1951 and had been working on dissolution procedures for alloy fuels. He made an important contribution to aqueous fuel reprocessing by determining the cause of explosions mentioned earlier when U-Zr alloy fuel was dissolved in nitric acid and showing that they can be avoided by adding a suitable amount of hydrofluoric acid to the system (ANL-5135). Bob was an excellent chemist and one of the memorable characters in the Division. He had lost the use of his legs through a bout with polio, and navigated about the building with a pair of canes and a stool on wheels. This disability seemed to have no effect either on his ability to work or his robust sense of humor. One thing in particular he is remembered for is his inexhaustible supply of limericks, none of which are printable. His loud voice and boisterous laugh once led Carl Crouthamel to comment that "Larsen reminds me of the Caracas bull—noted for its bellowing."

In some cases, new or modified analytical methods had to be developed. Laury Ross played a major role in much of this work. An example is an analysis for fission-product ruthenium, which was reported by Bob Larsen, Laury Ross, and Gwen Kesser.

In addition to his responsibility for supervising the Analytical Laboratory, Larsen maintained an ongoing interest in neutron cross sections and in burnup analysis of nuclear fuels. He became a nationally recognized authority in these areas and was one of the organizers of "round-robin" arrangements in which results from several laboratories on identical samples were compared.

In 1957 Bob Meyer, who had been involved primarily in spectrophotometry and X-ray analyses, joined the Analytical Group, where his specialties were spectrophotometry, polarography, EDTA titrations, radiochemistry, activation analysis, burnup determinations, and computer programming. He served as an assistant to Larsen, and several years later became a Group Leader in the Sodium Technology Program.

Before the 1950s, new analytical instrumentation had been slow to develop, but that situation began to change rapidly. Multichannel analyzers, coincidence counters, and lithium-drifted germanium (pronounced "jelly") detectors became available, greatly expanding the capabilities of radiation counting. Another example was a Cary Model 10 recording spectrophotometer that was procured by the Division. Alternatives to the old two-pan analytical balances, *e.g.*, the Mettler and Sartorius models, were introduced, and these were followed later by the fully automatic electronic balances. Solid-state digital readout instruments were not yet available in the 1950s, but were just around the corner.

Almost all of the research and development programs in the Division depended heavily on the Analytical Chemistry Laboratory for their experimental results. One interesting facet of this situation was that a large number of samples that contained uranium, plutonium, or other special materials were generated in the various experimental programs, and these ended up in waste solutions from the analytical lab. Nobody knew the exact amounts of these materials in the samples until they were analyzed, which created a complicated bookkeeping problem. A combination of good record keeping and Larsen's cooperation with the other group leaders fortunately produced material balances that were acceptable to the Special Materials people.

One unusual assignment given to the Analytical Chemistry Laboratory in the early 1950s was to train a group of young Du Pont people who were to become analytical laboratory technicians at the new Savannah River facility near Aiken, South Carolina.

Analytical Research and Nuclear Constant Measurements

Also located in B-Wing were a number of research programs that were somewhat related to the Analytical Chemistry Laboratory, but were not a part of it. These were originated for the most part by Carl Crouthamel, who had come to Argonne as a Senior Scientist from

Ames Laboratory in 1950. He was an expert in gamma-ray spectrometry and was also interested in the development of analytical methods for the various constituents of nuclear fuels and in capture-to-fission cross-section ratios for isotopes in fast breeder reactors. He played a major role in the acquisition of new analytical instrumentation as it came on the market.

Working with Crouthamel in the early 1950s was Carl Johnson, who left the Laboratory for a couple of years to obtain a Ph.D. degree at Michigan State University. Crouthamel and Johnson worked on scintillation spectrometry for fission-product analysis and developed spectrophotometric methods for the determination of uranium, molybdenum, technetium, tungsten, titanium, and niobium, using thiocyanates in an acetone medium. Some work was also done on paper chromatographic analyses of irradiated uranium. Various other individuals were involved in analytical development; for example, Sy Vogler and Roberta Shor worked out a procedure for zirconium analysis under Dr. Vogel's direction.

Stan Flikkema, who also appeared on the scene in the 1950s, was best known by his colleagues as a perfectionist, perhaps to a fault. He was engaged in several different areas of work, including studies of zirconium dissolution explosions, X-ray spectrophotometric methods for uranium and plutonium in solution, optical microscopy, and precision weighing on the microbalance. A revealing story about Stan's personality concerns a trip he made to the stockroom to get a bottle of ink. When Esmer Zeno produced the bottle, Stan became quite exercised and refused to accept it because it was slightly dusty. Esmer, with his usual tact, disappeared behind the shelves, polished up the bottle, brought it back and told Stan "Here's a clean one."

Crouthamel, Larsen, and others were interested in fast neutron cross sections because most of the existing information was on thermal systems, and data were needed for the EBR-II project. The Division was in an especially good position to do this research because it had access to irradiated fuel from EBR-I and a capability for identifying specific isotopes by radiochemical and counting techniques. Peter Kafalas, who was a specialist in this type of work, joined the group in the mid-1950s. Much of his effort was directed to neutron capture/fission ratios for uranium and plutonium and fission yields of cesium-137, which were important in determining breeding gain.

Much of the cross-section work was done in CP-5. On one occasion, Crouthamel had an irradiation going when something in the convertor system broke, contaminating a number of graphite stringers. The only practical way to remove the stringers was by manual manipulation and, as was frequently done in those days, a large number of people were used so no one person would receive more than an allowable radiation dose of a few seconds. Martin Steindler reminisces, "I lost a good pipe because I had stuck it into my back pocket and then added the gloves I had used to move the graphite, which turned out to be hot, but I didn't find this out until I got to the monitors in Bldg. 205. The pipe and the gloves, alas, had both become DAW (dry active waste)."

Especially Significant Publications

Because the 1950s were highly productive years for CEN, the journal publications, ANL topical and progress reports, book chapters, *etc.*, are far too numerous to cite in detail. A few of these, however, deserve special mention as landmark sources of information that were cited widely and used throughout the world's nuclear energy programs.

Much of the work done by members of CEN in the 1950s is reported in considerable detail in the proceedings of the 1955 and 1958

Geneva Conferences on the Peaceful Uses of Atomic Energy and the proceedings of the Brussels Conference in 1957. Reviews of CEN work may also be found in the *Reactor Handbook*, 2nd. Ed., Vol. II (Interscience), and in various volumes of the *Progress in Nuclear Energy Series* (Pergamon Press).

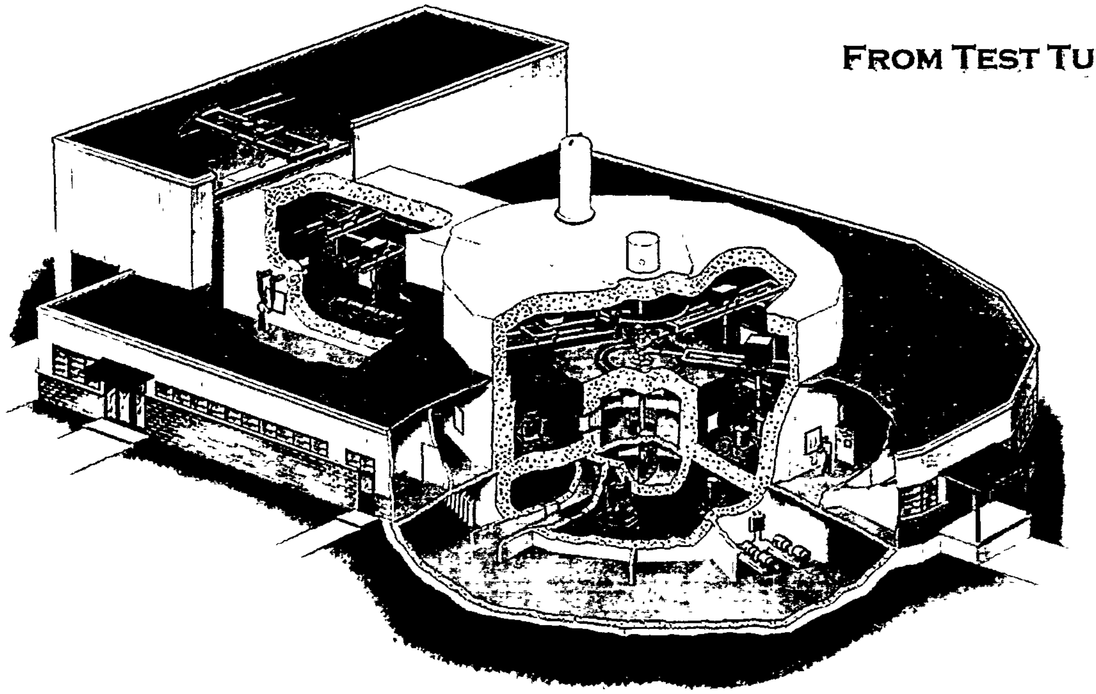
In the 1950s, thermochemical information on the compounds involved in fuel reprocessing, particularly for pyrometallurgical and fluoride volatility processes, was, in many cases, very sketchy or missing altogether. Alvin Glassner assembled essentially all the thermochemical data available at the time in a topical report, "A Survey of the Free Energies of Formation of the Fluorides, Chlorides and Oxides of the Elements to 2500 K," which was issued as ANL-5107 (August 1953). An updated and corrected version of this report appeared as ANL-5750 in 1957. These compilations, of necessity, contained many thermochemical values that were estimated, derived from theoretical principles, or based on analogy and were of questionable accuracy. Because of this, they were maligned later on by the calorimetrists and other "pure" scientists, but at the time they were extremely useful to those who had to predict how the individual actinide elements and fission products would behave in a process, and almost any information was better than none. On the whole, the actual performance of the processes turned out to be fairly close to what Glassner's compilation had predicted.

Because the fission-product spectra in fast reactors differ significantly from those for thermal reactors, information was needed to assess the impact of this fact on the reprocessing of EBR-II and other fast reactor fuels. Les Burris and Ira Dillon met this need by extensive fission-yield calculations that culminated in two ANL reports: "Estimation of Fission Product Spectra in Fuel Elements Discharged from the Power Breeder Reactor and EBR-II," ANL-5334 (October 1954) and "The Estimation of Fission Product Spectra in Discharged Fuel from Fast Reactors," ANL-5742 (July 1957). The distribution of activities was given for various cooling times of interest. Calculations of this kind are routine today, given the computer programs and data banks on cross-sections as a function of neutron energy, *etc.*, that are available, but they were long and tedious at that time. The results were essential in designing the shielding and heat-removal equipment for processing EBR-II fuel.

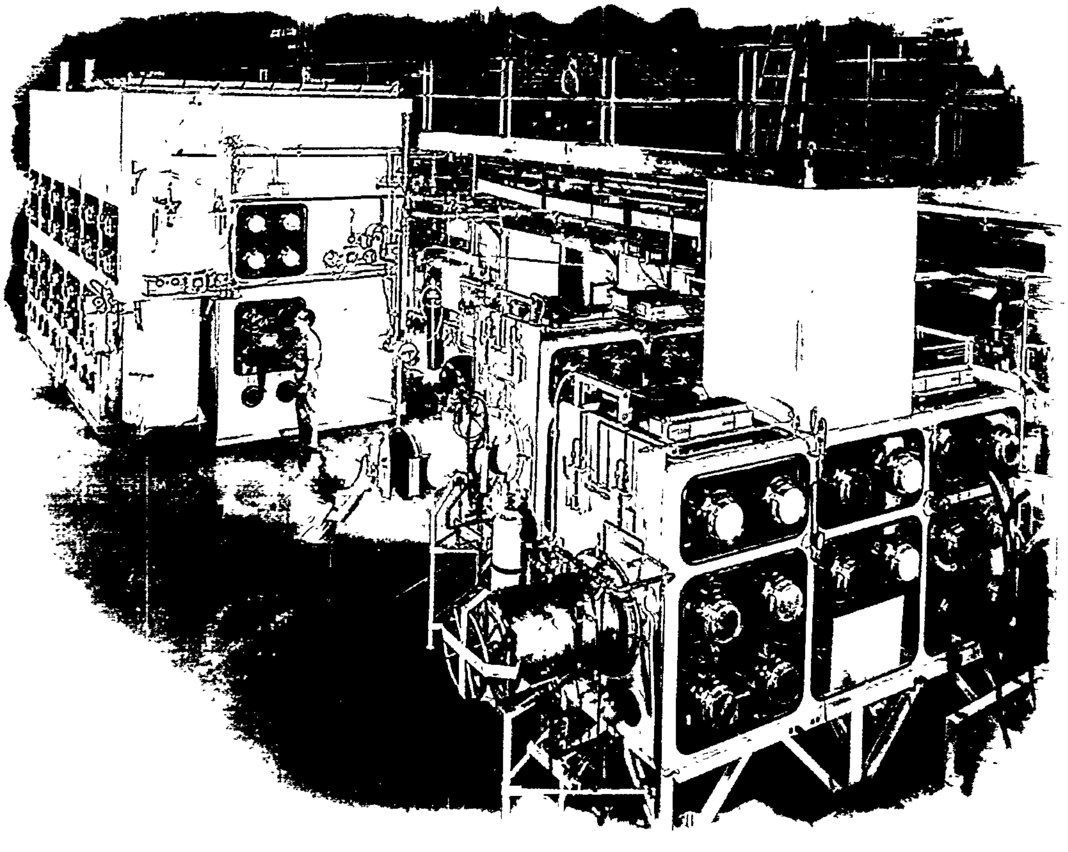
A book that was assembled and edited by Carl Crouthamel in the 1950s and published in 1960 is *Applied Gamma Ray Spectroscopy*, C. E. Crouthamel, ed., Pergamon Press (1960). One of the several valuable uses of this book was the identification of fission-product elements by the energies of their gamma ray emissions.

Perhaps the most widely recognized publication by CEN was a quarterly journal, *Reactor Fuel Processing*, which began in February 1958. In the late 1950s, several different types of reactor fuel were being touted, *e.g.*, metal, oxide, carbide, and even more schemes for processing them were proposed. The purpose of this journal was to "assist those interested in keeping abreast of important developments" in the reactor fuel reprocessing field. Dr. Lawroski had proposed the idea, and produced the publication for the AEC with the help of several CEN staff members. The information was timely, and one particularly interesting thing about it was that much of it appeared in unclassified form for the first time in that journal. In 1967, *Reactor Fuel Processing* was merged with *Power Reactor Technology*, which was also written by ANL staff, to a new quarterly called *Reactor and Fuel Processing Technology*. At this juncture, the nature of the publication changed in that it consisted of review articles rather than reports of current research and development. The Atomic Energy Commission (AEC) took over the publication in 1968 and it became *Reactor Technology* in 1970.

During the late 1950s and early 1960s, one of the largest and most important programs conducted by CEN was its role in the design and construction of the EBR-II Fuel Cycle Facility in Idaho. The excellent book that covers this work in detail, *The EBR-II Fuel Cycle Story*, written and compiled by Dr. Charles E. Stevenson, and published by the American Nuclear Society, La Grange Park, Illinois in 1987, was mentioned earlier.



1960-1970: TURBULENT TIMES



1960-1970

(top) Cutaway view of Fuel Cycle Facility. In the circular building (argon cell), fuel retrieved by dismantling EBR-II subassemblies in an adjacent air cell was processed and fabricated into new fuel elements for recycle to the reactor.

(bottom) Inert atmosphere glove-box facility in Bldg. 310, where large-scale studies were conducted on pyrometallurgical processes for EBR-II fuel.

3

1960-1970: Turbulent Times

The sixties was a decade of considerable turbulence in the United States and abroad. Dissention was in the air with four assassinations, bitter civil rights confrontations, war, political upheavals, international threats, riots, student uprisings, and challenges to the national mores of the time. The ANL Chemical Engineering Division was fairly well insulated from most of these problems, but it also underwent some major changes. In 1963, Dr. Richard C. Vogel succeeded Dr. Lawroski as the Division Director. The programs on aqueous fuel reprocessing had all but disappeared, but the fluoride volatility work continued at a strong pace with its main emphasis shifted toward oxide fuels, which were becoming the standard for commercial power reactors. A greatly expanded effort was placed on pyrometallurgical processes for the EBR-II Fuel Cycle Facility. This effort included not only the main-line melt refining process for the metallic EBR-II fuel, but also auxiliary processes for recovering melt refining skulls, extraction of plutonium from the metallic uranium blanket, and liquid metal-molten salt processes for other types of fuel. The chemical and engineering aspects of the liquid sodium coolant used in EBR-II became a major research program. The metal-air and metal-water reaction studies, calorimetry program, fuel-preparation studies, and high-temperature materials investigations continued to flourish. Basic chemical and engineering research studies were continued. On January 26, 1968, the AEC informed ANL that the AEC laboratories would be used for public health and environmental research, and on December 1, 1969, the Center for Environmental Studies was established at ANL. This was a forerunner of the Laboratory's environmental divisions. Shifts in the AEC priorities and accompanying funding cuts eliminated nearly all of the fuel-reprocessing work in the Division, necessitating some layoffs and transfers of personnel to other ANL organizations, including the group at Idaho. Some slack was taken up by new programs on batteries, coal combustion, and other work. A third Geneva Conference on the Peaceful Uses of Atomic Energy was held in 1964; CEN was well represented by papers on a variety of subjects.

THE DOMESTIC AND INTERNATIONAL CLIMATE

The American public, already concerned about the escalating possibility of a nuclear war with the U.S.S.R., was shocked by the news that a U-2 spy plane piloted by Gary Powers had been shot down by the Soviets on May 1, 1960. This incident killed plans for a Paris summit conference with Nikita Khrushchev, thereby increasing the tensions. The U.S.S.R. was known to be producing nuclear weapons and thought to be well ahead of the U.S. in the development and production of intercontinental ballistic missiles (ICBMs). Civil defense became an important subject and a few U.S. citizens, including Ed Rudzitis in CEN, constructed fallout shelters.

John F. Kennedy defeated Richard M. Nixon in the 1960 presidential election. Kennedy, keenly aware of the nuclear arms race and the so-called "missile gap," had a positive attitude toward U.S. nuclear and space programs. Early in his administration, Cuba became a problem with its confiscation of U.S. property, followed by the Bay of Pigs and the "Cuban Missile Crisis." This confrontation with the U.S.S.R. finally resulted in a partial nuclear test ban treaty and the "hot line" between Washington and Moscow.

On November 22, 1963, the nation was stunned by the assassination of President Kennedy at a parade in Dallas. At Argonne, the employees were given the rest of the afternoon off. The suspected assassin, Lee Harvey Oswald, was shot and killed by Jack Ruby, a Dallas nightclub owner.

Lyndon B. Johnson, the Vice President, assumed the presidency upon Kennedy's death and won the 1964 presidential election in a race against Barry Goldwater. On the domestic front, his concerns were mainly with civil rights and a collection of programs that was dubbed "The Great Society." Johnson's administration, however, was plagued by the highly unpopular Vietnamese war, race riots, and student uprisings as well as many other problems, and he opted not to run for reelection.

Richard M. Nixon was victorious in his presidential campaign against Hubert Humphrey in 1968. Nixon's forte was foreign affairs; he was successful during his first term in winding down the Vietnam war somewhat and in establishing relations with China. Neither Johnson nor Nixon seemed to have a strong pro- or anti-nuclear bias, but both recognized the necessity to maintain a strong nuclear defense and accepted the idea of nuclear power generation. During the Democratic primary campaign in 1968, Senator Robert F. Kennedy (John's brother and former U.S. Attorney General) was assassinated by Sirhan B. Sirhan in Los Angeles. Sirhan was convicted of murder.

Civil rights came to the forefront as a major movement in the 1960s. The decade began with peaceful demonstrations and massive rallies, although many of the participants were arrested. In 1965, Malcolm X, a black nationalist leader, was shot to death at a rally in Harlem, and the race issue exploded with extensive riots, first in the Watts section of Los Angeles, and later in several other cities. On April 4, 1968, Dr. Martin Luther King, Jr., was assassinated by James Earl Ray in Memphis, and this event ignited further rioting.

The Vietnam War began to heat up in 1964 when U.S. destroyers were supposedly attacked by North Vietnamese torpedo boats in the Gulf of Tonkin. The U.S. responded by bombing North Vietnam and sending the first combat troops to Vietnam in 1965. The U.S. troop strength escalated to 525,000 in 1967, and then to 540,000 in response to the North Vietnamese Tet offensive. That same year the North Koreans seized the crew of the U.S.S. *Pueblo*. Much dissatisfaction was expressed by U.S. citizens that the South Vietnamese were not doing their part in the war, so a "Vietnamization" was initiated in which the U.S. troop strength was reduced to 340,000 by 1970.

As if all the above troubles were not enough, the nation had to cope with the "Hippie" movement, Vietnam War protesters, and various student dissidents. Many young people fled to Canada to avoid the U.S. draft while others demonstrated nationwide against the Vietnam War, occupying campus buildings and destroying properties they regarded as targets. A graduate student was killed by a bomb at the University of Wisconsin.

The U.S. space program continued with the launching of Echo I, the first communications satellite, and Tiros I, the first weather satellite. The Soviets fielded two manned space missions in 1961, and the U.S. followed with its first suborbital flight by Alan Shepard. A series of space flights both by the U.S. and the Russians was conducted during the period. A tragic accident occurred in 1967 when three U.S. astronauts were killed in a test launch fire, and that same year a Soviet cosmonaut died during a reentry. The "space gap" was being closed rapidly by the Americans, especially with the introduction of the Apollo system in 1968, and on July 20, 1969, Neil Armstrong became the first man to walk on the moon.

Large-scale nuclear power finally came into its own in the 1960s. To the public, nuclear power was a new and arcane technology, and Alvin Weinberg, the director of Oak Ridge, referred to leaders in the field as a "nuclear priesthood." In 1963, Jersey Central Power and Light ordered a 620-MW plant and Fermi-I went critical. The General Electric Co. projected a cost of 4.3 mill/kWh for power produced in their Oyster Creek turnkey operation. The first big year for power reactor orders was 1965. The U.S. utilities ordered nine units [>6,000 MW(e)] and 16 other units were ordered by other nations. The trend continued with 20 reactors in 1966 and 31 in 1967, but began to wane with 16 in 1968 due to the increasingly long construction schedules and escalating costs. Argonne's EBR-II, a 62.5-MW(t) experimental fast breeder reactor, began operation in 1964. The "(t)" in MW(t) indicates thermal power, or heat; and "(e)" is used similarly in MW(e) to indicate electrical power.

Nuclear power was also becoming popular in foreign countries. In 1961, the first German power reactor, the Kahl plant supplied by the U.S., went critical, and Canada began a nuclear power demonstration with their heavy-water CANDU reactor in Ontario in 1962. Japan's JPDR 12.5-MW(e) boiling water reactor (BWR) demonstrated their first generation of nuclear power. The first Soviet RBMK reactor was commissioned in 1964. In 1967, France switched from gas-cooled to pressurized water reactors (PWRs). Belgian utilities, in 1968, ordered their first two power reactors, Doel-1 and Tihange-1, and nuclear electricity was produced for the first time in Spain and the Netherlands. Argentina contracted with Siemens in West Germany for their Atucha-1 reactor.

Some other nuclear highlights of the 1960s: The 1961 "Project Gnome" test was the first peaceful nuclear explosion under the Plowshare program. The N.S. *Savannah* went critical in 1962 and began commercial operations in 1965, but it generated little interest in the shipping industry or elsewhere, and was decommissioned in 1967. (The prefix "N.S." refers to a nuclear-powered civilian vessel in the same way that "S.S." denotes a steamship and "M.S." a motor ship.) Now moored at Charleston, South Carolina, the *Savannah* serves as a museum. In 1965, SNAP-10A became the first space reactor and in 1969, SNAP-27, a nuclear thermoelectric generator, was placed on the moon by Apollo-12 astronauts. The West Valley reprocessing plant, in which Walt Rodger played a major role, was opened in 1966. That same year, Weston, Illinois, was selected for the new accelerator facility that was to become known as "Fermilab." Preservation of certain foods by irradiation began to be accepted, starting with irradiated potatoes in Canada and the U.S.S.R. Other food irradiation studies continued in the U.S. under the auspices of the AEC and the Army.

Two significant reactor accidents occurred in the U.S. in the 1960s. In 1961, the first U.S. reactor fatalities resulted from a steam explosion at the SL-1 reactor at the Idaho Test Site, which killed three servicemen. The SL-1 was a prototype 3-MW(e) military reactor used for training, and the accident was attributed to a human operational error, but the details are not fully known (or at least made public). Recovery and handling of the bodies involved problems not faced before by emergency personnel because of the high radiation levels. The other accident, in 1966, was a meltdown of the metallic Fermi-1 core, which overheated when a vane in the liquid metal coolant system became dislodged. Two nuclear submarines were lost at sea due to accidents: the U.S.S. *Thresher* in 1963, and the U.S.S. *Scorpion* in 1968. It is not known whether these accidents were nuclear in nature. In 1969, a serious fire at the Rocky Flats Plant produced widespread plutonium contamination within the plant and to a lesser degree in nearby outside areas.

The antinuclear activists continued with protests, denouncing nuclear power and stalling reactor licensing wherever they could. The WASH-740 report was updated in 1964 with conclusions that were even more frightening than the original ones. The Atomic Industrial Forum (AIF) recommended that the conclusions not be published, and they were kept under wraps until David Comey, a nuclear critic, pried them loose under the Freedom of Information Act in 1973. Ernest Sternglass, in 1969, claimed that nuclear power would cause 400,000 infant deaths due to fallout. Arthur Tamplin from the AEC staff said that number was at least 100 times too high and he was backed up by John Gofman at Lawrence Livermore. The Sternglass-Tamplin-Gofman numbers were debated at length, but could neither be proved nor disproved conclusively because they were based on uncertain probabilities of accidents and gross extrapolations of data that were of questionable validity. The problem of nuclear wastes also began to rear its head seriously in the late 1960s.

REACTORS

The experimental reactor EBR-II first achieved dry criticality on September 30, 1961, and began operation with the sodium coolant on November 11, 1963. It produced its first electricity on August 18, 1964, and was dedicated, along with the adjoining Fuel Cycle Facility, on September 13, 1965. Most of the other new ANL reactors were special-purpose facilities that were not directly related to the programs in CEN other than the reactor-safety studies. BORAX-V, mentioned earlier, which was designed to feed superheated steam into a turbine, went into operation in 1962. JUGGERNAUT, a low-power [250 kW(t)] reactor that was started up on January 11, 1962, and designed mainly for nuclear research, was used to take some of the heavy research load being supported by CP-5. JANUS, another 250-kW(t) reactor, had two faces (hence its name), which provided two different levels of radiation. It reached criticality on August 3, 1964 and was the first reactor dedicated to biological research. A series of Zero Power Reactor (ZPR) critical assemblies was built at NRTS in Idaho to simulate reactor configurations for engineering studies. The Zero Power Plutonium Reactor (ZPPR), which went critical on April 16, 1969, was used for physics studies of liquid metal fast breeder reactors (LMFBRs) and could simulate such reactors having power levels as high as 1,000 MW(e).

THE DIVISION

The Chemical Engineering Division entered the 1960s with Dr. Lawroski as the Division Director, Dr. Richard Vogel and Dr. Walton Rodger as Associate Division Directors, and Victor Munnecke as the Assistant Division Director. In 1963, Dr. Lawroski became an Associate Laboratory Director. Although he was no longer a member of CEN, it was still under his jurisdiction, and he continued to maintain close contact with the CEN management and staff personnel. In 1969, Dr. Lawroski became a member of the National Academy of Engineering. Dr. Vogel took the helm from Dr. Lawroski as CEN Division Director in 1963. Dr. Rodger left ANL in 1960 to become a partner in a consulting firm, McLain-Rodger Associates, joined Nuclear Fuel Services as Vice President for Research and Development in

1962, was the General Manager of the West Valley Fuel Reprocessing Plant (W. R. Grace Co.) from 1962 to 1964, and then returned to consulting. Vic Munnecke departed from ANL in 1964, and was replaced by Frank Maston until Everett Proud arrived in 1966. Before joining CEN as a Section Head in 1963, Dr. Arthur Tevebaugh had been a chemist at the Knolls Atomic Power Laboratory (KAPL), operated by the General Electric Company, and was involved in fuel-cell development at the General Electric Research Laboratory. He was appointed Associate Division Director in 1969. Donald Webster, a chemical engineer from the Savannah River Laboratory (SRL), operated by the E. I. du Pont de Nemours and Co., was also appointed Associate Division Director in 1969. He had acquired extensive nuclear experience at the Met Lab, Oak Ridge, Hanford, and Idaho Falls before joining SRL.

In these new assignments, Tevebaugh was responsible for the electrochemical programs, high-temperature properties studies, calorimetry, and basic physical and chemical research. Webster directed the fluidized bed and coal-combustion work, engineering equipment research and development, and nuclear fuel reprocessing studies. Les Burris was a Section Head for pyrochemical processes and, in 1966, was appointed head of the Fuel Recycle Section of the Liquid Metal Fast Breeder Reactor Program Office at ANL. Bob Steunenberg replaced Les when he was transferred. Upon his return to CEN in 1969, Les became an Associate Division Director and Program Manager of Sodium Technology with Paul Nelson and Fred Cafasso, respectively, as Section Heads for Engineering and Chemistry. The following individuals served as Section Heads at one time or another in the 1960s:

Les Burris
Fred Cafasso
Elton Cairns
Carl Crouthamel
Al Jonke
Paul Nelson
Bob Steunenberg
Art Tevebaugh

Management changes were not limited to CEN in the 1960s; two new ANL Laboratory Directors came on the scene. Norman Hilberry announced his retirement, and Dr. Albert V. Crewe became the third Laboratory Director on November 1, 1961. Dr. Hilberry was elected president of the American Nuclear Society for the year 1965-1966. Dr. Crewe, born in England, had been a professor of physics at the University of Chicago with special interests in particle accelerators and high-resolution electron microscopy. He had served as Director of the Particle Accelerator Division (PAD) at ANL from 1958-1961. During these periods, he continued to conduct research on high-magnification electron microscopy at the University, and his work received wide recognition in the scientific community. At this time, interest in the EBR-II project was at its peak. Dr. Crewe, although not as outgoing as Hilberry, was approachable and seemed to relate reasonably well to the ANL staff. Crewe stepped down and later became the Dean of Physical Sciences at the University of Chicago. He was replaced on November 1, 1967, by Dr. Robert Duffield, ANL's fourth Laboratory Director. Dr. Duffield had been at the Los Alamos Scientific Laboratory (LASL), operated by the University of California, during the Manhattan Project. Duffield came to ANL during a difficult time when Laboratory funding was being reduced drastically, particularly for EBR-II and other fast breeder reactor programs, causing numerous layoffs. He reminded the ANL staff that research and development jobs funded by the government offer no guarantee of continuing employment; the staff people, of course, knew that, but didn't appreciate being reminded of it.

By 1960, the many people who had joined the CEN staff some ten years earlier had mostly settled down in a suburban life with a family, a mortgage, and often a dog, and seemed to be largely immune to the influence of the Hippies and Flower Children that was sweeping the country.

An ANL milestone of sorts was reached in 1961 when Branko Dokmanovic was issued Badge No. 10,000. With a few exceptions prior to 1952, ANL payroll numbers have been issued serially, and are never reassigned, so one can get a general idea of a person's length of service from his or her badge number. As one might guess, Badge No. 00001 was issued to the first Laboratory Director, Walter H. Zinn.

During the 1960s, a group of Senior Scientists formed the Argonne Senate. The stated objectives were to exchange technical information and improve the quality of ANL research programs, but some felt that the motivation was basically to inject more of an academic atmosphere into ANL, possibly with perks such as tenure and sabbaticals for senior staff personnel. This movement was viewed somewhat coolly both by the ANL administration and by those staff members who were not at the senior level. Making almost all the staff eligible for the Senate solved the latter problem, and the movement quieted down after a few years.

Another interesting event occurred when the American forces fighting in Vietnam were having an especially difficult time coping with the unorthodox tactics of the North Vietnamese army, such as their tunnel systems. Dr. Crewe, apparently in response to a Government request, called a meeting of the ANL staff and requested them to generate some technical solutions that might aid the American soldiers. Some people tried to comply, but it became quite obvious that ANL staff were neither well-versed in jungle combat nor in coming up with instant solutions. (The time available for implementation of any new ideas was two or three weeks.)

By 1960, some changes had begun to occur in the major programs of the Division. In the area of aqueous fuel reprocessing, existing processing methods were already in place for large-scale applications, and the Idaho Chemical Processing Plant (ICPP) was able to handle the lower-volume specialized fuels. Consequently, ANL could no longer justify a large research effort in this field.

In the pyrometallurgical program, development work on melt refining was nearly completed and process equipment was being installed in the FCF at the EBR-II site. The term "pyrometallurgical" was applied to these processes because the reactor fuel remained in the metallic state throughout the process. When the research effort was redirected nearly entirely to processes for recovering uranium from the melt refining skulls and extracting plutonium from the blanket, the term "pyrochemical" came into use to reflect the fact that many of the operations such as liquid metal-molten salt extractions, precipitation of products from liquid metal solutions, transport of fuel constituents as chlorides in molten salts, and distillation were more typical of chemical than metallurgical processes. Jim Battles, however, argues with some justification that the term "pyrometallurgical" is still valid because operations of this kind are used in the metallurgical industries. His opinion may be colored a bit by the fact that he is a metallurgical engineer. More recently, the term "pyroprocess" has come into vogue to cover all the bases, but it might be misleading, too, in that it implies any high-temperature process.

The emphasis in the fluoride volatility program was changing toward oxide fuels, the use of elemental fluorine, rather than an interhalogen as the primary fluorinating agent, and improved schemes for plutonium recovery. Much discussion was going on in the 1960s as to relative merits of metal, oxide and carbide reactor fuels and the relative suitability of aqueous, pyrochemical and fluoride volatility processes for the various fuels. This question was addressed in a report (ANL-7137) published by Milt Levenson, Virgil Trice and Bill Mecham in 1966. The report did not end the discussions, but did shed some light on the question. One of the uncertainties was in the types of reactors that would prevail in the future, *i.e.*, fast breeders (metal fuel), boiling and pressurized water reactors (oxide fuel), or high-temperature, gas-cooled reactor (carbide fuel). Oxide-fueled fast reactors were also under development in foreign countries.

The reactor safety work on metal reactions with air, water and other substances continued until the mid-1960s under Lou Baker and Dick Ivins, when a decision was made to transfer the program to the Reactor Analysis and Safety Division (RAS). At about the same time, the ANL sodium chemistry and technology programs were consolidated into a single entity in CEN.

Carl Crouthamel instigated a new area of work for CEN, which grew into a major program, when he became interested in regenerative galvanic cells. This work was supported strongly by Art Tevebaugh, who had been working on fuel cells at General Electric. This program was greatly enhanced by the arrival of Dr. Elton Cairns from the General Motors Research Laboratory. Elton was an extremely competent electrochemical engineer who had done his Ph.D. thesis work under Prof. Charles Tobias (a member of the CEN Review Committee for a period of time). He also seemed to know everybody who was doing serious electrochemical work in the U.S. and abroad and was well connected with key people in the government agencies. These connections were most helpful in seeking funding for the program.

The calorimetry work continued to thrive under Ward Hubbard and gained a valuable new staff member when Pat O'Hare, born and educated in Ireland, appeared on the scene. The Analytical Chemistry Laboratory, as well as the analytical research and nuclear constant studies, continued. Ben Tani became responsible for the X-ray laboratory. Jim Battles joined ANL in 1964 and began working with Russ Edwards on the chemical vapor deposition of tungsten on complex W-UO_2 cermets (part of the ROVER project for nuclear powered space vehicles) and other studies including high-temperature mass spectrometry of potential nuclear fuels. Hal Feder had the responsibility for several research programs, including Irv Johnson's extensive studies of liquid metal solubilities and thermodynamic properties of the solutions. As a Senior Scientist with wide-ranging experience, Hal served as sort of a mentor (and critic) for many of the staff members.

Feder was a stickler for accuracy and challenged almost every detail when one was writing a journal article; the authors began referring to this painful editing process as "Federization." Martin Chasanov, Marv Tetenbaum and Len Leibowitz investigated the thermodynamic properties of refractory metal compounds at high temperatures. John Gabor and others conducted a systematic study of the properties of fluidized beds, which became a major area of expertise for CEN. Vic Maroni, who also arrived in the 1960s, began his work on lithium-tellurium electrochemical cells and conducted spectroscopic studies of molten salt solutions. A significant effort was devoted to methods for the preparation of carbide reactor fuels.

The Division was requested to perform two special jobs supported by outside funding. One was the preparation of a small amount (30 grams) of isotopically pure ^{24}Mg metal from the oxide. This was accomplished successfully by Norm Chellew in his usual methodical, very careful (and slow) way with no significant loss of the valuable isotope. The other was to prepare high-purity ^{238}Pu metal suitable for space applications. That was a difficult job because the alpha activity of ^{238}Pu is about 300 times that of ^{239}Pu, and the neutron emissions from (α-n) reactions required special shielding. Jack Fischer and Paul Nelson took the lead in this project. At one point, Bob Steunenberg, who was then the Section Head, commented that this was a lot more demanding and expensive than working with ordinary plutonium. Les Coleman, the Division Safety Officer, replied sourly, "There is no such thing as 'ordinary' plutonium."

In the late 1960s, a young technician who decided to take some courses at the Illinois Institute of Technology in Chicago caused some excitement in the Division. Being concerned about his personal safety in that neighborhood at night, he started carrying a loaded derringer pistol in his pocket, which was understandable, but strictly forbidden by Laboratory rules. One day, in the men's locker room of Bldg. 205, the gun accidentally discharged, wounding the man in the forearm and scaring everybody in the area. Les Coleman, the Division Safety Representative, was highly upset, in part due to the fact that he had to deal with the DuPage County Sheriff. The employee was fired, due to the serious infraction of the regulations. Dr. Vogel's comment on the matter was that he would tolerate "no further gunplay in the locker room."

MANAGEMENT

One of the first things Dr. Vogel did when he became Division Director in 1963 was to move the Division office from L-Wing down to A-Wing. Although perhaps a symbolic move, it did in fact seem to bring the management and staff people closer together. Dr. Vogel, like Dr. Lawroski, was a demanding manager, and he insisted on quality work and reporting. Group reports were relaxed to a monthly schedule but were expected to be more comprehensive and of higher quality. Group Leaders almost routinely received copies of their preceding monthly reports with Dr. Vogel's comments written in the margins. It was obvious that he was staying on top of the work in the Division. He was a strong supporter of Joe Royal's Technical Editing Group. Just a few days after Dr. Vogel had moved into his A-Wing office, the Radiation Safety people detected a small spot of activity on one of the chairs in a routine survey. He became quite

Fig. 3-1. Richard Vogel

upset over the matter, and everybody who had been in the area was called in to have his pants checked, but no culprit was found. He sometimes kidded about putting up a print of El Greco's menacing painting, *View of Toledo*, behind his desk to intimidate visitors to his office.

The Assistant Division Director had a strong influence on the general tone of the Division because he handled the mundane administrative affairs and interacted with everybody. In the early 1960s, everyone was used to Vic Munnecke, who had been there since the Division's inception, and was a fairly "laid back" person. Frank Masten, who replaced Vic, was a businesslike individual who did his job rather quietly. Everett Proud, who replaced Frank, however, shook things up a bit. He had been at KAPL at one time (along with Tevebaugh) and had held several responsible management positions before he came to ANL from the Sperry Rand Research Center. He had a gruff manner, and his appearance and demeanor reminded one of a tough military officer (which he had been in WWII, and then in the Army Reserve). When one approached him for something such as a blackboard or bookcase, for example, Everett's immediate response was usually to growl "no way"—and then it would suddenly appear a few days later. Actually, he was effective in solving administrative problems and went to bat for CEN people on many occasions. At one time, office occupants were allowed to choose the color when their rooms were repainted, and a secretary at the east end of A-Wing selected a brilliant flamingo pink. The next morning, when Dr. Vogel arrived at work, the sun was creating a hot pink glow all down the length of A-corridor, and he told Everett to have that office repainted by the end of the day. It was. The same policy applied to the laboratories, and when Bill Walsh's lab needed repainting, he had it done in a subdued version of the blue and gold colors of the University of Notre Dame. Some wondered if Jim Battles in the lab next door would opt for Alabama crimson, but he didn't.

Argonne, like business firms, was attempting to stay on the leading edge of new management trends, as they became popular. Many CEN supervisory personnel attended training sessions, seminars, and short courses both on and off-site. Carter Johnson of the Personnel Department, an enthusiastic, friendly young man, handled most of these activities and became acquainted with many CEN people. When the Program Evaluation and Review Technique (PERT) along with the Critical Path Method (CPM) was just coming into its own in the early 1960s, John Vogel introduced these techniques to the CEN staff in one of the most entertaining seminars in the history of the division. He went into considerable detail in illustrating how these planning and management tools could be used to set up a moonshining operation in the Tennessee hills. The next major fad in management circles was MBO (Management by Objectives), and the group leaders and section heads were duly instructed in these methods.

Up to about 1960, the regular staff personnel had little direct interaction with the AEC managers in Washington, but that began to change gradually. Those managers were beginning to require a more detailed accountability in the form of program reviews, special progress reports, *etc.*, but the situation had not yet become what one would call onerous.

A major shock wave struck the entire nuclear community in 1965 when Milton Shaw was appointed Director of Reactor Development and Technology (RDT) at AEC Headquarters. He was an alumnus of Admiral Rickover's operation, and told the Joint Committee on Atomic Energy (JCAE) that the AEC laboratories under his jurisdiction "would be converted from a research orientation to one stressing disciplined engineering application." He felt that, once the light reactors were commercialized, the federal research effort should be placed on advanced concepts such as the fast breeder. Research was downplayed in favor of engineering. The Loss of Fluid Test (LOFT), which was to have been a sacrificial reactor to study safety problems in light reactors, was rescheduled to test standards of reactor design. Shaw believed there could be no safety problems if the engineering was done right. The strong deemphasis of research and safety upset many people, particularly at NRTS and ORNL, and the safety issue escalated to a national level in the JCAE, Congress, the nuclear industry, and the general public. When Shaw was appointed, ANL felt the effects almost immediately. The Chemical Engineering Division began receiving several directives per day. Early in the Shaw regime, Milt Levenson served as sort of a lightning rod for the Division because he had intimate knowledge of the EBR-II project; he was also articulate and quick on his feet. The net effect, however, was that the fast breeder fuel processing work in CEN and other laboratories began to wane and was essentially phased out by the end of 1969. Representatives from various laboratories who attended a conference titled "Symposium on the Reprocessing of Nuclear Fuels" at Ames, Iowa, in August 1969 felt as if they were participating in a technical wake.

Shaw was not the only harbinger of heavy-handed micromanagement that was going to be emanating from Washington. The cognizant AEC person for the sodium programs in the late 1960s had an authoritative, hypercritical attitude toward the ANL work.

As mentioned earlier, project management and control methods began receiving greater emphasis in the 1960s. Detailed milestone schedules were (and still are) required in proposals for future work and in the monitoring of current projects. Although a legitimate management tool when applied responsibly, they give the researchers a problem of "inventing on schedule," particularly where highly creative work is needed. The predictable tendency of the funding agencies was to accept a proposed set of milestones, but then insist that they be met in a shorter time and on a lower budget. There was sometimes a temptation to accept a demanding milestone schedule with inadequate funding in order to keep a program alive.

BUILDING ADDITION

By the 1960s, the Division had outgrown its available space. Offices were filled to capacity, the B-Wing labs were occupied by the analytical work, and the increasing volume of bench-scale work had filled all the space in the A-Wing labs. The high-bay areas, originally designed for solvent-extraction studies, had been adapted to other work. A new addition, located at the ends of A- and B-Wings, which was built in 1961-1962, covers an area of about 18,000 square feet. The core of the new addition consisted of eight large general-purpose laboratories (one of which was divided in half), which were designated as "X-Wing." X-Wing was surrounded by extensions of the A- and B-Wing corridors and offices plus a corridor with a string of about 30 offices and a conference room across the east end, which was named "W-Wing." A service floor was built under the entire addition. Although a number of purification systems for glove-box atmospheres, various other equipment installations, and storage areas are located in this service area, it still has sufficient open space to serve as a tornado shelter for Bldg. 205.

The laboratories were provided with all the usual services and were sufficiently capacious to be used either for bench-scale work or for larger scale operations requiring large glove boxes and vacuum-frame hoods. Most of this laboratory space has been devoted to the basic research, electrochemical, and calorimetry programs.

The new wing closed off the open area between A- and B-Wings, creating the present courtyard. This introduced some new maintenance problems in that lawnmowers and other equipment had to be brought in through the building's corridors. After a while, weeds began to take over the area, which became rather unsightly. Everett Proud decided at one time to solve the problem by applying a heavy mulch of cocoa nut hulls, which were highly odoriferous and were located under the building air intakes. For a few days, the building occupants felt as if they were being gassed, but the sun, air and rain disarmed the hulls after a few days and the problem disappeared. Some years later, Herb Brown, aided by several volunteers and with the cooperation of ANL grounds people, installed the present arrangement of walkways, planters, landscaping and picnic tables, which finally transformed the courtyard into an attractive asset, although it has deteriorated somewhat in recent years.

TOOLS OF THE TRADE

Everybody in the Division was affected by the many technological innovations that were introduced to the marketplace in the 1960s—Xerox® copiers, IBM Selectric® typewriters, electronic analytical instrumentation, digital readouts, and computers that, although not yet quite "user friendly," were no longer downright hostile. Color television was maturing, and several CEN people assembled large-screen sets at home from Heathkits®, which were much less expensive than the retail models if one didn't count the assembly time. The circuits still used vacuum tubes, and nearly every drugstore had a tube tester along with a convenient supply of overpriced new tubes for sale.

A major breakthrough in computer miniaturization occurred in 1958, when an American engineer, Jack Kirby, devised the first truly integrated circuit. His prototypes consisted of a germanium wafer with integrated transistors, resistors, and capacitors. By the 1960s, the technology had developed rapidly, using less expensive silicon chips with many more components on each chip. The first large-scale integration (LSI) used hundreds of components on one chip. The next step was very large scale chips with 100,000 components, and today it appears that ultra large scale integrated chips will contain as many as 10 million components on a 1-cm-square chip. Although integrated circuits began to find wide application in the 1960s, they did not develop into computer microprocessors until the 1970s.

By about 1960, CEN staff people were beginning to use the large mainframe computers in the Applied Mathematics Division (AMD). Their first big commercial machine was an IBM 704, and before long they converted to a CDC 1600. Dean Pierce describes the situation at the time: "I had repetitive calculations to reduce the data from many dissolution-rate experiments. The programmer from AMD worked with the equations that Shelby Miller and I presented and wrote a Fortran program to do the calculations. She debugged the program and gave us a deck of cards and a format for our data. We had their keypunch operators punch our data cards. They always double-checked their work and I never had an error."

Several people began to take computer courses, mostly at AMD, but also at schools such as the College of DuPage, to learn programming. The main languages were Fortran and Basic and AMD had an extensive library of scientific subroutines. Packaged software as we know it was not available, and programming was nearly from scratch. Some individuals found that programming could be fun to the point of becoming addictive. A few became hobbyists who put together improvised computers at home and had to learn about machine and assembly languages to make them work. Irv Johnson was one of those people.

The first real computer capability within CEN came about when four Wang desk calculators were purchased and put into operation. These could handle the normal math functions such as exponentials and logarithms, polynomial equations, and trigonometric functions, and the programs were saved on punched cards. The Wangs were useful for stage calculations and other purposes at the time, but they could not serve very many people and seemed to be subject to quite a bit of down time. As CEN people requested more computer availability, Mel Foster was appointed to seek solutions to the problem. One such solution was a real-time phone-line connection between a commercial General Electric computer and Teletype® machines in CEN. A system called "Rescue" allowed one to use either Fortran or Basic. Access to the mainframe computer at AMD was becoming more convenient, and Stanley Cohen of ANL developed a more-or-less plain language program called "Speakeasy." About that same time, cardpunches became available in Bldg. 205. Martin Steindler tells an amusing story about that. He had purchased a tire at a Standard Oil station on a credit card and sent in the payment along with the enclosed remittance card when the bill arrived. The next few months, he kept receiving the same bill and no phone calls or letters could stop the process. Finally, in desperation, he brought the last remittance card to work, added a few random keypunches and sent it in. Shortly thereafter, he got a frantic phone call with the message that his bill was settled and an admonition to never, ever do that again. When AMD got their CDC machine, Mel set up a satellite station in CEN where input could be sent to AMD by punch cards or paper tape and the output could be picked up in Bldg. 205, which saved a lot of running back and forth.

The introduction of xerographic copying was a major innovation of the 1960s. The concept of xerography (from the Greek, meaning "dry writing") was invented in 1938 by a physicist, Chester F. Carlson, who sold the commercial rights to the Haloid Company in 1947, and 13 years later the company, later named the Xerox Corporation, introduced its first office copier to the market. Prior to the introduction of the Xerox copier, a variety of thermographic and chemical copying systems had made a brief appearance, but these were expensive, slow, and required special papers that had several shortcomings (gray backgrounds, curling, thick paper, slick surfaces that were difficult to write on, and unpleasant odors). It wasn't long before nearly all the office copying in CEN was being done with Xerox machines or clones produced by other manufacturers. For large layouts such as shop drawings, "whiteprint" processes such as Ozalid® had largely supplanted blueprints.

By the mid-1960s, solid-state technology was coming on strong and all kinds of new electronic instruments and devices were becoming available. This made it possible for researchers to rig up systems for automated data collection. An early example of this was an oscillating-cup viscometer that Dean Pierce was using to measure the viscosities of molten metals in which the viscosity could be calculated from the decrements of the oscillations. Lad Prucha (Doreen's husband) wired a cardpunch to the system to produce a card deck for computer input. Lou Baker and his people in their reactor-safety experiments, as well as researchers in the coal-combustion program were using automated data-collection systems. Real-time output of processed data, however, was still awaiting the availability of desktop computers.

Because of the increasing importance of electronic devices in the experimental programs, several individuals availed themselves of a course by Heathkit aimed specifically toward scientists and engineers. This course consisted mostly of hands-on experience but also included some textbook material.

For the secretaries, the big event of the 1960s was the introduction of the IBM Selectric typewriter, in which the printing element was a ball that moved back and forth and rotated to print the desired character while the carriage remained stationary. The balls were easily replaceable (also breakable), so font changes were easy. At this point, we were about half way through the typewriter sequence:

> Mechanical → Electric → Selectric → Word Processor → Computer

CENHAM GLOVE BOXES

In the late 1950s, a simple, inexpensive, versatile glove box design for work with plutonium and other hazardous materials was developed by Dick Malecha, Harry Smith, John Schraidt, John Natale, Norman Ross, and Herb Brown. The acronym, "CENHAM," is derived from its full name, Chemical Engineering Hood, Alpha Modular. A major design goal was modularity. Modular structural elements allowed construction of glove-box arrays of various lengths and heights to accommodate the needs of a wide variety of experimental programs.

A drawing of a two-module glove box of this type is shown in Fig. 3-2. The basic module is 42 inches in depth, width, and height. It rests on a 36-in.-high steel angle frame. The safety glass windows are 3/8-in. thick. The internal ventilation system allows either for a once-through or a circulating gas atmosphere with an external purification system. The rubber gloves (not shown) are attached to the glass windows by standard ANL 8-in.-dia plastic glove rings sealed to the glass. When the gloves are not in use, the ports are covered by aluminum covers similar to a flanged, deep-dish "cake pan."

A salient feature of the CENHAM glove box is the use of automobile-type weather-stripping to seal the safety glass windows to the metal frames of the box. The glove boxes are usually operated at a slightly negative pressure (about –1 in. of water pressure) so that any air leakage is into the box. In-leakage rates of air have been very low with automobile-type window seals. Moreover, the windows can be removed and replaced relatively quickly. Depending on the requirements of the experimental work, a variety of inert atmospheres, *e.g.*, argon, helium, nitrogen, or dry air can be maintained in the glove box.

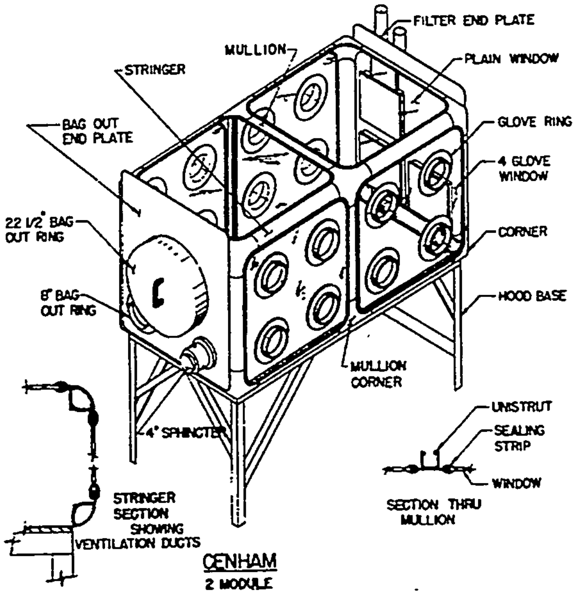


Fig. 3-2. Two-Module CENHAM Glove Box

Other features of the glove-box assembly shown in Fig. 3-2 are the following:

1. Three ports for transferring materials in and out of the box—a large 22.5-in. lock, an 8-in. port, and a small 4-in. sphincter port. In using this latter port, a 4-in.-dia canister is pushed through wipe seal rings until the opening of the canister is just inside the box. When the canister is full, it is pushed into the box by a replacement canister and later bagged out through one of the large ports.
2. A filter housing in which high efficiency filters were installed to filter exhaust gas.
3. Electrical feedthroughs and pipe couplings for connection to external fluid sources (usually water for cooling). Inexpensive construction materials such as carbon steel sheet or plate were used for the box structure.

Many different accessories have been attached to the boxes, depending on the requirements of the work. In some cases, small electric hoists are installed on rails in the boxes to raise, lower, or move heavy items. Furnaces that open into glove boxes are often attached to the floor of the box by water-cooled flanges. Large air locks are often attached to the ends of boxes containing inert atmospheres.

Figure 3-2 shows a simple two-module assembly. Much larger glove box units, some multitiered, have been constructed. The CENHAM glove boxes are in wide use at ANL, and can be seen in many of the laboratories throughout Bldg. 205.

TECHNICAL PROGRAMS

EBR-II Fuel Cycle Facility

There is little question that the most exciting program for the Chemical Engineering Division in the 1960s was the construction and operation of the EBR-II Fuel Cycle Facility (FCF) at the Idaho site. By 1960, CEN and other divisions at ANL-E had completed most of the research and development work that led to this facility. (The practice had begun of referring to the ANL site in Illinois as Argonne East, ANL-E, and the site in Idaho as Argonne West, ANL-W.) Detailed design work by the H. K. Ferguson Company had been initiated in 1957, construction work was started in 1959, and the facility was completed in 1962. The EBR-II reactor went critical in 1963 and was placed in full operation at reduced power in 1964. The power was increased stepwise until it reached the design level of 62.5 MW(t) [20 MW(e)] in 1969.

The Chemical Engineering Division had primary responsibility for the FCF during its construction phase. Charlie Stevenson, who had been in charge of the Idaho Chemical Processing Plant (ICPP), operated by the Phillips Petroleum Company, was appointed Manager of the EBR-II Fuel Cycle Facility in 1960, and held that position until he returned to CEN as a Senior Chemical Engineer in 1969. Milt Levenson was the Resident Lead Project Manager in 1961-1962, followed by John Schraidt in 1962-1963 and Neill Carlson in 1963-1964. In 1964, operating responsibility for FCF was transferred to the ANL-W personnel.

Several CEN personnel, including Don Hampson and Phil Fineman, were transferred to the Idaho site for permanent positions. Many others had shorter-term assignments at the site, and there was a great deal of commuting both by air and rail between Chicago and Idaho Falls, which is somewhat off the beaten track. Those transferees who had always lived in an urban environment generally experienced some initial culture shock with the remoteness of the area, the pervasive Mormon influence, and lack of amenities a big city has to offer. Most of them, however, began to enjoy the excellent outdoor recreational opportunities, such as camping, fishing, hunting, boating, and skiing that the area has to offer. Almost everybody used the buses to commute the 30 miles or so between Idaho Falls and the EBR-II site; bridge games on those buses are legendary, with the players occasionally overshooting their destinations to play out a hand.

Approximately 160 ft from the EBR-II-FCF complex, there was an additional building that housed the analytical laboratories and other auxiliary operations. The analytical facilities included six 20-Ci, 1-MeV gamma radiation caves with American Machine and Foundry (AMF) Mod 8 manipulators and two conventional wet analytical laboratories with fume hoods for hot work. Bill Sovereign, John McCown, and Earl Ebersole were the principal operators of this facility.

The layout and a brief description of the Fuel Cycle Facility were given in the previous chapter. The following is a more detailed description of the fuel-reprocessing operations. The discharged fuel assemblies, after cooling in the reactor, were passed from a shielded air cell to the circular argon cell and continued in a counter-clockwise direction (as viewed from above) through a sequence of workstations. The new subassemblies were then transferred back out through the air cell for reinsertion into the reactor. The fuel-processing operations, all of which were conducted remotely behind 5-foot-thick walls of concrete shielding, were as follows:

1. After a minimum of 15 days of cooling, the fuel subassemblies were moved, one at a time, to the air cell in the Inter-building Transfer Coffin. In transit, each subassembly was washed thoroughly with water to remove adhering sodium coolant, and was then dried.
2. The subassemblies were disassembled, and the fuel elements (stainless steel clad fuel pins) were separated from the other components, which were discarded. The fuel elements were transferred to an argon cell for further processing.
3. The stainless steel cladding was removed from the fuel pins by a spiral cutter, and the pins were chopped into 3/4-in. segments.
4. A 10-kg batch of pin segments was charged into an induction-heated CaO (lime)-stabilized zirconia (ZrO_2) crucible where it was melted and held at 1400°C for three hours. The liquid metal was then poured into a graphite mold with two small holes in the bottom to form an ingot with protrusions, which were broken off and used as analytical samples.
5. The melt refining "skull," a mixture of unpoured metal and oxides, was converted to a powder by oxidation at 700°C through a controlled addition of oxygen, and the resulting powder was poured out of the crucible.
6. The U-235 content of the product ingot from melt refining was brought back to the original concentration by adding a small amount of highly enriched uranium. These materials were melted together in a graphite crucible coated with yttria. New fuel pins were then formed by evacuating the system;

lowering precision-bore Vycor (quartz) tubes, closed at the top and containing a thin thoria (ThO_2) wash on the inside surface, into the liquid metal; and repressurizing to force the metal up into the tubes. This procedure was called "injection casting." After cooling, the Vycor was removed from the pins by crushing, and the pins were cropped to the desired length.

7. New fuel elements were fabricated by inserting the uranium pins into stainless steel jackets, adding the sodium thermal bond in the annulus, and sealing the jackets by welding. The finished fuel elements were subjected to a series of rigorous quality-control tests.
8. The fuel elements were inserted into new subassemblies for return to the reactor.

The melt-refining process resulted in a fission-product decontamination factor of about three, the low value being due to fact that the noble metals were not removed. Composite results from a large number of runs in the FCF, shown in Table 3-1, give the distribution of the various fuel constituents after melt refining. The recoveries of uranium and plutonium ranged between 90 and 95%. Noble metals were not separated from the uranium by melt refining but were maintained at a satisfactory equilibrium concentration by the 5-10% of the metal removed with the skull, which served as a "dragout" stream. The fission-product gases, Xe and Kr, were collected for controlled disposal. The melt-refining crucible had a Fiberfrax® (formulated asbestos) lid, sometimes called a "top hat," that collected vaporized species by a combination of condensation and chemical reaction. A "skull reclamation" process had been developed and tested on a pilot-plant scale in CEN. Some skull-reclamation equipment was installed in the FCF, but it was not used due to an AEC policy decision to recover the skull material by aqueous processing in ICPP. Work on a process for recovering plutonium from the blanket fuel was also well on the way toward application, but it, too, was terminated.

Overall, the FCF demonstration was an outstanding technical success and a tribute to the ANL engineers and scientists who developed it. The EBR-II operated for about five years, using the recycled fuel, which

Table 3-1. Melt Refining Results from the EBR-II Fuel Cycle Facility

Off-gas	Fume Trap	Skull	Crucible	Product
Xe 100%	Cs 100%	U 5-10%	Y 5%	U 90-95%
Kr 100%	Cd 100%	Pu 5-10%	RE 5%	Pu 90-95%
	Rb 100%	NM 5-10%	Ba 90%	NM 90-95%
	I >75%	Y 95%	Sr 90%	
	(Na) 100%	RE 95%	Te 10%	
		Ba 10%		
		Sr 10%		
		Te 90%		

(Na) = Sodium from thermal bond.
NM = Noble metal fission products.
RE = Rare earth fission products.