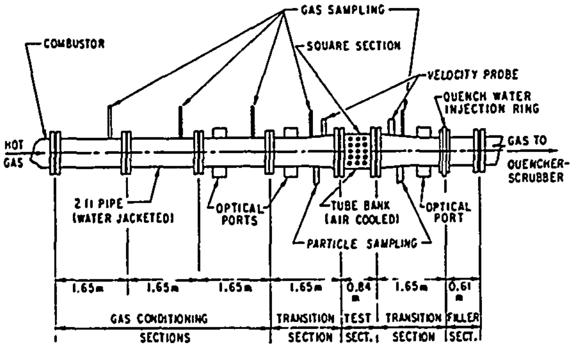


Fig. 5-13. Test Train for Fouling Tests in Fossil Energy Users Facility

coefficient. Gas temperatures between 1100 and 1300°C produced dense, adherent deposits that were difficult to remove by soot blowing

Argonne developed a model for calculating the fouling efficiency (gas-side, heat-transfer coefficient of fouled tube divided by that of a clean tube) of a convective heat exchanger operating at temperatures below about 1,300°C. As shown in Table 5-7, calculated and measured fouling efficiencies were in good agreement.

Table 5-7. Measured and Calculated Fouling Efficiencies

Test	Fouling Efficiency		
	Measured	Calculated	Difference, %
1	0.80	0.82	2.5
2	0.85	0.75	12
3	0.73	0.77	5.5
4	0.69	0.69	0

FOLLOW-UP APPLICATIONS OF FEUL

When MHD studies using FEUL waned in the late 1980s, FEUL was used to investigate (1) SO_x-NO_x control in slagging combustors, which were being developed for potential application to coal-fired gas turbine systems and for retrofitting existing gas- and oil-fired boilers, and (2) char combustion.

In the slagging combustion studies, an investigation of SO_x-NO_x was conducted in a staged cyclone coal combustor with limestone injection. The tests were performed in the FEUL coal-fired test leg, which consisted of a primary combustion stage into which coal and primary air were injected, and a secondary combustion stage. Funding was provided by the Coal Technology Corp. and the Illinois Coal Industrial Committee. Limestone and a pressure-hydrated limestone were used to getter SO_x. Best results (80% reduction of SO_2 emission) were realized when the first-stage combustor was operated in an oxygen-deficient mode (60 to 70% of stoichiometric air), and the second stage was operated with excess air (160 to 170% of stoichiometric). This work also showed that satisfactorily low NO_x emissions could be achieved in slagging combustors.

The pyrolysis (or mild gasification) of coal yields volatiles that are recovered for their chemical value and a clean char that can be utilized in industrial or utility boilers. In FEUL, very stable combustion of a low-volatile char was realized. Combustion efficiencies ranged between 91 and 96%, which is lower than the 99.5% required for boiler application. The work was halted before conditions that might have increased the combustion efficiency could be explored.

RECOVERY OF POTASSIUM CARBONATE SEED MATERIAL

The primary function of the MHD seed-reprocessing system was conversion of K_2SO_4 discharged from the radiant boiler to K_2CO_3 for recycle to the coal combustor. The most promising chemical process was high-temperature reduction of K_2SO_4 to K_2S and conversion of the K_2S to K_2CO_3. With minimal funding in 1980 and 1981, CMT limited its efforts to managing seed-reprocessing studies by industrial firms and to developing a computer code for single- and three-stage contactors. A sharp reduction of total MHD funding in 1982 forced termination of this work. Seed-recovery work was resumed again in 1988 for one year when CMT investigated the reduction of K_2SO_4 in a molten pool of sulfates and sulfides contained in a ceramic-lined reactor. A process flowsheet based on thermodynamic studies was developed and provided to Babcock and Wilcox for testing by them.

SUPPORTING STUDIES

Thermodynamic Support Studies. Thermodynamic support studies were conducted in 1980 and 1981 to investigate reactions between slag constituents and K_2SO_4 and to evaluate the characteristics of the seed-slag deposits in the radiation heat boiler. At temperatures from about 2000 down to 1400°C, the K_2SO_4 reacted with the slag to form potassium silicates, aluminates, and aluminosilicates. Recovery of potassium from these materials was judged to be very difficult, and probably uneconomical. Because of these reactions, it was estimated that 6-10% of the potassium would be unrecoverable.

Other support studies included electron-probe analyses of the slag-seed deposits, thermal diffusion of potassium in the slag, and thermodynamic modeling of coal-seed-slag interactions. This work was also a casualty of the sharp reduction of MHD funding in 1982.

Materials Studies. Corrosion of heat-exchanger tube materials by MHD combustion gases was investigated in 1987 and 1988. Austenitic and ferritic steels were exposed to MHD conditions for up to 2,000 hours in autoclave tests. Austenitic steels performed satisfactorily under steam superheat conditions; corrosion rates of ferritic steels were unacceptably high. Neither austenitic nor ferritic steels performed acceptably at the temperatures of an intermediate air heater. The work was terminated before tests of other candidate alloys could be done.

PERSONNEL

Terry Johnson was in charge of this work. Because of its highly interdisciplinary nature, many individuals from other divisions were involved. Those from CMT included Paul Blackburn, Carl Johnson, Stan Johnson, Jiri Klinger, Bali Misra, Mike Myles, Charlie Schoffstall, Atul Sheth, Eugene Smyk, Bill Swift, Doug Warinner, and Stan Zwick.

Energy and Municipal Waste Technology

ENERGY FROM MUNICIPAL WASTE

In 1982, Argonne was designated as the lead laboratory for DOE's Energy from Municipal Waste program. The purpose of the program was to undertake research that would enhance the ability of the private sector to complete the development, demonstration, and commercialization of technologies for deriving energy from municipal solid waste (MSW). The principal CMT tasks were to (1) investigate the basic thermodynamic mechanisms associated with the pyrolysis of MSW, (2) evaluate the catalytic upgrading of pyrolytic liquids, and (3) analyze the external combustion of MSW as a supplemental source of energy for a conventional steam boiler.

Pyrolysis of MSW. Although pyrolysis of MSW had not previously been technically or commercially successful, the possibility that MSW could be degraded to produce stable, transportable gaseous and liquid fuels continued to be considered seriously. The basic mechanisms of pyrolysis were not understood. In CMT, a variety of cellulosic materials—paper, newsprint, packing materials, wood wastes, grass clippings, *etc.*—were pyrolyzed in a bench-scale reactor. Gases were analyzed by mass spectrometry. Liquids were analyzed by gas chromatography and by gas chromatography/mass spectrometry. So complex were the liquids that complete identification of molecular species was not possible, but they appeared to be substituted furfurals and furfurols. Various amounts of tars and chars were also produced in the pyrolysis experiments. The reactor experiments were supplemented by determination of activation energies obtained by thermogravimetric analysis.

Two subcontractors, the Solar Energy Research Institute (SERI) and the University of Arizona, were also involved in this effort. Using a flame pyrolyzer with a molecular-beam, mass-spectrometer analyzing device, SERI studied the influence of reactor conditions on the compositions of solid and gaseous products at low pyrolysis temperatures. Investigators at the University of Arizona performed pyrolysis tests in a high-pressure autoclave reactor. Studies of MSW pyrolysis were phased out in 1988.

External Combustion of MSW. In a large-scale combustion demonstration of the use of MSW as a supplemental fuel in existing steam boilers, a refuse-derived fuel (RDF) has been cofired with coal. Preparation of the RDF resulted in difficult storage and transportation problems with high capital and maintenance costs. Co-firing of RDF with coal was, therefore, not economically beneficial. The CMT Division investigated an alternative—burning the coal and MSW in separate units. The gaseous combustion products would be combined with those from combustion of coal for generation of steam. Economic analyses of MSW combustion in a dedicated unit showed that the cost of MSW-derived power would be competitive with that from coal.

In 1988, a computer model was developed to simulate combustion of MSW in a combustor shown schematically in Fig. 5-14. The MSW pyrolyzes and burns as it is transported horizontally along the grate from left to right. Part of the heat from burning the waste is recovered in water walls that line the flame zone. The remainder of the heat in the flue gases is used for generation of steam. The model provided valuable information on the effects of dimensional and operating variables.

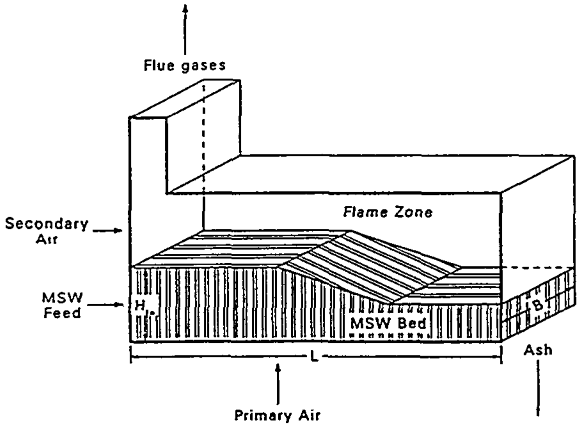


Fig. 5-14. Municipal Solid Waste Combustor

HAZARDOUS ORGANIC WASTES

The technical feasibility of a microwave-assisted chemical process for detoxification (conversion to harmless materials) of hazardous organic wastes, such as trichloroethylene (TCE), polychlorobiphenyls, dichlorobenzene, and ethyl ketones, was investigated in the late 1980s. Initial results showed that more than 80% of the TCE adsorbed on active carbon (loaded with copper and chromium catalysts) was detoxified in one pass when heated by microwave radiation to temperatures approaching 400°C. At 500°C, more than 98% was detoxified.

The work was extended to testing detoxification in a microwave-induced plasma reactor. A stable plasma was first established at atmospheric pressure, after which a chlorohydrocarbon-bearing vapor was introduced. In a single pass, 95.9 to 98.3% conversion of C_2H_3Cl and C_2HCl_3 was achieved.

Shabir Ahmed, Amrit Boparai, Jack Demirgian, Jim Helt, Richard Henry, Romesh Kumar, Mike Myles, John Schneider, Ravi Varma, Ronald Wingender, and John Young worked on this program.

TREATMENT/DISPOSAL OF REACTIVE WASTES

Work was performed in the late 1980s on development of an integrated process for conversion of waste sodium, including sodium-containing radionuclides, to a glass form. In the process, shown in Fig. 5-15, sodium was injected into the reactor, using nitrogen as an aspirator and atomizer. An air stream containing a suspension of glass-forming materials was introduced to oxidize the sodium. Molten glass was formed directly in the reactor.

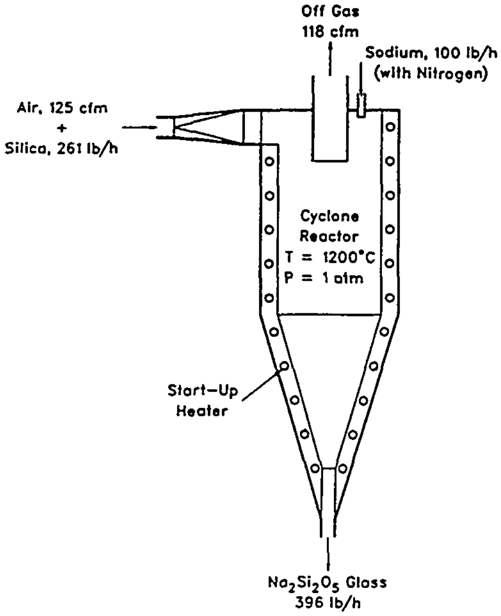


Fig. 5-15. Cyclone Reactor for Converting Sodium to Glass

If no radioactive contaminants were present, a simple soda-silica glass was a suitable waste form. If radioactive contaminants were present, other constituents, such as B_2O_3, Al_2O_3, and CaO, had to be added to provide a glass waste form having high resistance to leaching of the radioactive contaminants by water.

Argonne provided technical assistance to commercial demonstration of the process. Chemical Technology personnel in this program were Alan Brown, Jim Helt, Romesh Kumar, John Rajan, Ravi Varma, and Don Vissers.

Solar Energy

The ANL solar energy research program, which was a joint effort among several divisions, continued in the 1980s. This program supported the presidential goal in 1978 of achieving 20 quads of energy production by the year 2000 from solar energy. (A quad is 10^{15} Btu.) The Chemical Technology Division's activities included solar collector development, ice storage, and thermal storage. The solar energy program was somewhat unusual in that the results of the development studies were adopted quickly by industrial firms, some of which had been industrial participants, and placed on the market as commercial hardware in many cases. Funding for the solar-collector work, which was a large part of the CMT program, was being withdrawn gradually, and in 1983 the CMT program was transferred to the EES Division along with Bill Schertz, who had spearheaded the effort.

SOLAR COLLECTOR DEVELOPMENT

Three major types of solar collectors were under consideration: (1) flat plate, (2) evacuated tube, and (3) parabolic trough. Each had its problems. The flat-plate collectors had inadequate performance characteristics, the initial cost of the evacuated-tube collectors was too high, and those parabolic reflectors that tracked the sun had operational and maintenance problems. The non-imaging compound parabolic concentrator developed by CMT appeared to show the most promise, and the Solar Energy Group in CMT, having become the acknowledged leader in this technology, was the focus for commercialization activities, hardware tests and evaluations, and support for establishing standards. The group served as a clearinghouse for manufacturers and other solar researchers in universities and other government laboratories.

A study of seven first-generation collector designs showed optical losses of about 5-20% because of a necessary gap between the absorber and the collector. Most of the designs also had a low solar absorbance of approximately 0.8. Second-generation design studies at ANL resulted in two concepts—a four-facet "gaplossless" collector and a generalization of it, the multifacet gaplossless collector, both of which were modifications of the classic compound parabolic concentrator cusp. The concept was developed at ANL and patented by DOE. A third design overcame the problem of low solar absorbance by making an absorber-reflector system an optical cavity with increased absorbance through multiple-plate reflections. The final design to be studied employed a multifacet gaplossless reflector as a secondary concentrator coupled to a conventional focusing parabolic trough. This combination permitted a relaxation of the accuracy requirements for the primary mirror shape, with a resulting cost reduction.

Tests were conducted on nine collector modules: (1) three first-generation ANL prototype units, (2) three first-generation industrial units, and (3) three second-generation designs by ANL and the General Electric Company. The results showed that the ANL computer programs gave accurate predictions of the performance of all the designs, and that the optical losses were indeed recouped by the gaplossless and enhanced absorption designs.

By 1982, the nonimaging concentrating collectors developed at ANL had been introduced to the market and were being sold commercially, so the research program was phased out. A small follow-on effort continued, however, on the computer modeling, and evaluations were made on advanced coating materials that showed promise of increasing the absorptivity from about 0.78 to 0.92. The mode of operation was also being changed to allow steam generation in the collector instead of an organic heat-transfer fluid. Tests of a prototype steam-generating collector demonstrated 50% conversion of sunlight to steam at 135°C.

ICE STORAGE

The objectives of the ice storage program were outlined in the preceding chapter. The general idea was to develop passive refrigeration devices for heating and cooling buildings, using solar power. The near-term program objective was to determine the feasibility of the concept through theoretical and experimental studies. The longer-range goal was to develop the technology to the research-prototype stage, at which point it could be taken over by the industrial sector.

This work continued in the early 1980s, primarily on materials and hardware design. Cylindrical heat pipes were replaced by Roll-bond® panels (a proprietary product in commercial use), which are basically copper or aluminum sheets with integral fluid channels. The immediate objective was to increase the surface area available for deposition of ice and for heat transfer, and the new material was used both for the evaporators (underground) and the condensers (above ground). Several full-scale heat pipes were fabricated for outdoor use during the winter. The evaporator consisted of four Roll-bond heat pipes attached to a plastic cylinder. Each evaporator unit had about 3 m^2 (32 ft^2) of surface area. The aboveground condenser units consisted of Roll-bond panels having an area of about 15 m^2 (160 ft^2).

Initial attempts to operate the facility were unsuccessful in that the "freeze and release" procedure used on the laboratory scale did not perform properly in the scaled-up equipment. After suitable modifications, however, the system did function satisfactorily, and about 18 tons of ice was produced in 1982. Mathematical models of the freezing process were developed to permit extrapolation of the experimental results to other system designs.

THERMAL STORAGE

Three projects on thermal energy storage were in progress in 1980: (1) Stratified Storage and Analysis, (2) Testing of Latent Heat Storage Units, and (3) Development of Thermal Energy Storage Devices Using Cross-Linked, High-Density Polyethylene.

Estimates by others had indicated that thermal stratification in storage tanks could improve the performance by 5-15% over fully mixed systems. Typical tanks behave as mixed systems, and special designs were required to achieve stratification. Semiempirical modeling studies were conducted to predict accurately temperature-time and -space behavior within tanks under a wide variety of operating conditions.

Approximately 12 manufacturers had latent heat-storage units on the market or nearly ready to be marketed in 1980. Because the manufacturers' test procedures were not uniform, the performance results were inconsistent. This project consisted of testing available units in cooperation with Oak Ridge National Laboratory (ORNL) to assess the industry-wide performance of heat-storage units and to develop testing standards. Oak Ridge was then to do full-scale testing, using the final test procedure, and the results were to be published jointly by ORNL and ANL.

A cross-linked, high-density polyethylene (HDPE) developed jointly by Monsanto Corp. and the University of Dayton was of interest as a latent heat storage medium due to a phase change at 130°C involving a latent heat of about 40 cal/g. The material does not change shape or fuse at temperatures up to 150°C. A heat-storage device using this material could be used for solar-powered air conditioners ("chillers") and industrial processes requiring heat at temperatures up to 150°C. A prototype unit was designed for a 3-ton chiller. Ethylene glycol, water, or a combination of the two would be used as the heat-transfer fluid.

PERSONNEL

The solar programs were headed up by Bill Schertz, and CMT personnel involved in those programs in the 1980s included John Allen, Anthony Gorski, Arthur McGarity, and Alvin Wantroba. About 10 people from other divisions were involved.

DESICCANT STUDIES

A small program was started in 1982 on the use of solid and liquid desiccants for dehumidification in heating, ventilating, and air-conditioning systems. The DOE at that time was stressing the development of novel desiccants that would remove moisture with a minimum expenditure of energy. The work began in the solar energy group headed by Bill Schertz and was performed by Sidney Bourne, Jack Demirgian, Tony Fraioli, Jiri Klinger, Wally Kremsner, and Jack Parks.

In the initial studies, a promising family of solid desiccants, two manganese oxides, ε-MnO_2 and Mn_3O_4, were identified, and it was found that the rectangularly tunneled microfiber structure of these compounds results in minimum energies for their water-adsorption characteristics. There appeared to be a possibility that the weak adsorbate-adsorbent interactions of the microfibers might be used to provide easy mass transport of water into the interior of silica gel structures, which are limited in capacity by pore blocking during the water adsorption cycle. Composites of silica gel particles were prepared with MnO_2 and metal fibers as additives to determine their mass-transport and heat-transfer characteristics.

The concept behind the liquid desiccants was to develop a system that could be regenerated by a liquid-liquid separation, thereby avoiding the energy cost of vaporizing water. A search was initiated for organic liquids whose mixtures with water have the requisite phase-separation properties, and a computer model was developed to aid in predicting the performance of such systems. The organic compound N-cyclohexyl-2-pyrrolidone (CHP) had the necessary water-adsorption and liquid-phase separation properties when mixed with water, but there was a need to improve the degree of CHP-water separation. Work was done on pertinent phase diagrams and other properties to determine the effects of various additives. The water-miscibility properties of six amines and seven amides were determined. The phase diagram for water-diisopropylamine indicated that an excellent liquid-liquid separation occurred on heating to 65°C .

Nuclear Fusion Energy Research

Unlike many other CMT programs, the work on fusion energy, under the leadership of Vic Maroni, remained at a relatively constant level of effort (approximately 10 people) throughout the 1980s. This activity fell under the purview of Fred Cafasso, an associate division director, who transferred to the Chemistry Division in 1983. Dieter Gruen of the Chemistry Division was then given overall responsibility for Vic's group and the basic research group headed by Milt Blander.

The program continued to consist of (1) systems analysis and engineering experimentation, (2) materials research and development, and (3) neutron dosimetry and damage analysis. Some significant changes of emphasis, however, were in the wind. There was an interest in replacing the liquid lithium in the tritium breeder blanket with a solid lithium-bearing material. The Division was being asked to play a larger role in national and international fusion reactor designs, and joint projects with other ANL divisions, other laboratories, and industry. Ongoing work on neutron dosimetry and damage analysis was to be expanded. Work was to be discontinued on liquid lithium blanket processing and hydrogen isotope permeation, and operation of the lithium processing loop was curtailed.

SYSTEMS ANALYSIS STUDIES

Studies of fusion reactor systems, which had been in progress since 1969, had established the Division as an internationally recognized leader in the design and analysis of tritium-processing systems. In 1980, CMT personnel participated in several major design studies for tokamak fusion reactors, including the STARFIRE commercial reactor, the Engineering Test Facility (ETF), and the International Tokamak Reactor (INOR). In this international project, STARFIRE was managed by Argonne, ETF by Oak Ridge, and INOR by the International Atomic Energy Authority (IAEA), which involved the U.S., the European Community, the U.S.S.R., and Japan. These studies included the establishment of tritium-supply guidelines for fusion-reactor startup projections, design of a complete tritium fuel-processing facility, a parametric analysis of the STARFIRE vacuum system, design of a solid tritium breeder blanket, and evaluation of the effects of physical and chemical parameters on tritium (spill) cleanup systems.

A special study was conducted to consider mechanisms involved in the recovery of tritium from a solid breeder blanket. What seemed to be needed was a low-density blanket material having a fine grain size (about 1 µm) and a bimodal pore distribution, that is, small grains and fine porosity within fairly coarse particles (about 1 mm) with a much coarser porosity between the particles. This design study identified critically needed data such as the solubility of T_2O (H_2O) in Li_2O; compatibility of breeder material, coolant, and structural alloys; thermal conductivity and radiation stability of the breeder material; and the kinetics of tritium release. Properties databases were developed for the candidate materials.

Several major design studies were made in 1982. One study was aimed toward achieving a world-wide consensus on tokamak fusion reactor designs. Another study was focused on blanket design and involved both solid blankets (Li_2O) and liquid metal blankets (lead-83% lithium). In addition, the Division participated in a study sponsored by the Electric Power Research Institute (EPRI) to assess the risk factors involved in the tritium fuel cycle. The main CMT effort in that study was to define the tritium systems that would be needed in a fusion reactor plant.

In 1983, CMT participated in a blanket comparison and selection study and tritium systems work in support of mirror and tokamak designs. Both liquid metal and solid blankets were included. Because the blanket must generate tritium and convert the energy from the lithium transformation reaction into sensible heat, areas of concern were tritium recovery and inventory in the blanket, and thermal-hydraulic effects. The tritium systems work was concerned with processing the tritium and deuterium to fuel the plasma, the water coolant, and the atmosphere in the tritium areas. A flowsheet was developed for a continuous tritium-processing system for the upgraded Mirror Fusion Test Facility (MFTF-B) at Livermore National Laboratory.

It was recognized that an order of magnitude improvement in performance was necessary to make fusion power an attractive commercial energy source. Two design assessments were made in 1985 on (1) the technical and economic benefits of using polarized fuels in tritium-deuterium reactors and (2) the benefits of using high-temperature, high-pressure helium as a heat-transfer medium. Neither concept appeared to offer a good possibility of achieving the desired performance. The economic aspects of fusion power were explored further in a 1986 study based on three fusion reactor designs. The bottom line was that the bus-bar cost of electricity could be about 32 mill/kWh in 1986 dollars, assuming a developed fusion technology. This value compares with a cost of about 52 mill/kWh in 1985 for Illinois electricity produced by coal and nuclear plants.

The Tritium Systems Test Assembly (TSTA) at Los Alamos National Laboratory was a full-scale test of tritium handling systems to be used in fusion reactors. A joint team involving ANL, Los Alamos, and the Japan Atomic Energy Research Institute (JAERI) was formed to study the addition of a breeder blanket interface (BBI) to the TSTA. Three types of blankets were considered: (1) liquid lithium metal, (2) solid Li_2O, and (3) an aqueous salt solution containing lithium. By 1989, BBI reference designs had been developed for items (2) and (3), along with development schedules and estimated costs. Funding was not available for ongoing development work on all the options, and at the end of the year, strategies were being planned to determine the most cost-effective paths to pursue.

Although fusion reactors would not produce the large quantities of highly radioactive wastes characteristic of fission reactors, waste disposal is still an important factor and a matter of public concern.

Therefore, a study was conducted on the reprocessing and disposal requirements for prototype fusion-reactor modules using liquid metal or solid breeder blankets. Reprocessing of the structure would require remote handling methods and, for some systems (depending on the details of the reactor design), residual activity may be too high for shallow land burial. Reprocessing of a lithium metal blanket would result in no major costs or disposal problems.

In 1981, as part of a U.S./Japan exchange program, Patricia Finn of CMT spent six months in Japan, mostly at JAERI. Pat is very knowledgeable about high-temperature, refractory oxide systems and other pertinent technology, having been a major contributor to CEN's programs on the thermodynamics and other physical properties of such systems, and also to applied programs such as the fuel-cell work. The experimental program at JAERI was directed toward Li_2ZrO_3 and Li_2TiO_3 as solid breeder blanket candidates. The work included studies of fabrication methods, thermal diffusivity and conductivity, compatibility with structural materials, and tritium-release behavior after irradiation.

Chemical Technology personnel who were involved in these systems-analysis studies were Rob Clemmer, Pat Finn, Carl Johnson, Ralph Leonard, and Bali Misra. Many people from other divisions also contributed.

MATERIALS RESEARCH AND DEVELOPMENT

Liquid Breeder Blanket Processing. In 1980, the work on processing of liquid lithium breeder blankets and the corrosion studies continued, but the interest had turned more toward solid breeder blankets, so the lithium-processing and hydrogen-permeation studies were de-emphasized. An investigation of possible causes of the LPTL leak that caused the fire mentioned in Chapter 4 revealed that iron crystallites and other solids had built up in the area of the electromagnetic pump. These deposits might have restricted the liquid metal flow, thereby producing cavitation and erosion of the channel walls. The location was in a region of high residual stress from cold working during fabrication. Crystals of the compound Li_xCrN_y were found, which verified a suspicion that nitrogen had a role in the mass-transfer corrosion of stainless steel in lithium loops. The LPTL was repaired, but further operation was curtailed due to other priorities.

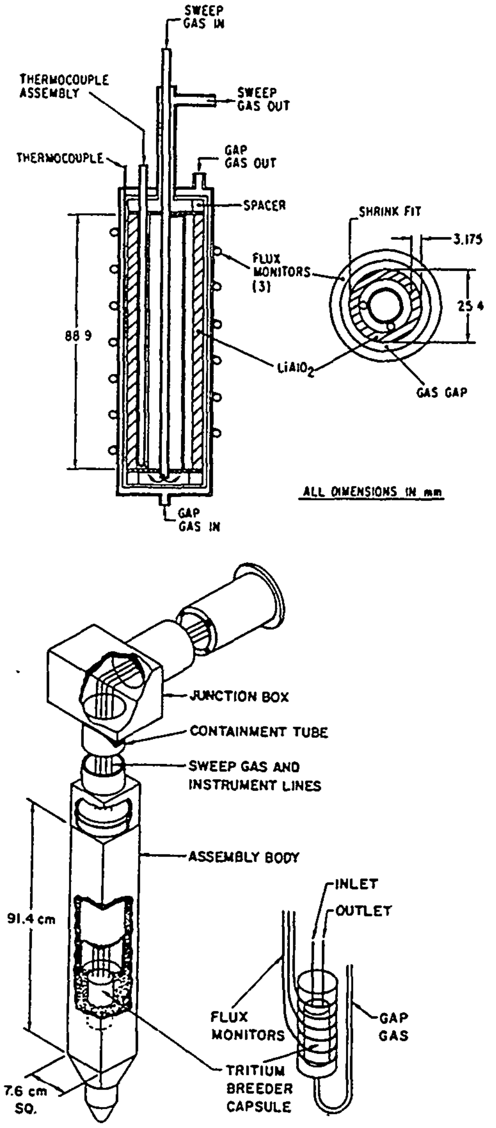
Liquid lithium-lead-bismuth (Li-Pb-Bi) alloys were considered as a possible alternative to lithium as a blanket material. Potential advantages were a relatively high breeding ratio (>1.2), a thinner breeding zone, a melting temperature 30 to 40°C lower than that of lithium, and less susceptibility to contamination by air or water vapor. Compositions of 10 and 15 at.% Li in Pb/Bi at a mole ratio of 0.773 were found to be totally liquid at 131 and 136°C, respectively.

Hydrogen Permeation Studies. An extensive survey of hydrogen permeation data for pure iron, ferritic alloys, and martensitic alloys revealed that alloys containing small amounts of aluminum had lower permeabilities than aluminum-free alloys. Experiments on iron-chromium (Fe-Cr) alloys showed that small aluminum additions of 2 wt% reduced the hydrogen permeation rates of the alloys by as much as a factor of 200 in an oxidizing atmosphere.

SOLID BREEDER BLANKETS

Although liquid lithium metal seems at first glance to be the obvious choice for a fusion reactor breeder blanket, it has several serious drawbacks: (1) safety, due to its flammability, (2) corrosion, (3) electrical conductivity, which makes it difficult to pump through magnetic fields, and (4) high chemical reactivity, which attracts impurities such as water vapor, oxygen, and nitrogen from cover gases. Most of these problems can be overcome (and a few new ones introduced) by the use of a solid breeder blanket. Lithium-bearing ceramic materials such as Li_2O, $LiAlO_2$, Li_2ZrO_3, Li_4SiO_4, Li_2SiO_3, and Li_2TiO_3 were considered for this purpose. Two key engineering areas were involved in research on processing solid blankets: *in situ* tritium recovery and thermal-hydraulic performance in the breeding zone. In processing the solid blanket, the breeding medium remains stationary, and tritium is recovered by sweeping a purge gas (helium or nitrogen) through channels in the solid bed. The temperature must be kept high enough to achieve acceptable diffusion rates, but also low enough to avoid sintering or other microstructural changes in the bed.

The TRIO Experiment. Early work on solid breeder blanket processing was focused on comprehensive in-pile tests of a miniaturized blanket assembly, which were assigned the somewhat strained acronym, TRIO (Tritium Recovery in-Pile), at the Oak Ridge Research Center (ORR). Figure 5-16 shows the experimental configuration of the TRIO-01 experiment. This experiment was designed to simulate conditions in an operational solid fusion reactor blanket on a miniaturized scale. A lot of development work and verification testing had to be done in preparation for the experiment. An "engineered microstructure" with the desired bimodal pore distribution was developed for the γ-$LiAlO_2$ blanket material, and extensive chemical analyses were performed to identify trace contaminants. A gas loop was used to verify performance of the gas-analysis system. In addition, neutron fluxes and energy spectra, as well as tritium production rates, were determined in a sample of γ-$LiAlO_2$.



The solid breeder material (γ-$LiAlO_2$, about 70% dense, bimodal pore structure) is in the form of a hollow cylinder, and the purge gas is swept past the inside surface. Temperatures, monitored continuously, are varied over a range of 400-1000°C with less than a 150°C gradient across the solid. Neutron flux is monitored continuously by self-powered neutron detectors and by dosimetry wires. The assembled capsule fits into a cylindrical hole in an aluminum core piece. Sweep-gas lines pass upward out of the reactor to a gas-analysis package where tritium levels and the chemical composition of the sweep gas are measured.

Fig. 5-16. Tritium Breeder Blanket Experiment (TRIO-01) for Fusion Reactor

The irradiation phase of the TRIO experiment was conducted at Oak Ridge in 1983. Thirty-three tests were made at various temperatures and sweep-gas compositions. With a helium-0.1% hydrogen sweep gas, tritium released from the assembly was easily recovered, and tritium retention in the blanket was extremely low. Nearly all of the tritium was recovered in the reduced form as T_2 or HT. (From an overall tritium handling standpoint, it would be desirable to have the tritium in an oxidized form, namely, T_2O or HTO.)

The experiment also tested the heat-transfer performance of the assembly. The temperature profiles across the solid bed were within 10°C of those predicted by heat-transfer computations. Post-test examination of the solid bed indicated no significant changes in the porosity or microstructure of the γ-$LiAlO_2$. Between the irradiations and analytical work involved in the TRIO experiments, quite a few CMT people were involved in this phase of the fusion program. Pat Finn and Rob Clemmer were group leaders. Others included Del Bowers, Al Fischer, Larry Greenwood, Myron Homa, Rob Klemmer, Ralph Leonard, Dick Malecha, Bali Misra, Gerry Reedy, Mike Slawecki, Shiu-Wing Tam, and Sy Vogler. Tony Scandora from Electronics Technologies (ELT) was assigned to CMT.

Thermodynamics and Kinetics of Solid Breeding-Blanket Materials. It was becoming apparent that removal of tritium from an oxide breeder blanket was a complex process that would require thermodynamic studies of equilibrium reactions, solubilities, phase relationships, *etc.*, and investigations of the kinetics involved in diffusion, adsorption-desorption, and other rate-limiting processes. In the case of tritium produced in a Li_2O bed by the neutronic reaction $^6Li(n,\alpha)$, the tritium was expected to be released from the bed by dehydration of LiOT and to pass into the helium purge stream. An experimental study was undertaken to determine the solubility of tritium in Li_2O and to determine the phase relationships and vaporization behavior of the Li-O-T system. Because of the difficulties involved in handling tritium, the studies were actually conducted on the Li-O-H system, which is thermodynamically very similar to the Li-O-T system. The reaction of water vapor with Li_2O produces lithium hydroxide (LiOH), which dissolves in the Li_2O, causing a lower activity of LiOH and reduced partial pressures of gaseous LiOH and H_2O over the system. This effect is an important consideration in establishing conditions for retention or release of tritium in the Li_2O blanket. The solubility of LiOH in Li_2O was, therefore, measured as a function of water-vapor partial pressure and temperature. The solubility of LiOH (or H) in Li_2O proved to be proportional to the concentration of water vapor in the helium carrier gas.

Measurements were also made on the vaporization of Li_2O (as LiOH) in the presence of water vapor: $Li_2O + H_2O(g) \leftrightarrow 2\ LiOH(g)$. The experimental results can be expressed as follows: $\log p(LiOH) = 9210/T + \log p(H_2O)$, where p is in atmospheres and T is in degrees Kelvin.

The SOLGASMIX computer code was used to study the use of a H_2-H_2O mixture to exploit isotopic exchange as a means of enhancing tritium recovery from blanket material at temperatures of about 600 and 1000°C. The addition of small amounts of hydrogen and/or moisture to the tritium purge gas strongly affected both the chemical form of the released species and the residual tritium in the solid material. For γ-$LiAlO_2$ breeder material and an oxygen activity of about 10^{-15}, a temperature of 600°C was more favorable for tritium release than 1000°C, and most of the tritium was in an oxidized form. Higher tritium release, although in the reduced form, could be achieved at both temperatures by using low oxygen activities ($<10^{-25}$). This study was then extended to evaluate the relative performance of three candidate blanket materials with respect to tritium release, which turned out to be $LiAlO_2 > Li_2O > Li_4SiO_4$. On the basis of these results, further work was initiated on the thermodynamics and kinetics of tritium release from γ-$LiAlO_2$.

Both calculational and experimental methods were used to characterize further the mechanisms involved in the recovery of tritium from γ-$LiAlO_2$. One study was focused on the dissolution, adsorption, and desorption of gaseous H_2O. Isotherms were developed for surface adsorption of H_2O and the solubility of OH^- in $LiAlO_2$ as a function of $H_2O(g)$ partial pressure. The nature of the adsorption curves indicated that more than one type of surface site was involved in the process. Further work showed that physisorption occurred at low temperatures, but chemisorption became dominant at higher temperatures. Computer models were devised to predict tritium release from a ceramic breeder, and more detailed studies of adsorption-desorption and other phenomena involved in the process were continued through the end of the 1980s.

The thermal conductivity of a ceramic breeder material is important because it determines the temperature difference between the interior of the solid breeder material and the coolant/breeder interface. The thermal conductivity of 85% dense γ-$LiAlO_2$ at temperatures of 827-1127°C was about 2.5 W/(m·°C). The effects of porosity and temperature proved to be complex, however, because of different heat-conduction mechanisms involved. This finding suggested that caution be exercised in extrapolating γ-$LiAlO_2$ thermal conductivity data to other temperatures and/or porosities.

The effects of the blanket configuration on the thermal conductivity were investigated. The use of beryllium or its oxide in the form of microspheres as a neutron multiplier in "sphere-pac" $LiAlO_2$ blanket beds was evaluated by a computer study. Both mixed-sphere (γ-$LiAlO_2$-BeO) and coated-sphere (γ-$LiAlO_2$ coated with BeO) systems were studied. The coated-sphere arrangement resulted in a higher thermal conductivity.

This was a rather wide-ranging effort that included many individuals: Bob Blomquist, Wally Calaway, Norm Chellew, Rob Clemmer, Larry Curtiss, Pat Finn, Al Fischer, Carl Johnson, Bob Land, Len Leibowitz, Vic Maroni, Bali Misra, John Shearer, Shiu-Wing Tam, Marv Tetenbaum, Erv Van Deventer, Ewald Veleckis, and Bob Yonco.

AQUEOUS BREEDER BLANKET

The International Thermonuclear Experimental Reactor (ITER) project included various efforts to produce conceptual designs of a tokamak reactor that could be used to test components for a prototype fusion reactor. As a part of this study, CMT researchers examined the technical requirements for an aqueous lithium salt blanket (2 *M* LiOH or $LiNO_3$) in which tritium fuel could be bred. The study included corrosion effects in the blanket and a breeding blanket interface (BBI) for recovering the tritium product. The BBI was a complex system which required a sizeable design effort, but no experimental work was done in this area.

DOSIMETRY AND DAMAGE ANALYSIS

Work continued on the effects of the intense radiation fields in fusion reactors on component materials. The primary goal continued to be a characterization of (1) the neutron fluence and energy spectrum of neutrons produced in reactor and accelerator test facilities and (2) the damage effects on materials, including nuclear displacements, internal gas production, and transmutation rates. The group in the Chemical Technology Division, led by Larry Greenwood, had a lead role in collecting and correlating this type of information, which was essential because the irradiations were being conducted at several different facilities, including those at ANL.

The principal reactors used as irradiation facilities at the time were the Oak Ridge Research Reactor (ORR) and the High Flux Isotopes Reactor (HFIR) at Oak Ridge, the Experimental Breeder Reactor (EBR-II) at ANL-W, and the Omega West Reactor at Los Alamos National Laboratory. Accelerators can also produce high fluxes of 14-MeV neutrons similar to those in a fusion reactor, so irradiations were conducted in several accelerators—the Rotating Target Neutron Source (RTNS) at Lawrence Livermore National Laboratory (LLL), the cyclotron at the University of California at Davis, and the newly commissioned Intense Pulsed Neutron Source (IPNS) at ANL. As information was accumulated in the extensive data files at CMT, it was forwarded to the National Magnetic Fusion Energy Computer Center (NMFECC) at LLL.

Each facility had its own unique neutron flux, energy spectrum, geometry, *etc.*, so dosimetry measurements were required in order to put the irradiation effects on a common basis. To perform the dosimetry measurements, small wires or foils were included with the materials to be irradiated, and the radioactive products were measured in each sample by gamma-ray spectroscopy. The activation rates for up to 38 different nuclear reactions were then used to adjust the neutron flux spectrum, which was obtained by a neutronics calculation. This was the same technique used to characterize the neutron environment in the TRIO experiments. The cross-section data are also essential for fusion reactor diagnostics and the handling of long-lived wastes.

By 1981, extensive data files of damage parameters had been generated for 36 isotopes, including six key elements for which damage parameters up to 50 MeV had been obtained from accelerator irradiations. Prediction of damage in fusion reactor materials required prior calculation of neutron-energy-dependent cross sections, which were used to determine the number of atomic displacements and transmutations at each neutron energy. In 1982, new theoretical treatments were developed to include (n,γ) capture reactions and β-decay, and all the files were updated accordingly. The Chemical Technology Division pioneered these dosimetry and damage techniques at higher neutron energies (50 MeV) for accelerator neutron sources.

Two new activities were undertaken in 1984. One involved a joint program with the Princeton Plasma Physics Laboratory in which cross sections for the reactions ^{54}Fe(n,2n)^{53}Fe and ^{27}Al(n,2n)^{26}Al were measured near 14 MeV. Since both reactions have thresholds near the fusion neutron energy of 14 MeV, their yields are highly sensitive to the plasma temperature, which determines the neutron spectrum near 14 MeV, and the yields of the reactions can be used for plasma diagnostics. They are also useful in calculating the radioactivity levels of activation products in fusion-reactor wastes. The other new program was the measurement of spallation yields of specific isotopes to determine the neutron spectrum. The utility of this technique was demonstrated in collaborative experiments between IPNS and the Los Alamos Meson Physics Facility (LAMPF). Work then continued on cross-section determinations for a variety of isotopes of interest to the fusion program. Vanadium, iron, copper, nickel, and molybdenum were of particular interest.

The formation of helium by (n,α) reactions in structural materials was studied by experiments with nickel, copper, and zinc. As an example, helium concentrations up to about 100 ppm were generated in copper in a neutron fluence of 6×10^{22} n/cm^2. Subsequent work showed that more helium than was expected was produced in iron samples.

By the end of the 1980s, the fusion research group in CMT had become well known nationwide and internationally for its comprehensive experimental studies and computations relating to radiation damage from the neutrons in fusion systems. Their SPECTER computer code was used to determine atomic displacements, gas production, and other transmutations in a wide variety of materials. Near the end of the decade, a part of the program effort took an interesting twist when it was realized that their work had possible applications relating to the Strategic Defense Initiative, and several avenues of investigation were proposed in the area of nuclear arms treaty verification.

The people who were active in this program were Rob Clemmer, Don Graczyk, Larry Greenwood, Ray Popek, Chuck Seils, and Bob Smither.

"COLD FUSION"

Early in 1989, two electrochemists, Stanley Pons of the University of Utah and Martin Fleischmann of the University of Southampton, England, startled the scientific community with an announcement that they had achieved "cold" (room-temperature) nuclear fusion by electrolyzing heavy water (D_2O), using platinum and palladium electrodes. They claimed that the cell produced more heat than could be accounted for by the chemical reactions alone, and they thought they observed gamma rays at energies typical of fusion, although that result was disputed. Because of the important scientific and technological implications of these results, laboratories all around the country started trying to reproduce the experiments, generally with negative or ambiguous results.

At CMT, Laszlo Redey, Mike Myles, Dennis Dees, Mike Krumpelt, and Don Vissers became interested in the subject and conducted two series of experiments: (1) differential temperature analysis of identical light- and heavy-water electrochemical cells and (2) calorimetric measurements on operating heavy-water cells. Wrought palladium cathodes and platinum anodes were used in both cases. The first series of experiments was unsuccessful because identical electrochemical conditions could not be maintained in the two cells. In the second series of experiments, cells were operated in a calorimeter sensitive enough to detect the levels of excess heat reported by Pons and Fleischmann. The results of the energy-balance measurements and calculations showed no significant excess heat.

Efforts to reproduce the cold fusion experiments at various laboratories gave mixed results, but generally tended to be unconvincing (for example, no neutrons were detected). There were (and still are) some scientists, however, who believe that the phenomenon is real. Toward the end of 1989, the CMT workers proposed a joint research effort with Case Western Reserve University, where they had seen some evidence of excess heat in their experiments, to investigate the matter more thoroughly, but the proposed program had to be dropped for lack of funding.

Steel Research Initiative

In 1987, a program that resulted from a joint steel industry/federal laboratory research initiative was aimed at reducing equipment, operating, and energy costs in the steel industry through the use of new, innovative technologies. The purpose of the ANL program was twofold: (1) the development of an electromagnetic process for the continuous casting of various grades of steel in large-aspect-ratio shapes such as steel strip and (2) the development of an economical process for the purification of ferrous scrap. Although this program was under the general direction of Jim Battles, essentially all the work was done in the Energy and Environmental Systems, Electromagnetic Technology, and Materials and Components Technology Divisions. Bali Misra of CMT also contributed some effort to this program.

ELECTROMAGNETIC CASTING OF STEEL

In the production of steel strips, sheets, and other shapes, liquid steel from the production furnace is either cast into large ingots or slabs, or fed into a continuous casting process, and then subjected to rolling and other operations to produce the final product. Electromagnetic continuous casting involves the use of magnetic fields to form a liquid sheet of the metal, which is levitated until it is solidified by cooling. The electromagnetic continuous casting studies were focused on levitation experiments, development of a caster design, fluid-flow analysis and experimentation, heat-transfer analysis, and sensors for on-line monitoring and process control.

Levitation Experiments. The experimental work was directed initially toward the development of a combination of high-frequency magnetic fields and eddy currents. Tin, which has a melting point of about 250°C, was used as a stand-in for steel to permit a more convenient operating temperature. A test magnet, 20 cm wide and 13 cm high with a 30-cm-long ferrite core, was designed and built to study the magnetohydrodynamic stability of the liquid metal. The experiment was started by inserting a sheet of tin into the magnet and melting it by eddy-current heating. The liquid tin sheet was disrupted before levitation, apparently due to a mismatch between the electrical conductivities of the stainless steel window and the liquid tin. Somewhat better results were obtained when the stainless steel was replaced by copper or Monel metal, but the results indicated that the low frequency (10 kHz) and power output (30 kW) of the equipment would both have to be increased.

Electromagnetic Design. A computer code (PE2D) was used to evaluate various magnet geometries for a horizontal electromagnetic caster. A cross section of a conceptual design for a bench-scale unit is shown schematically in Fig. 5-17. The window-frame design was expected to yield a very uniform horizontal field (± 0.2%). Special design features were the copper shields and the side guards. The frequency of the AC field was such that it penetrated less than one-third the thickness of the steel sheet. The steel levitated due to longitudinal eddy currents normal to the direction of the AC field, and the magnetic force generated by interaction of the eddy currents with the AC field.

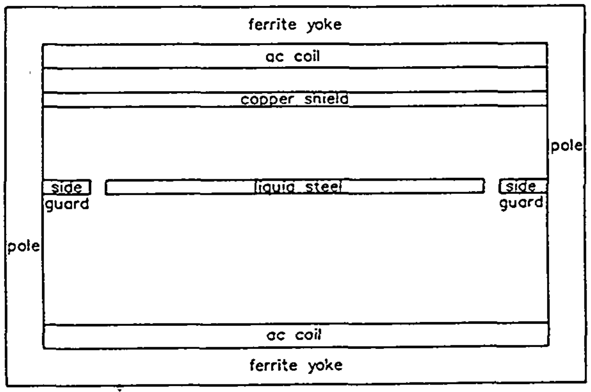


Fig. 5-17. Cross Section of Conceptual Horizontal Caster

Feed System Development. It was assumed initially that a conventional liquid metal feed system would be suitable for a bench-scale caster. Preliminary analysis, however, showed that low turbulence levels are required to achieve good stream quality and steady-state flow, and means are necessary to remove inclusions and minimize heat loss. A parametric study using a three-dimensional computer code, COMMIX, provided design guidance for the feed system.

Test results from a series of experiments on wave formation at a gas/liquid metal interface showed that a magnetic field could damp out waves formed on a liquid metal surface by a nitrogen gas stream. A second series of experiments, using a water model, indicated that the geometric characteristics of the nozzle affecting the shape and velocity distribution of the emerging liquid stream were (1) the aspect ratio of the nozzle cross section, (2) the area contraction ratio from inlet to exit, (3) the length of the straight section, and (4) the corner curvatures of the exit cross section. To evaluate the effects of these geometrical factors, eleven Plexiglass® nozzles of various geometries were built and tested. To obtain further design information, an experimental feed system for recirculating liquid tin was designed and fabricated. That system was used to investigate the flow of molten metal through different types of nozzles.

Heat-Transfer Analysis. A key element in the casting process was the necessity to cool the molten metal quickly as it left the caster so it maintained the desired dimensions and shape as it solidified. Radiative cooling was insufficient, so convective cooling had to be provided. That had to be done in such a way, however, that it did not disturb the flow of the liquid steel. To proceed with a parametric investigation of the problem, a set of reference conditions had to be established. These included items such as the outlet temperature, thickness of the steel strip, casting speed, coolant pressure, electromagnetic heat flux, emissivity of the steel, coolant gas, coolant velocity, magnet length, and coolant channel height. A literature review revealed a variety of cooling-enhancement techniques, including the addition of fine water droplets to a coolant gas, which was highly effective.

Sensors and Process Control. The initial effort in this area was focused on sensors and control systems for on-line process monitoring and automatic control of the casting process. A wave detector based on capacitance changes was developed for quantifying and characterizing surface-wave formation caused by the coolant gas. A spectrophotometer was modified and fitted with fiberoptic light guides for measurements of tracers and water-jet thickness variation. A review of sensor and control needs indicated that certain components were available commercially, but that further research and development would be required in some cases.

STEEL SCRAP BENEFICIATION

The purpose of this work was to develop processes that will produce high-quality, deep-drawing steels from low-grade ferrous scrap material. The Institute of Scrap Iron and Steel at that time estimated a ferrous scrap inventory of about 750 million tons, and that inventory was growing in spite of the fact that more units of steel were being produced from scrap than from ore in the domestic production of steel. A major impediment to greater use of scrap was the presence of undesirable residual elements such as copper and tin, which degrade the quality of steel. This part of the steel research was done by Milt Blander and his coworkers and might be more appropriately placed in the basic research studies, but it is germane to the general area of steel production.

Removal of Copper from Scrap Steel. In the common types of ferrous scrap material, copper is present in concentrations of about 0.2 or 0.6 wt%. For deep-drawing steel, the allowable copper content is 0.1 wt% or less; for steel tubing or pipe, it is 0.2 wt%; the lower grade rebar steel can contain 3 wt% or more. Thus, to produce high-grade steel from low-grade scrap, the copper content must be reduced by a factor of six or more.

With the common steel-making slags in an electric-arc furnace, all of the copper remains in the molten metal. Thermodynamic data indicate that the copper could be extracted into the slag by the addition of sulfides. The reaction $FeS + 2\ Cu \leftrightarrow Cu_2S + Fe$ can be driven to the right by using a slag in which Cu_2S has a low activity coefficient, such as a polyvalent sulfide, *e.g.*, an Al_2S_3-FeS slag. With this type of system, distribution coefficients (wt % Cu in slag/wt % Cu in metal) as high as 30 were obtained. Even with this large distribution coefficient, however, a slag volume about equal to the metal volume would be needed to decrease the copper content by a factor of ten. This copper-extraction procedure leaves some sulfur in the steel. This sulfur is removed by exposing the steel to metallic calcium or aluminum.

Preliminary economic analyses of the above procedure indicated a potential saving of about 20% for the production of liquid steel, and savings up to 30% may be achievable if the spent slag is reprocessed and reused.

Removal of Tin and Other Tramp Elements. Tin is present in ferrous scrap material at concentrations of 0.05 or 0.02 wt%, depending on the type of scrap. Permissible levels for tin are 0.01 wt% in deep-drawing steel, 0.02 wt% in pipe and tubing steel, and 0.03 wt% or more in rebar steel. Calcium reacts with more electronegative metals such as tin, *i.e.*, Ca + Sn → CaSn, and the literature reports that calcium can be used to remove tin and sulfur from molten steel. Preliminary experiments with *in situ* electrochemical generation of calcium for this purpose were promising.

Sodium Technology

From the late 1960s through the middle 1970s, the major efforts in sodium technology at Argonne were on development of continuous on-line impurity monitors and improved chemical analytical procedures for the major impurities of concern in sodium, namely, oxygen, hydrogen, and carbon (as Na_2O, NaH, and Na_2C_2). These were to be applied at the FFTF (Fast Flux Test Facility), then under construction at Hanford, Washington. When prototype monitors and the improved analytical procedures were tested at EBR-II, it was found that the concentrations of these impurity elements were much lower than had previously been measured by much less sensitive analytical methods. Moreover, the cold traps on the primary and secondary sodium systems maintained essentially constant concentrations of oxygen and hydrogen. This finding eliminated the need for the expensive on-line monitors and costly facilities to house them.[1] In the Chemical Technology Division, work was shifted to optimization of cold-trap design, *in situ* regeneration of plugged cold traps, purification of sodium to reduce the level of radioactive contamination, and disposal of radioactive sodium and sodium-containing wastes. This program was managed by Chuck McPheeters.

OPTIMIZATION OF COLD TRAP DESIGN

Sodium impurities, particularly sodium oxide and sodium hydride, are normally controlled by low-temperature precipitation and deposition of the precipitates in cold traps. In a cold trap, the sodium enters at the top of an annular section created by a circular divider that extends to near the bottom of the cold trap, and then flows upward through the central section. Both the central and annular sections are packed with wire mesh, which provides nucleation sites for the impurity precipitates. In the cold trap the sodium is cooled to a temperature of about 125°C. When a cold trap becomes filled with precipitates, a sharp increase in the pressure develops across the unit. Only a small fraction of the main sodium flow (2% or less) is diverted through a cold trap for removal of oxygen and hydrogen

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[1] Work did continue on the development of hydrogen leak detectors in the Components Technology Division for long-range applications to liquid metal fast breeder reactors, but the hydrogen leak detector was not required on FFTF because it was not equipped with a steam generator.

impurities. In large LMFBRs, hydrogen produced by water-side corrosion of steam-generator tubes diffuses into the secondary sodium system at a high rate. Although the hydrogen is removed continuously by the secondary system cold trap, much of it diffuses through the intermediate heat exchanger into the primary system, where it is removed by the primary system cold trap. The major impurity deposited in the primary and secondary system cold traps is sodium hydride (NaH). Cold-trap lifetime is limited by the deposition of sodium hydride in the primary and secondary system cold traps.

In the CMT Division, work was undertaken to increase the cold-trap capacity, and hence, its useful lifetime by optimization of the design. A one-dimensional computer model was developed with which distribution of impurity deposits within a cold trap was calculated from temperature profiles, impurity concentrations, wire-mesh packing density, and geometrical dimensions. This model was tested using small, simple cold traps installed on AMPS (Apparatus for Monitoring and Purifying Sodium). The cold traps consisted of 19-mm-dia tubes, 560 mm long, with thermocouples along the centerline and air cooling along the exterior to establish a temperature gradient along the trap's length. The cold traps were packed with wire mesh to different densities to provide extended surface area for impurity nucleation and growth. The amount of impurity deposited in a trap was determined by continuously measuring inlet and outlet impurity concentrations. These measurements were made using on-line oxygen and/or hydrogen meters.

After an impurity-deposit experiment, the cold trap was cut into segments to determine mass distribution within the trap. The distribution of NaH precipitates was in excellent agreement with model predictions, but that for Na_2O was not. The difference was attributed mainly to poor adherence of the Na_2O crystals on the stainless steel surfaces. Inaccurate or drifting oxygen-meter calibration may have been a contributing factor.

A two-dimensional model was then developed to aid in optimizing cold-trap design for maximum capacity. This model, named MASCOT (Model for Analyzing Sodium Cold Traps), was used to determine, by means of a parametric study, which cold-trap design variables have the greatest impact on capacity. The base case was the cold-trap design for the Clinch River Breeder Reactor (CRBR). The results of this study are shown in Fig. 5-18, where capacity, defined as percent of mesh volume filled with impurity, is plotted as a function of the L/D (length/diameter) ratio and the ratio of annular downflow area to the central upflow area (ANN/CEN). The other curves are cases of different mesh packing densities. The most important factor is the ratio of the annular area to the central area. The capacity can be increased about threefold by increasing the ratio from 1.0 to 80 (large annular area, small central sodium return pipe).

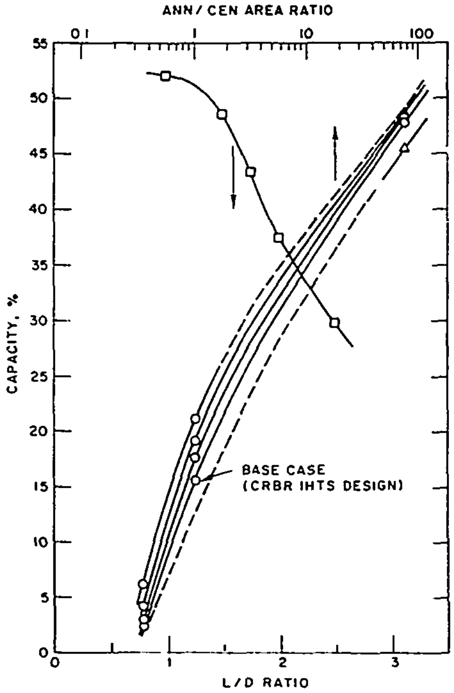

Fig. 5-18. Cold Trap Capacity as a Function of Area and L/D Ratios

The L/D ratio is also important and should not exceed about 1.5. The CRBR cold-trap design was revised to reflect the results of this study.

To verify the accuracy of the MASCOT computer model, calculated and measured sodium hydride distributions were compared for cold traps from actual operating systems. These included the primary system cold trap of the Fermi reactor, two industrially fabricated cold traps used on experimental systems by the General Electric Co. and Mine Safety and Appliance Co., and two experimental cold traps operated on an ANL system. In all cases, the measured and calculated sodium hydride distributions were in excellent agreement.

The MASCOT was subsequently used to design cold traps having volumes of 3,000 to 7,000 L to satisfy the needs of liquid metal fast breeder reactors ranging in size from 1,000 to 3,500 MW(t).

IN SITU REGENERATION OF COLD TRAPS

A method of increasing cold-trap life is *in situ* regeneration, which is achieved by thermal decomposition of NaH, the bulk constituent, under a vacuum. The feasibility of *in situ* regeneration was demonstrated in small-scale tests in 1981, so plans were made to demonstrate the procedure on a full-size, plugged cold trap that had been removed from the EBR-II secondary system in 1970 and placed in storage.

Chemical Technology Division staff designed, fabricated, and installed the regeneration system (see Fig. 5-19). In the regeneration test, approximately 13,200 L of gas, predominantly hydrogen, was removed in 97 h. This represented 97-98% of the original quantity of hydrogen in the trap.

Subsequent efforts were directed to selecting a viable, safe, and economical method for treating the gas, which also contained some tritium, for disposal. A variety of processes were reviewed for separation, concentration, conversion, and stabilization of the tritium-contaminated hydrogen. The most direct, cost-effective approach was to consider the hydrogen and tritium gases as one entity, convert them to water (H_2O and T_2O), and incorporate the water into concrete formed in a steel drum. Chemical Technology Division staff recommended that the gases be processed as they exited the regeneration unit. The Sodium Technology Program was terminated before gas conversion and immobilization of the tritium-contaminated water in concrete could be demonstrated.

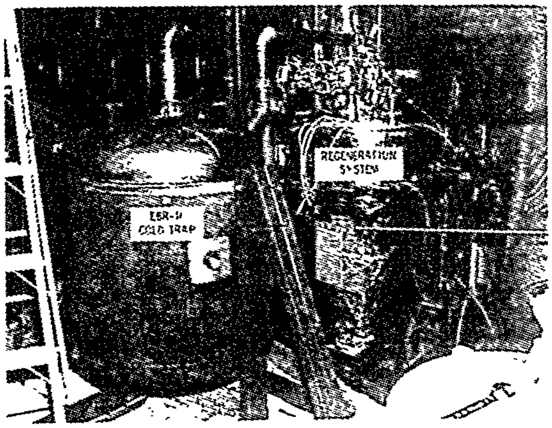

Fig. 5-19. Cold-Trap Regeneration System

SODIUM PURIFICATION BY DISTILLATION

Operation of LMFBRs, particularly with some fraction of breached fuel elements, results in contamination of sodium with radioactive fission products. Decontamination of the sodium should aid in the rapid detection of additional fuel-cladding failures and also allow easier future reuse of sodium after reactor decommissioning. The radioactive species of major concern are cesium-137, barium-133, fuel particles, and various fuel-coolant reaction products.

The CMT Division explored several methods for decontaminating sodium. These included soluble gettering, reaction with various solids (including graphite), and low-pressure distillation. A reticulated vitreous carbon trap had been used successfully at EBR-II for removing ^{137}Cs, but it is specific only for cesium and risks introduction of carbon-bearing species into the sodium. The Division selected low-pressure distillation for development.

The feasibility of separating ^{137}Cs and ^{133}Ba was first demonstrated in a small, total-reflux distillation column 100 mm in diameter and 610 mm long. This small column was packed with wire mesh, and the reboiler was filled with 7.7 kg of sodium spiked with ^{137}Cs and ^{133}Ba. The decontamination factor for ^{137}Cs (concentration ratio of that in top product to that in the reboiler) was 200. The ^{133}Ba reacted with small amounts of Na_2O to form BaO, which plated on the column surfaces.

These encouraging results led to construction of a larger (204-mm ID) column consisting of three 0.61-m-high packed sections with a reboiler at the bottom and condenser at the top. Contaminated sodium was fed between the bottom and middle sections; and product sodium was withdrawn from between the middle and top sections. When the column was operated, ^{137}Cs in the product stream was below the background level, so an accurate decontamination factor could not be determined. Again, BaO plated out on the column surfaces.

A series of runs was made with $Na^{131}I$ in an attempt to determine the HETP (height equivalent to a theoretical stage). As nearly as could be determined, the HETP was in the range of 100 to 300 mm.

Development of the distillation process was concluded with a test using primary sodium from the Fermi reactor. The ^{137}Cs level in the product was again very low, 3×10^{-6} ppm, which is much lower than the concentration of approximately 52 ppm permitted for shallow land burial.

SODIUM WASTE TECHNOLOGY

In 1980, the Division provided technical support to ANL-West on development of a melt/drain, evaporation, calcination (MEDEC) process for disposal of radioactive waste containing elemental sodium. The MEDEC process was to be incorporated into the Sodium Process Demonstration plant planned for construction at ANL-West to demonstrate the safe treatment of wastes containing metallic sodium. The process consists of (1) melting and draining sodium from waste and scrap, *e.g.*, a cold trap, (2) evaporation to remove residual sodium, and (3) calcination to convert sodium into Na_2O. Incorporation of Na_2O into a high-sodium glass was subcontracted to Battelle Pacific Northwest Laboratory. Development work by CMT on the calcination step was completed in about 1980 and is described in Chapter 4.

The sodium evaporation step required work in three areas: (1) treatment of tritium gas released during removal of sodium from a cold trap,[2] (2) development of sodium-vapor-detection instrumentation for determining the end point of an evaporation cycle, and (3) determination of the effects of organic waste items (plastic bags, paper wipes, *etc.*) inadvertently mixed with the waste. The Argonne Chemistry Division conducted work on the treatment of tritium-containing gases.

For the sodium-evaporation step, four methods were tested for detecting the end point of the evaporation step: (1) measurement with ordinary vacuum gauges, (2) use of atomic absorption, (3) determination of breakdown voltage, and (4) use of a quadrupole mass spectrometer. The quadrupole mass spectrometer proved to be the most reliable and

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[2] This reprepresents a situation in which *in situ* regeneration is not practiced, and the cold trap is slated for disposal. It is assumed, however, that the bulk of the hydrogen and tritium was removed by thermal decomposition.

effective method. The design and operating procedure for it were prepared for ANL-West.

Organic materials added to the sodium did not cause rapid or violent reactions at temperatures up to 450°C and under an argon atmosphere. Nor did they interfere with the detection of the evaporation end point. However, a carbonaceous residue accumulated in the boiler, and it was recommended that organics be removed to the extent possible before the processing of sodium-containing wastes.

SODIUM-CONCRETE REACTIONS

In some of the modeling scenarios of core-meltdown accidents, liquid sodium containing heat-generating debris comes in contact with the concrete basement of the containment vessel. In such a case, water emanating from the concrete would react with the sodium, thereby producing NaOH and other reaction products. The resulting phase relationships among the non-gaseous species are complicated, but literature data indicated that they had been well characterized at temperatures below about 550°C. No experimental work, however, had been reported above that temperature, so an experimental investigation of the $Na\text{-}Na_2O\text{-}NaOH\text{-}NaH$ system was undertaken.

Equilibrium hydrogen pressures were determined as functions of temperature and hydrogen content above mixtures with fixed Na:O ratios. Four isotherms obtained from a sample having a Na:O ratio of 1.983 provided information on the boundaries between the various phase fields. Due to other priorities, no further work was done in this area.

PERSONNEL

The sodium program was in Fred Cafasso's part of the division, and then under Martin Steindler. Chuck McPheeters and Verne Kolba had Group Leader responsibilities. Others in the program were Joanne Fink, Vic Kremesec, Len Leibowitz, Bali Misra, Don Raue, Stan Skladzien, Charles Smith, Marv Tetenbaum, and Ray Wolson.

Nuclear Separations Technology

ANALYTICAL SUPPORT FOR LWBR PROOF-OF-BREEDING

The program to provide analytical support for determination of the extent of breeding in the Light Water Breeder Reactor (LWBR) at Shippingport, PA, continued into the 1980s (see Chapter 4). The role of CMT was to analyze segments of fuel rods for total uranium, individual uranium isotopes, and certain fission products, the latter to enable a determination of burnup. The fuel segments were cut from precisely located positions along a fuel rod. The work was carried out under the direction of Bettis Atomic Power Laboratory (BAPL), which had the responsibility for determination of breeding.

Delayed neutron profiles of fuel rods selected for analysis by CMT were obtained by BAPL, using a Production Irradiated-Fuel Assay Gauge (PIFAG). The CMT analyses enabled Bettis to calibrate the PIFAG so that it could be used later to obtain total uranium and the amounts of uranium isotopes (U-232 and U-233) in 500 fuel rods statistically selected from a total of 17,192 fuel rods discharged from the reactor after four years of irradiation (end-of-life). From these measurements, Bettis could obtain the fissionable uranium content of the entire core.

Analyses of the fuel rods started with precision shearing of the rod into segments by a specially designed shear that simultaneously pulverized the fuel and freed it from the cladding during the shear stroke. Segment lengths ranged from 17.5 to 53.3 cm. From the initial boundary of the segment, small lengths of the fuel rod (about 1/4 in.) were sheared until the final boundary of the segment was reached. All of the material from an original segment was collected in an aluminum sample can, and the entire can and contents were dissolved in a 13.6 *M* HNO_3-0.06 *M* HF solution at 195°C and a pressure of 125 psig in a tantalum-alloy dissolver. The dissolver solutions were analyzed for total uranium and uranium isotope abundances by a combination of mass spectrometric isotopic dilution (MSID) and alpha spectrometry. High-precision, high-accuracy analyses were required.

Following tests of a prototype dissolver, two complete dissolver systems were installed in one of the manipulator-equipped M-Wing caves in Building 200. Each dissolver system consisted of a tantalum alloy vessel mounted in a stainless steel shell, associated liquid and gas handling equipment, and electronic balances for weighing the fuel charge. Tantalum alloy vessels were required to provide corrosion resistance to the highly corrosive nitric-hydrofluoric acid dissolver solution.

Computer programs were developed for automation of the dissolving operation. After dissolution of a fuel segment, a dissolver was thoroughly cleaned before dissolution of the next segment. Cross-contamination was less than 0.005%, well within the 0.01% stipulated by BAPL.

The campaign for destructive analysis of seventeen fuel rods of various types (core, blanket, and reflector) began in August 1985 and, with 24-hour operation during weekdays, was concluded in November 1986. The fuel recovery on shearing of the fuel rods averaged well above the minimum of 99.75% required by BAPL. The fuel dissolution procedure consistently provided 99.99% recovery of each fuel segment. Performance of the analytical operations was also outstanding. Analyses of two separate dissolver samples from dissolution of 135 fuel-bearing segments by the MSID method showed an average difference of only 0.01%. Measurements of precision and accuracy for cesium-137 and cerium-134 also exceeded requirements. (Analysis for zirconium-95 was dropped.)

The BAPL staff stated that they were very pleased with the high quality results achieved in this program, which made possible a "fine-tuned" calibration of the PIFAG. Later, BAPL reported breeding ratio values in the LWBR that were slightly greater than one (1.013 and 1.015), but too low to be of practical interest.

One task remained—disposal of the 700 L of dissolver solution produced in the end-of-life campaign. The dissolver solution was mixed with cement in 5.7-L cans to produce a monolithic solid. Excess lime was used to ensure acid neutralization. Two primary cans were placed in a secondary can, which, in turn, was loaded into a 55-gal drum containing a specially designed shielded cask. Suitable for ultimate disposal as transuranic (TRU) waste, they were first shipped for interim storage (up to 25 yr) at a site operated by the Rockwell International Corp. at Richland, WA.

This program required a sizeable group that included Roy Benson, Ron Brock, Tom Cannon, Phil Deeken, Jim Fagan, Don Graczyk, Joe Hoh, John Kincinas, Ralph Leonard, Fred Martino, Bob Meyer, Bob Nelson, Jack Parks, Don Raue, Lewis Ruppert, Glen Tomlinson, Verne Trevorrow, Charlie Wach, Prince Walker, Irv Winsch, and Tony Ziegler. Norm Levitz had the overall responsibility for the program.

TRUEX PROCESS DEVELOPMENT

Process Description. In 1984, the CMT Division began a cooperative program, under the leadership of George Vandegrift, with the Chemical Separations Group of the ANL Chemistry Division (CHM) to develop the TRUEX (Transuranic Extraction) process. This process, which was invented by members of the Chemical Separations Group led by Phil Horwitz, uses an extractant, abbreviated CMPO, in combination with tributyl phosphate (TBP), the conventional Purex process extractant, and a diluent. The diluent is typically a normal paraffinic hydrocarbon, such as dodecane, which is used as the TBP diluent in the Purex process, or a nonflammable chlorocarbon, such as carbon tetrachloride or tetrachloroethylene.

The chemical structure of CMPO is shown in Fig. 5-20. The name for it is octyl(phenyl)-N,N-diisobutyl carbamoyl phosphine oxide. Its discovery was the result of basic research studies in the Chemistry Division on a series of neutral, phosphorus-based bifunctional extractants.

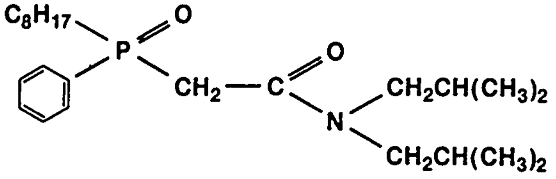


Fig. 5-20. Chemical Structure of CMPO Extractant Used in Purex Process

The distinguishing feature of CMPO is its ability to extract trivalent elements from nitric acid. The intended application of the TRUEX process was for processing a variety of Hanford wastes to remove the transuranic (TRU) elements, specifically neptunium, plutonium, and americium. In nitric acid solutions, these elements exist predominantly in the trivalent state or can easily be put in the trivalent state. In the Purex process, neptunium and americium (and a small fraction of the original plutonium) report to the first-cycle aqueous waste. Transuranic wastes, because of their long half-lives, must be disposed of in a deep geologic repository. Removal of the TRU content of a waste to below 100 nCi/g of solid makes it a "nonTRU waste" eligible for less expensive, near-surface burial. Application of the TRUEX process to nuclear wastes in the United States would (1) greatly lessen the amount of waste that must be buried at the Waste Isolation Pilot Plant (WIPP), (2) recover substantial amounts of TRU elements, *e.g.*, plutonium, that otherwise would be lost, and (3) alleviate long- and short-term problems with waste storage that threaten to curtail the production of plutonium.

In concept, the TRUEX process is the same as the Purex process. The solvent-extraction step consists of the conventional extraction, scrubbing, and stripping operations.

Because of their small size and high throughput, centrifugal contactors were an integral part of implementing the TRUEX process. One advantage of centrifugal contactors is that they can fit into conventional glove boxes. Another advantage is that the number of stages allocated to the extraction, scrubbing, and stripping operations, all of which are conducted within the same unit, can easily be changed to achieve desired process objectives and to accommodate new process flowsheets.

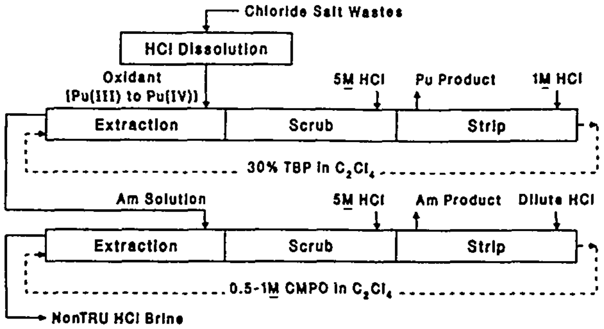
Plutonium Finishing Plant Waste. In 1985, a flowsheet was developed and tested for removal of americium and plutonium from Plutonium Finishing Plant (PFP) waste, one of the wastes at the Hanford site. This waste, which contains americium and plutonium in low concentrations, is generated when plutonium-bearing scrap is converted into concentrated plutonium nitrate solutions. The flowsheet was demonstrated in a 14-stage centrifugal contactor (five extraction, two scrub, four americium stripping, and three plutonium stripping stages). Results were excellent. The aqueous waste contained <10 nCi of TRU per gram of solid. The americium and plutonium product streams contained >99.9% of that in the feed solution.

In 1987, CMT personnel assisted Hanford personnel in making the first TRUEX process tests, using actual PFP wastes. No problems were encountered in operating the centrifugal contactors and in implementing the PFP flowsheet.

Processing of HCl/Brine Solutions. In 1985, work was started on the development of a solvent-extraction process to remove plutonium and americium from chloride salts generated at Los Alamos in pyrometallurgical processes for recovering and refining plutonium. A two-cycle flowsheet (Fig. 5-21) was devised in which plutonium, oxidized and maintained in the tetravalent state by sodium chlorite, was extracted from a water solution of the salt waste into TBP with 25 vol% tetrachloroethylene (TCE) solvent in the first cycle. In the second cycle, americium was removed from the brine solution into a 0.5 *M* CMPO-TCE solvent. In each cycle, the solvent extracts were scrubbed with 6 *M* HCl, and the products were stripped into a dilute HCl solution.

The CMT Division had the responsibility for developing the first cycle, which is a Purex-type cycle. The Chemistry Division developed the TRUEX second cycle. During 1987, the Purex-TCE cycle was installed in a glove box at Los Alamos. The separation was made in a 16-stage contactor fabricated largely of Hastelloy C276 (see Fig. 5-22). Very good plutonium recoveries were achieved, and the Purex-TCE cycle was adopted for production use. Some corrosion of the Hastelloy C276 occurred, and an ANL-type contactor made of Kynar® was fabricated for Los Alamos by a French firm, Robatel.

The TRUEX-TCE cycle was not put into operation, primarily because americium recovery was of secondary importance, and because glove-box space was not available for its installation.



This flowsheet exemplifies the manner in which a Purex solvent-extraction cycle can be coupled with a similar TRUEX cycle to achieve a three-way separation of uranium, plutonium, and TRU elements. A separation of this type could be useful in developing processes for treating nuclear wastes.

Fig. 5-21. Process for Recovery of Americium and Plutonium from Chloride Salt

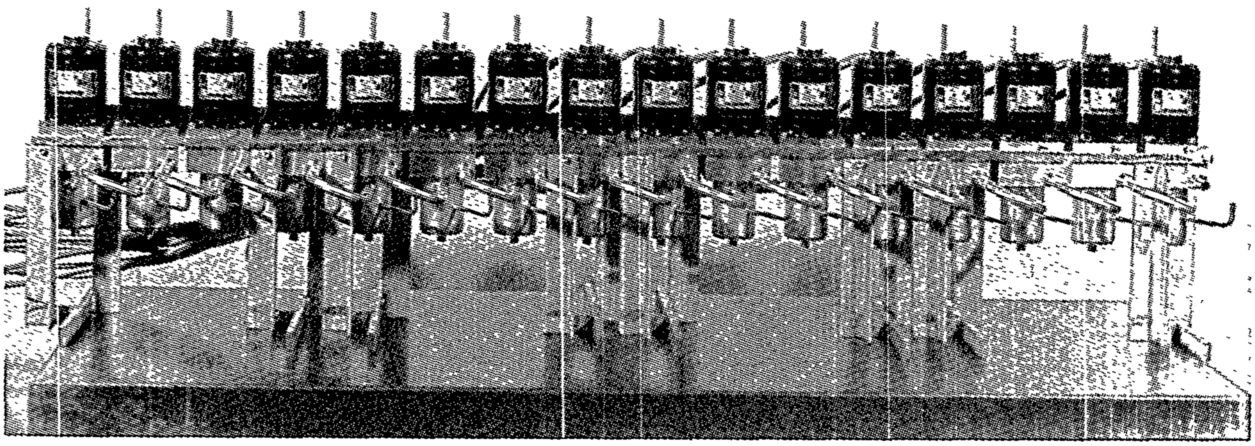


Fig. 5-22. Sixteen-Stage Centrifugal Contactor Used in TRUEX Process

Generic TRUEX Model. Because of the wide variety of actinide wastes in the United States, a large effort was devoted to developing a generic TRUEX model by which distribution coefficients of the key elements could be determined from a knowledge of the waste composition. Flowsheets based on the distribution coefficients could then be developed. The model enabled determination of stagewise composition changes in countercurrent multistage contactors.

Considerable success was achieved with the model. Curves A, B, and C in Fig. 5-23 show the ultimate agreement between the model and experimental data as successive improvements in the model were made. Figure 5-24 shows the close agreement between experimental and calculated values for stage-to-stage concentrations of nitric acid in the aqueous phases of a 14-stage centrifugal contactor.

Radiolytic and Hydrolytic Degradation of the TRUEX Solvent. If the TRUEX process were used to extract TRU elements from the first-cycle waste of the Purex process, the TRUEX solvent would be degraded by radiolysis and hydrolysis. The extent of solvent degradation by these mechanisms was determined by changes in the americium distribution coefficient between 2.0 *M* nitric acid and the TRUEX solvent (CMPO diluted with a paraffinic hydrocarbon). The extent of degradation is similar to that for TBP in the Purex process. Degradation by hydrolysis was approximately one-thirtieth of that by radiolysis.

Extensive studies of radiolytic and hydrolytic damage to CMPO were also made at nitric acid concentrations of 0.01 and 0.05 *M* and at temperatures of 70 and 95°C. From these, G values (molecules of CMPO destroyed per 100 eV of absorbed radiation) were obtained, and rate constants for hydrolysis of CMPO at any temperature could be derived. Algorithms expressing the amount of decomposition of CMPO by radiolysis and hydrolysis were incorporated into the Generic TRUEX model. Washing a degraded TRUEX solvent with a carbonate solution effectively removes the degradation products.

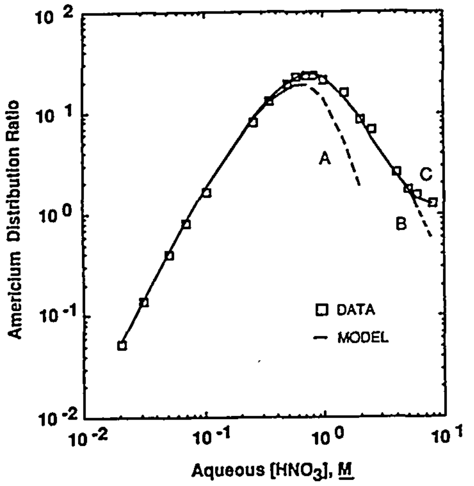


Fig. 5-23. Effect of Nitric Acid Concentration on Extraction of Americium by TRUEX Process (A, B, and C show successive model refinements.)

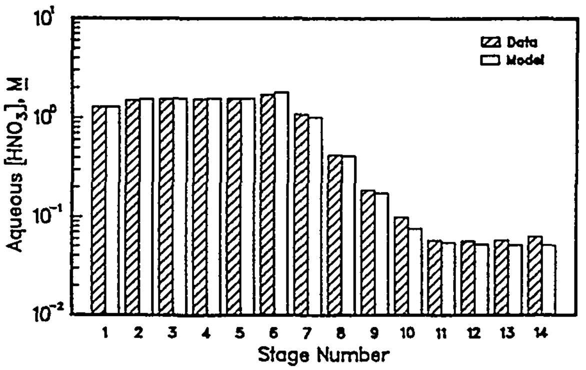


Fig. 5-24. Experimental and Calculated Values for Nitric Acid Concentrations in 14-Stage Centrifugal Contactor

Centrifugal Contactor Development. Because of the importance of centrifugal contactors in the TRUEX process, continued improvements were made in their design and operation. One of these was the design of a remotely operable contactor for operation within a glove box or a shielded cell facility.

Provisions were made for easy installation and removal of major components, such as the motor-rotor assembly. Several contactors were designed and fabricated at ANL for installation at other DOE sites, including Hanford, Y-12 at Oak Ridge, and Los Alamos.

To permit design modifications to accommodate different flowsheets, models were developed for calculating aqueous and organic flow through the contactor and vibrational parameters of spinning rotor-motor combinations.

Personnel. George Vandegrift was in charge of the CMT work on TRUEX. Other members of the group were Natalie Blake, David Chaiko, David Chamberlain, Lorac Chow, Clifford Conner, Jacqueline (Leddin) Copple, Don Fredrickson, Eddie Gay, Ray Jaskot, Jane Kwok, Ralph Leonard, Frank Mrazek, John Rajan, Monica Regalbuto, Lucinda Reichley-Yinger, Carmen Sabau, Wally Seefeldt, Ian Tasker, Verne Trevorrow, Pui-Kwan Tse, Erv Van Deventer, and Jake Sedlet.

Ralph Leonard was in charge of the centrifugal contactor effort, which also included George Bernstein, Bob Frank (TD), Ralph Pelto, Ron Wigeland, and Tony Ziegler.

RECOVERY AND SEPARATION OF MOLYBDENUM-99

In 1985, the Division began a small program, under the leadership of George Vandegrift, to assess the feasibility of substituting low-enriched uranium (LEU, 20% ^{235}U) for high-enriched uranium (HEU, 93% ^{235}U) for production of the fission product ^{99}Mo. This substitution was required by the United States government to prohibit export and internal use of HEU because of its potential use in nuclear weapons. Most of the world's supply of ^{99m}Tc for medical-diagnosis applications is produced from ^{99}Mo.

Molybdenum-99 decays with a half-life of 66 h to metastable technetium-99, which has a half-life of 6.5 h. Targets containing ^{235}U need to be irradiated for five or six days to reach a steady-state concentration of ^{99}Mo. The targets must then be processed rapidly to produce a ^{99}Mo source from which ^{99m}Tc may be stripped periodically. For example, an alumina column on which ^{99}Mo has been deposited could be "milked" several times to remove ^{99m}Tc before most of the ^{99}Mo has decayed.

Targets of HEU consisted of uranium aluminide in curved plates, uranium-aluminum alloys in modified fuel rods, and electrodeposited films of UO_2 on the inside surfaces of cylinders. Substitution of LEU for HEU would require dissolving and separating ^{99}Mo from nearly five times more uranium. The greater amount of uranium would also likely affect the removal of other impurities from the ^{99}Mo. To overcome partially the low concentration of ^{235}U in LEU while maintaining the same target geometries, denser uranium targets were sought. The objective of the Division's work was to evaluate alternative target materials and to develop procedures for dissolving them, and for separating ^{99}Mo from the bulk of the uranium and other target material constituents.

Early consideration was given to U_3Si_2 dispersed in aluminum and clad in aluminum. Although dissolution procedures for the target material constituents were developed, they were cumbersome and unattractive, and the presence of large amounts of silicon caused downstream processing problems. Another candidate was electrodeposited uranium to form freestanding hemispherical shells. Don Vissers was achieving some success in producing dense deposits, but lack of sufficient funding precluded further pursuit of that approach. As the decade ended, the search for suitable target materials was continuing.

The individuals involved in this work included Del Bowers, Ed Huff, Samson

Marshall, Laszlo Redey, George Vandegrift, and Don Vissers.

Integral Fast Reactor Electrometallurgical Process

THE INTEGRAL FAST REACTOR CONCEPT

The Integral Fast Reactor Concept evolved from a growing awareness of the potential of metal fuels in fast reactors. This was based on the following two discoveries at the Experimental Breeder Reactor II (EBR-II), a sodium-cooled, pool-type fast reactor in which a uranium-fissium[3] metal fuel alloy was employed.

1. High fuel burnups (in excess of 10%) could be achieved by providing annular space in the fuel element to accommodate fuel expansion during irradiation.
2. Metallic fuels provide a high degree of inherent safety. Sharp temperature rises in the fuel resulting from loss of flow in either the primary or secondary sodium systems cause the metal fuel assemblies to expand and the fuel elements to move apart. This slows down the chain reaction, and the reactor shuts itself down without human intervention.
3. Although initially proposed as a breeder, an IFR could also be designed instead to "break even," *i.e.*, generate an amount of plutonium equal to that burned, or to consume more plutonium than is generated (a converter reactor).

The success achieved with metal fuels in EBR-II spurred Chuck Till to inquire of Les Burris and Bill Miller about the possibility of reviving the melt-refining process, which had been successfully employed in the early years of EBR-II operation in the adjacent Fuel Cycle Facility to recover discharged fuel. Burris noted that the melt-refining process would not be practical for recovery of high-burnup fuel because a large fraction of the fuel (30 to 50%) would have to be removed for separate processing to remove noble metal fission products. In a subsequent search for a process suitable for IFR fuel, Bill Miller came up with the idea of using electrorefining, which had been investigated by the French in the 1960s for the purification of unirradiated uranium.

Electrorefining soon became a major focus of research and development work in CMT. The Division was given the responsibility for developing, under the direction of Les Burris, an on-site process for recovering plutonium and uranium from core and blanket materials, removing fission products from them, reenriching the core alloy with plutonium bred in the blanket, and disposing of wastes. Integrating the process into a closed cycle for recycling fuel from an IFR became a major feature of the IFR concept. The close coupling of the recovery process with the reactor accounts in large measure for the name, Integral Fast Reactor.

Because the fission products would be completely removed in the electrorefining process, a new alloying metal was sought that would confer the same benefits to the fuel as does fissium. Zirconium was found to be equally effective, and a fuel alloy consisting of uranium, plutonium, and zirconium in the proportions of 70/20/10 wt% was chosen as the IFR driver fuel. Zirconium has the additional advantage of raising the melting point of the fuel. With this fuel, burnups greater than 18.5% were achieved in EBR-II,

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[3] Fissium is a mixture of noble metal fission products, molybdenum, ruthenium, rhodium, and palladium, which was present in EBR-II driver fuel at a total concentration of 5 wt% in ratios corresponding to their fission yields. Fissium produces an equiaxed metal grain structure in uranium, which, under irradiation, expands uniformly in all directions.

far exceeding the design burnup of 10%. The composition selected for the blanket material was uranium-10 wt% zirconium.

PROCESS FLOWSHEET DEVELOPMENT

Two basic steps were incorporated in the original process flowsheet: (1) electrorefining for removal of fission products from core and blanket material and (2) halide slagging for concentrating plutonium in the blanket material from a concentration of about 5 wt% or less to a value sufficient to enrich the driver fuel (30 to 40 wt%). In this flowsheet, metallic fuel-element segments were dissolved in liquid cadmium at 500°C, leaving behind the cladding hulls. The resulting solution of uranium in cadmium was made the anode of an electrolytic cell. Under an applied voltage, uranium was transferred through a molten chloride salt electrolyte to a solid metal cathode. The molten salt electrolyte was the LiCl-KCl eutectic (m.p., 352°C) containing a few percent UCl_3 to facilitate uranium transport. The uranium deposit was recovered mechanically and melted to form an ingot for preparation of new fuel and blanket pins. In halide slagging, the blanket material was melted under a molten salt consisting of barium and calcium chlorides and a small amount of UCl_3, which oxidizes plutonium preferentially into the salt phase. The salt was then added to the electrorefining electrolyte for plutonium enrichment of the core material. The operating temperatures for the electrorefining and halide slagging steps were 500 and 1250°C, respectively.

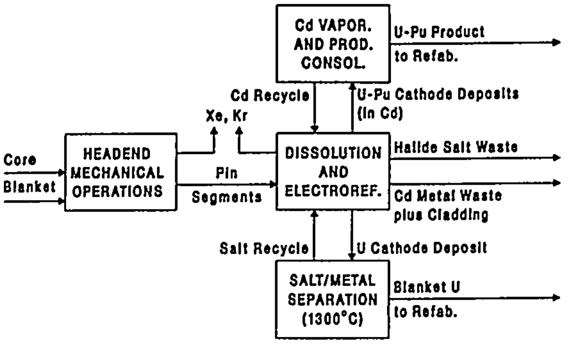
The following changes and improvements in this flowsheet were made to overcome some difficulties with it and to incorporate more efficient process arrangements:

1. The solution rate of uranium in cadmium was found to be intolerably low. To overcome this problem, the anode basket containing fuel or blanket segments is moved into the salt phase. Under an applied voltage, uranium and plutonium are oxidized to their chlorides as, simultaneously, an equivalent amount of uranium is deposited on the cathode.
2. Plutonium accumulates in the salt phase and is not transportable to a solid metal cathode when uranium is present because $PuCl_3$ is substantially more stable than UCl_3 (by about 20 kcal/mol). Electrotransport of plutonium requires use of a liquid cadmium cathode. In cadmium, plutonium has a low activity coefficient of 10^{-4}, which makes its transport to cadmium possible.
3. Halide slagging, which was shown to work in accord with theoretical predictions, was found to be unnecessary. Blanket fuel could also be processed by electrorefining. Plutonium accumulates in the salt phase as $PuCl_3$ while uranium is deposited on the cathode. Plutonium is removed later from the salt to enrich core material. The simplified process is shown in Fig. 5-25.

PROCESS FREASIBILITY AND DEMONSTRATION

Two inert-atmosphere glove boxes with instrumentation and argon purification systems were installed in Laboratory G-118 for conducting electrorefining and the previously mentioned halide-slagging experiments with plutonium-bearing materials. The principal investigators were Bill Miller and Ziggy Tomczuk. Ray Wolson was responsible for maintaining the facility and keeping plutonium accountability records.

In the early electrorefining experiments, uranium was transported from a cadmium solution to a solid iron mandrel. Important



Pin segments of core or blanket material are contained in a basket suspended in the electrolyte salt. Under an applied voltage, uranium and plutonium are dissolved anodically, with uranium transporting to a solid metal cathode and the plutonium reporting to the salt. Subsequently, plutonium, along with some uranium, is transported to a liquid cadmium cathode.

In this flowsheet, the role of the cadmium pool in the bottom of the electrorefiner changes from that of an anode to a collector of any noble metal fission products and zirconium that might escape from the anode basket. It would also collect any uranium that might fall from the dendritic deposit of uranium on the solid cathode. The electropositive fission-product elements (alkalis, alkaline earths, rare earths, and yttrium) collect in the salt, as does sodium used as a thermal bond in the fuel elements. Iodine also reports to the salt.

The product metals are recovered by vaporizing cadmium and any adhering salt, and melting them into ingots for manufacture of new fuel pins.

Fig. 5-25. Electrorefining Process for Driver and Blanket Fuel of the Integral Fast Reactor

results of these early studies were the following:

1. High uranium recoveries (greater than 99%) were demonstrated.
2. Uranium and plutonium were distributed between salt and metal phases in accord with theoretical predictions. Their total concentrations in the salt and metal phases could easily be adjusted by using cadmium chloride ($CdCl_2$) as an oxidizing agent or lithium as a reducing agent.
3. Fission products behaved as predicted. The noble metal fission products remained in the cadmium. The electropositive elements transferred to the salt. A uranium decontamination factor of 240 was realized in a run spiked with a small amount of irradiated uranium.
4. The low-carbon steel vessel used to contain the molten salt and cadmium phases showed no evidence of corrosion after one year at 500°C.

Because plutonium reports to the salt electrolyte, consideration was given to using a cup containing liquid cadmium as the cathode for deposition of both uranium and plutonium. On codeposition of uranium and plutonium, uranium dendrites grew out of the cadmium surface when the cadmium became saturated with uranium. The activity coefficient of uranium at its saturation concentration in cadmium is one, the same as that for uranium metal, so the pronounced tendency for dendrite formation is understandable. These dendrites had a fern-like structure and, on growing out of the cadmium cup, they short-circuited the cell when one of them came in contact with the cradle holding the cathode cup. Various methods for preventing dendrite growth (stirring, cutter blades, *etc.*) were unsuccessful.

As the process evolved, uranium was removed on a solid metal cathode, and plutonium was removed by transport to a cadmium cathode. It was found later that by maintaining a sufficiently high ratio of plutonium to uranium in the salt, saturation of the cadmium with uranium would not occur and, hence, dendrite formation would not occur. If the activity of plutonium in the salt was greater than that of plutonium in the plutonium-saturated cadmium, plutonium could be "pumped" into the cadmium, with the intermetallic compound, $PuCd_6$, precipitating as the additional plutonium was transferred.

A small amount of rare earth elements will be deposited along with the plutonium in a cadmium cathode. The decontamination factors for cerium and neodymium in two experiments are shown in Table 5-8. These decontamination factors are low, but ample—in fact, desirable. The high radiation level resulting from contamination of the plutonium product with rare earth fission products is a strong deterrent to diversion of plutonium to weapons production.

The TRU elements, americium, curium, and neptunium, were found to accompany the plutonium quantitatively. They can, therefore, be recycled with plutonium to the reactor where they are consumed by fission and contribute to the energy generated by the reactor. The absence of these elements in the electrorefining waste streams is a major advantage of the electrorefining process.

LARGE-SCALE DEMONSTRATION OF ELECTROREFINING

Justified by the successful electrodeposition of uranium on a 300-gram scale, a large-scale electrorefiner with a capacity of 20 kg of uranium was installed in a large, inert-atmosphere glove box in Laboratory J-118. Only the deposition of uranium was investigated. Work with plutonium was prohibited because the amounts of plutonium that would be required far exceeded the laboratory and building security limits. Eddie Gay was in charge of operating this facility.

Cross-section diagrams of the large electrorefiner are shown in Fig. 5-26. A close replica of this unit was designed and built for installation in the EBR-II Fuel Cycle Facility. The purposes of the large electrorefiner were to (1) demonstrate fuel dissolution, deposition of 10-kg amounts of uranium on an iron-mandrel cathode, and product handling, (2) establish the duty cycle for the electrorefiner, and (3) evaluate equipment performance.

Dissolution in cadmium had been attempted, but, as noted previously, the rate of uranium solution was impracticably low, so anodic dissolution became the norm. Successful demonstration of the deposition of 10 kg of uranium was carried out many times. Figure 5-27 is a photograph showing the highly dendritic deposit of 10 kg of electrodeposited uranium.

Several other uranium-deposition options were examined. Approximately 4 kg of uranium was successfully transported into liquid cadmium, but this was not an efficient method for uranium transport. Chemical deposition into liquid cadmium was also tried with limited success. Neither of these options was considered further for uranium collection.

The deposition of 10 kg of uranium required 40 to 50 h. That is much too long for practical application of electrorefining. Reducing the uranium deposition time was identified as a challenge to the researchers as the process development moved into the 1990s.

Table 5-8. Decontamination Factors for IFR Electrorefining Process

Experiment	Ratio	Discharged IFR Fuel	Cathode Product Ingot	Decontamination Factor
ENG 20	Nd/Pu	0.069	0.012	5.8
ENG 21	Nd/Pu	0.069	0.022	3.1
ENG 20	Ce/Pu	0.043	Not obtained	--
ENG 21	Ce/Pu	0.045	0.0085	5.3

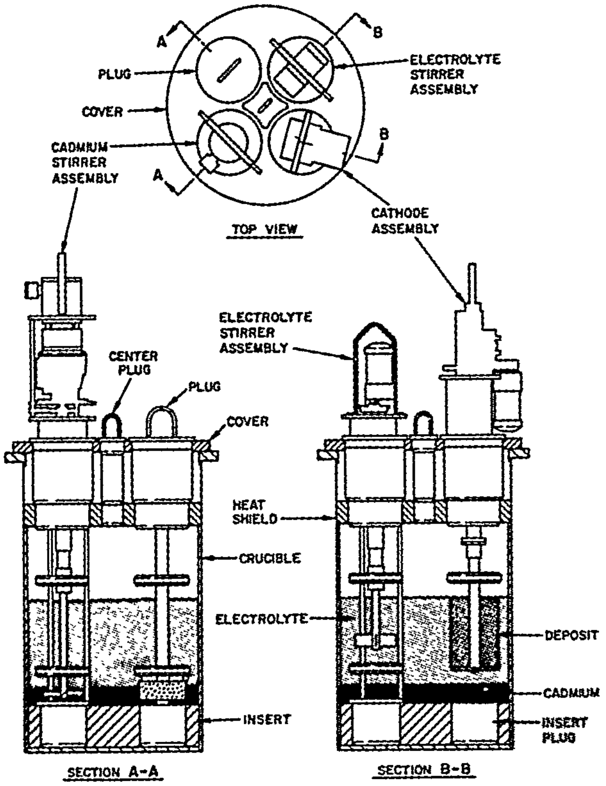


Fig. 5-26. Large-Scale Electrorefiner for Spent Nuclear Fuel

Fig. 5-27. Dendritic Uranium Deposit (~10 kg) from Electrorefining

IFR WASTE MANAGEMENT

Nearly all the fission products in the electrorefining vessel are in the anode basket and the electrolyte salt. These become part of the two major waste streams resulting from the electrorefining—a metal waste stream and a salt waste stream.

Metal Waste. The anode basket contains most of the noble metal fission products, zirconium (the alloying element in core and blanket fuels), and stainless steel cladding hulls. To this are added fuel assembly hardware, waste ceramic materials from preparation of new fuel pins and from operations to consolidate the uranium and plutonium products produced in electrorefining, and cadmium waste streams. The change from fuel dissolution in cadmium to anodic dissolution did not significantly alter the composition of the metal waste stream. One of the cadmium waste streams is produced in treating salt wastes to remove the TRU elements. It contains transuranic and rare earth elements and yttrium. Also, even with anodic dissolution, some cadmium must be removed occasionally from the cadmium cathode pool in the electrorefiner. Cadmium, however, is only a temporary constituent of the metal waste, since it is vaporized and condensed for recycle.

Initially, the metal waste was encapsulated in a heavy-walled steel container for disposal in a repository. In a later innovation, copper powder was added to the metal waste in a copper canister, and the mixture was compacted by hot isostatic pressing before being placed in a steel canister for final disposal.

Salt Waste. In the initial waste flowsheet, actinide elements in the salt removed to waste were extracted into cadmium with a Cd-1 mol% Li alloy. Most of the electropositive fission products also transferred to the cadmium. Only cesium, strontium, and iodine remained in the salt phase. The cadmium was combined with other metal wastes.

Figure 5-28 shows the distribution coefficients of several metals as a function of lithium concentration in cadmium. The distribution coefficient is defined as D(M) = Y_M/X_M, where Y_M is the mole fraction of MCl_3 in the salt, and X_M is the mole fraction of M in the liquid cadmium solution. These data, and other data for transuranic elements, indicate that a single contact with a Cd-1.0 mol% Li alloy should produce an actinide concentration of less than 1 ppb in the salt. In practice, however, such low values could not be attained. This was attributed to the presence of small amounts of uranium and plutonium oxide or nitride impurities in the salt. Although the actinide content of the treated salt could be low enough (less than 100 nanocuries per gram) to classify the salt as non-TRU, the presence of cesium and strontium would still require its burial in a deep geologic repository.

The major difficulty with the above treatment of salt waste was the loss of several percent plutonium to waste. Work was therefore begun on separating the actinides from the rare earths to enable recovery of the actinides. The large differences between the actinides and the rare earths (see Fig. 5-28) show that they can be separated by a multistage extraction process that employs cadmium containing a small amount of uranium as the extractant. Calculations showed that more than 99% of the actinides accompanied by less than 20% of the rare earths could be achieved in five to six equilibrium stages of countercurrent contact. Work was therefore initiated on development of suitable centrifugal contactors for this operation.

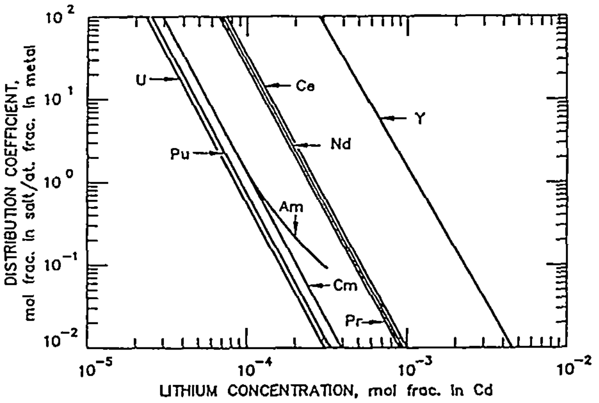


Fig. 5-28. Distribution of Actinides and Rare Earths between Salt and Cd-Li Alloys

After actinides and rare earths had been removed from the waste electrorefiner salt, the treated salt was dispersed in a Portland cement mortar (salt concentration about 10 wt%) and cast into a corrosion-resistant container for disposal. Although the resistance of the cement mortars to water leaching was satisfactory, hydrogen and chlorine were produced by electrolysis. The resultant pressurization of the container was a major concern. Therefore, disposal of the salt in cement mortars was abandoned, and attention was turned to investigating other media, such as zeolites, for immobilization of the salt waste.

PERSONNEL

Les Burris was the leader of the IFR effort until his retirement, when Jim Battles assumed that responsibility. Others in the program were John Ackerman, Jack Arntzen, John Basco, George Bernstein, Del Bowers, Erv Carls, Don Fischer, John Gabor, Eddie Gay, John Heiberger, Bob Heinrich, Joe Herceg, Ed Huff, Ken Jensen, Jerry Johnson, Irv Johnson, Terry Johnson, Bill Kann, Bob Kessie, Michele Lewis, Len Leibowitz, Dick Malecha, Bill Miller, Bali Misra, Tom Mulcahey, Dave Poa, Nick Quattropani, Don Raue, Jack Settle, Mike Slawecki, Bob Steunenberg, Ziggy Tomczuk, Dave Warren, and Florence (Williams) Smith.

PLUTONIUM RESIDUE RECOVERY (PuRR) PROCESS

The Plutonium Residue Recovery Process (PuRR), although not a part of the IFR

Program, had an indirect relationship to it in that it utilized pyrochemical procedures and was concerned with plutonium. It involved a joint effort between Lawrence Livermore National Laboratory (LLNL) and ANL to develop an effective process for the recovery of plutonium from intractable residues, and, later on, to remove transuranic elements from wastes to a non-TRU level to simplify their disposal. An adjunct effort between Savannah River Laboratory (SRL) and ANL was directed toward the use of a pyrochemical head-end treatment to convert intractable residues into a form suitable for subsequent aqueous processing.

The experimental program, which began in 1988, concentrated on the reduction of PuO_2 in the residues by a liquid metal-molten salt system to produce a solution of metallic plutonium in the liquid metal, which is a more convenient material for plutonium recovery either by pyrochemical or by aqueous processes. Reductions of PuO_2 by this technique had been well established in earlier pyrochemical programs using combinations such as zinc-magnesium as the liquid metal and molten $LiCl-KCl-MgCl_2$ as the salt.

Potential feed materials for the PuRR process included any of 22 categories of weapons-production residues. The most intractable of these materials, acid-leached LECO® analytical crucibles (ground) from SRL and incinerator ash heels from Rocky Flats (calcined and ground), were selected for the studies. The plutonium contents of these materials ranged from >1 wt% to about 20 wt%.

Several solvent/reduction systems were considered; initial experiments were conducted with Cu-Mg-Ca and Zn-Mg reductants for the LLNL effort (Rocky Flats material), and Al and Al-Mg for the SRL material. The salt used for the Cu-Mg-Ca system was $CaCl_2$-15 wt% CaF_2, and for the Zn-Mg and Al-Mg systems it was $MgCl_2$-22 wt% NaCl-19 wt% KCl-4 wt% MgF_2. Good reductions of the PuO_2 (98% or higher), which were achieved in nearly all cases, far exceeded recoveries by aqueous processes. Additional reduction studies resulted in plutonium recoveries averaging 98.0% after one reduction stage and 99.4% after a second stage, based on analyses of the salt, but these results could not be confirmed by analysis of the metal ingot products, which was difficult because of the heterogeneous nature of the product.

Savannah River then requested a determination of whether plutonium remaining in the slag from bomb reductions of PuO_2/PuF_4 by calcium could be extracted by pyrochemical procedures, and also asked ANL to design and fabricate a heated transfer line for transferring molten salts and metals. (Such lines had been developed earlier at ANL in pyrochemical research and development programs.)

Much of the effort in 1989 was concerned with the CaO byproduct resulting from the use of calcium as a reductant. To eliminate the CaO waste and simultaneously recover the calcium for recycle, work was begun on incorporation of a calcium electrowinning step in the process. Regeneration of the calcium metal was performed successfully. The use of carbon anodes resulted in the production of CO or CO_2, rather than oxygen or chlorine, as the by-product of the electrolysis and also reduced the operating voltage.

In spite of the promising results, this program was phased out around 1990 because of a political realization that large quantities of plutonium would become available from reduction of the nuclear weapons stockpile, and there was little incentive to recover more of it. The effort was diverted to the use of this technology to convert wastes into a non-TRU form for disposal, as mentioned earlier.

The individuals working on this program included Jerry Johnson, Irv Johnson, Tom Mulcahey, Dean Pierce, and Dave Poa.

Nuclear Waste Management

YUCCA MOUNTAIN PROJECT

The proposed site for the first high-level waste repository in the United States is in the tuff beds of Yucca Mountain, Nevada. The site is unique among those being characterized internationally because it lies several hundred meters above the water table in a zone unsaturated with water. Investigators in the CMT Division studied the reactions of glass and spent irradiated reactor fuel under anticipated repository conditions. The general focus was on the post-containment period, *i.e.*, that period following canister deterioration (estimated to be 300 to 1000 years after emplacement of the waste), during which time the waste glass monolith is exposed to the repository environment.

Waste Glass Studies—Unsaturated Tests. Although large amounts of water are not expected to contact the waste during the repository lifetime, water vapor or small amounts of transient water may contact the waste at any time after emplacement. Unsaturated tests were designed to study glass/steel/fluid interaction under those conditions. Groundwater from the Yucca Mountain site was dripped onto a model waste package composed of a glass cylinder (SRL 165) sandwiched between two perforated stainless steel disks at 90°C. The rate of water introduction was varied from one drop every 3.5 days to one drop every 14 days. The glass was doped with actinide elements (uranium, plutonium, neptunium, and americium). The nature and degree of reaction were assessed from solution analysis and inspection of the waste package surface by various analytical techniques, such as scanning electron microscopy.

The test apparatus is shown schematically by components in Fig. 5-29. Both batch- and continuous-mode testing were done. In the batch mode, the tests were terminated at selected 13-week intervals. In the continuous mode, the test package, along with any adhering water, was transferred to a new test vessel, and the test was continued in that manner until little additional information could be learned from further exposure.

Forming on the glass surface was a layer of clay, which spalled off, allowing further reaction. This ongoing, cyclic process plays a major role in glass erosion. The release of lithium, present in the matrix glass at a concentration of about 1 wt%, was a good monitor of the extent of glass reaction because little or no lithium is incorporated into secondary phases that form on the glass surface.

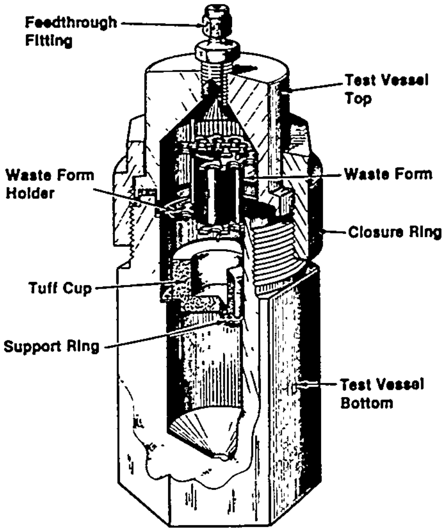


Fig. 5-29. Test Apparatus for Unsaturated Zone Testing

Hydration of Glass by Water Vapor. Before high-level nuclear waste is contacted by liquid water, it will be contacted by water vapor. Some water will be sorbed on the glass surface. Hydration will occur between the glass and this small amount of sorbed water, which will release alkali metals into the sorbed film, decreasing the vapor pressure and allowing further sorption of water. By this mechanism, significant quantities of water may condense on, and subsequently react with the glass. As the glass reacts, released species quickly approach their solubility limits, and precipitates form in the solution. These are incorporated into a potpourri of mineral phases—predominantly zeolites and silicates that form on the on the outer surface of the glass (see Fig. 5-30). The vapor-hydration experiments were extremely useful in projecting performance of glass because they disclosed the mineral phases that control the reaction rate.

Vapor/Hydration Leach Experiments. The extent of vapor hydration or aging of glass is a function of the glass composition, relative humidity, reaction time, and temperature. Of interest was whether aged glass reacted differently to liquid water than fresh glass. The difference in reaction rates was striking. Aged glass reacted significantly faster with liquid water than did fresh glass. Even more striking, however, was the behavior of plutonium and americium. Very little plutonium or americium appeared in solution in leaching tests using fresh glass. In contrast, with aged glass, considerable amounts of plutonium and americium were found in the solution as colloidal precipitates. This effect is illustrated by the data in Table 5-9. The two types of glass are a Westinghouse Savannah River Co. (WSRC) glass and a West Valley Demonstration Plant (WVDP) glass. The importance of this finding is that groundwater transport of colloidal suspensions may differ greatly from that of dissolved materials.

Static Leach Experiments. After high-level wastes have been enclosed in a repository, the most likely scenario for release of waste constituents is through leaching and transport in groundwater. Two sets of static leach-rate tests were conducted by the CMT Division in the 1980s: (1) general leach-rate characterization studies in the early 1980s and (2) studies in the late 1980s that were pertinent to the Yucca Mountain repository. Two techniques were used to measure the small amounts of radioactive materials leached from the wastes: (1) neutron-activation analysis (NAA), and (2) solution analysis after spiking the waste form with radioactive tracers. These methods complemented each other because there are instances when NAA is not

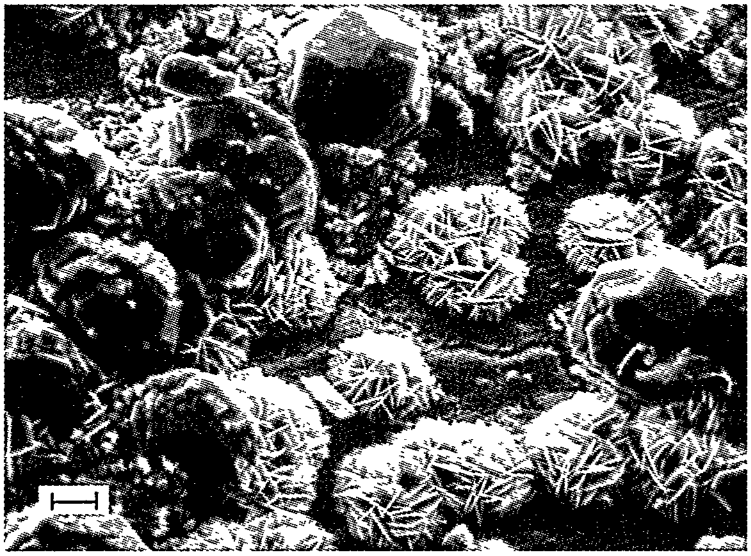


Fig. 5-30. Scanning Electron Image of Hydrated Glass Surface Showing Complex Silicate Precipitates

Table 5-9. Release Rates of Elements from Fresh and Hydrated Glasses

Elements	Normalized Release, g/m^2			
	WSRC Glass		WVDP Glass	
	Fresh	Hydrated	Fresh	Hydrated
B, Li, Na	1.5	30	10	25
Am, Pu	0.1	2	0.001	0.2
Np, U	0.6	15	2	10

applicable. The close agreement between NAA and spiking for amounts of selected constituents from a Savannah River Laboratory (SRL) glass, SRL-211B, is illustrated in Fig. 5-31.

Leach tests were conducted on three Savannah River glasses, 131A, 211B, and 211C. Glass samples prepared for leaching were spiked with radiotracers from the four major classes of fission products (alkali, alkaline earth, rare earth, and noble metal), as well as the actinide elements (uranium, plutonium, neptunium, and americium). Static leach tests were conducted, following procedures specified by the Materials Test Center, namely, contact with deionized water at 90°C for 3, 7, 14, 28, and 42 days. Some tests, however, were run for up to 546 days to gain insight into the long-term nature of glass leaching. In one of the 546-day tests of an SRL-131 glass, six distinct layers were found by analytical electron microscopy.

After about one year, there was little further accumulation of any element in the leachate. Effective leachate saturation was reached by formation of a "protective" gel layer on the glass surface. This occurred because of saturation of some elements in solution and formation of precipitates. For each glass, the matrix elements of the glass (Si, Na, Li, B, Al, Ca, and Fe) leached at about the same rate, but the nature of the gel layer, the composition of the precipitates, and the behavior of the waste elements differed greatly among the glass compositions. It was concluded that the behavior of waste elements must be determined in tests using glass having the same composition as that of the actual waste. Uranium and neptunium continued to leach from the glass and were not found on the glass surface, whereas plutonium and americium accumulated slowly in the leachate, their concentrations stabilizing after 28 days.

The Yucca Mountain leach tests were performed with leachants characteristic of the tuff repository. These tests showed that the ratio of the glass surface area to the leachant volume is a critical parameter in static leach experiments because it affects the rate at which the solution becomes saturated or approaches saturation by various glass components and,

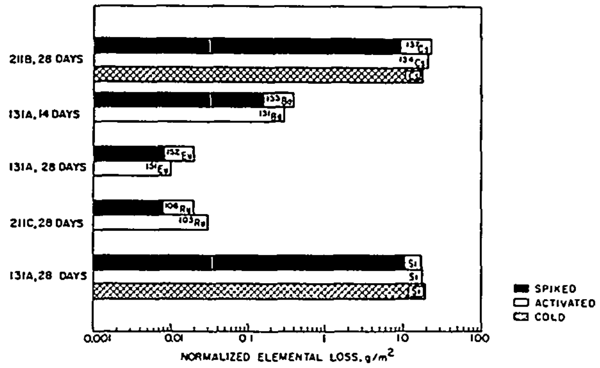


Fig. 5-31. Losses of Representative Elements from Simulated Glass Wastes

therefore, the eventual composition of precipitated phases. Release rates of elements were controlled more by solubility than by the existence of a protective layer.

Natural Analog Studies. Naturally occurring glasses are useful for validating both predictive computer codes for long-term waste performance and laboratory experiments used to accelerate glass reactions. The experimental alteration by water vapor of basalt and obsidian glasses, whose compositions are similar to synthetic waste glasses, was investigated and compared with the alteration of synthetic glasses under the same conditions. The amount of water sorbed and, hence, the extent of glass alteration increased with relative humidity at all temperatures. Reactions occurred in a thin film of condensed water, and precipitates formed in only a few days due to rapid saturation of the small amount of water by dissolving constituents of the glasses.

Spent Fuel Studies. Although most of the work on storage of nuclear wastes in the 1980s was concerned with the storage of high-level radioactive wastes immobilized in glass, a study was initiated in 1988 to determine the release of radionuclides from spent fuel samples (from light water reactors) exposed to varying amounts of water following breach of containment in a repository. The high level of ionizing gamma radiation causes a reaction of oxygen and nitrogen in the air to form nitric oxide, which then combines with water to form nitric acid. The nitric acid causes corrosion of the fuel storage canister. Relative rates of corrosion of candidate cannister materials were Cu>Cu-Ni>Al-bronze>> Inconel 825. Isotopic exchange of U-235 and U-238 could be determined with high precision by mass spectrometric isotope dilution. This program was continued into the 1990s to determine the behavior of fission products and actinide elements.

ANALOG EXPERIMENTS FOR PROPOSED HANFORD REPOSITORY

In the early 1980s, one of the candidate repository sites was at Hanford, Washington, in underlying Pomona basalt. Borosilicate was the solid waste form, and bentonite plus basalt was the backfill around a canistered waste form. Analog experiments were performed in which the migration of elements from the glass waste by a water stream was followed through a sequence of materials, *i.e.*, waste form, bentonite clay, and the host basalt rock. The laboratory experiments are illustrated in Fig. 5-32, and Fig. 5-33 shows the distribution of neptunium from water at 90°C flowing at a rate of 250 m/yr, which is higher than that expected in a repository. At the water flow rates expected in a repository, neptunium would migrate about 200 m per 1,000 years. The Hanford site for a repository was eliminated from further consideration in 1984, so the analog experiments were stopped. This work was part of the geoscience program conducted by Martin Seitz and Neil Sturchio with Rex Couture and George Vandegrift.

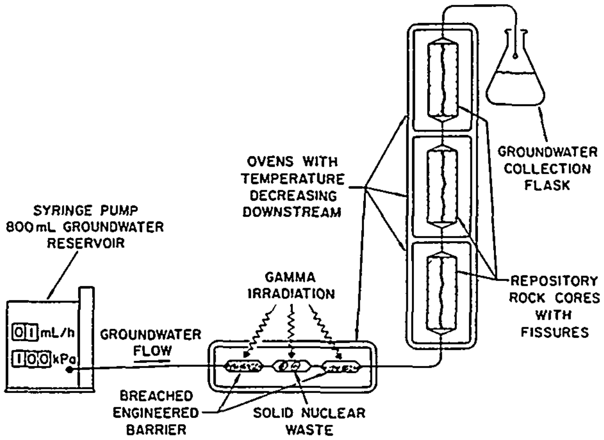


Fig. 5-32. Design of Groundwater Stream Simulation Experiment

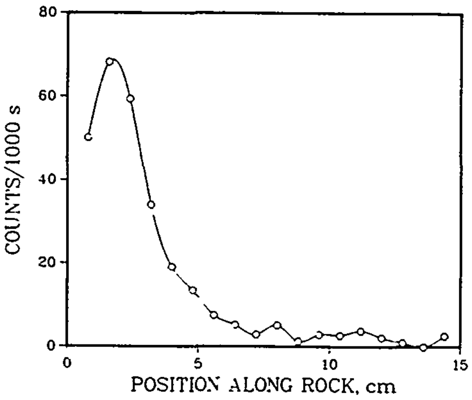


Fig. 5-33. Distribution of Neptunium-237 on a Basalt Core Surface

BRITTLE FRACTURE STUDIES OF SOLID WASTES

Because mechanical impacts to solid wastes might occur during processing, handling, storage, and transportation, the CMT Division began the development of a generalized methodology for characterizing the impact fracture of brittle materials for evaluation of material properties and use in accident analysis of full-size waste forms. Fracture of a solid waste would increase the surface area available for leaching of fission products by groundwater and produce a quantity of respirable particulates (<10 μm).

A preliminary model was developed on the basis of a particle-size distribution resulting from impacting small Pyrex® cylinders (38-mm dia by 100-mm length) by a drop weight. The particle-size distribution was lognormal. Subsequently, simulated waste glasses (SRL-131 and PNL-76-68), several Synroc formulations, and conglomerate brittle materials such as sandstone were tested. For the materials tested, all were found to follow a lognormal particle-size distribution. A similar lognormal distribution was found at Pacific Northwest Laboratories (PNL) for free-fall impact tests of full-scale canisters (0.61-m dia by 2.3-m length), indicating that the CMT model may be applicable to full-size waste forms. In the PNL tests, the respirable fraction was found to be 0.15 wt%. This CMT study was terminated in 1982. These studies were done by Bill Mecham, Wally Seefeldt, and Martin Steindler.

NUCLEAR METHODS OF OIL WELL LOGGING

Workers in CMT investigated the application of nuclear oil well logging methods to determine the amount of oil remaining in an underground formation after removal of the easily available oil. In the proposed method of logging an underground reservoir, the radioactivity of the reservoir is first determined by a gamma-sensitive probe. Then, water containing a gamma-emitting radionuclide is injected, and gamma logging is repeated. The difference in measured radioactivity can be related to the residual oil content. The difference in radioactivity between an oil-saturated core and an oil-free core on injection of water containing Na-22 is shown in Fig. 5-34. This work was not continued beyond demonstration of the feasibility of the method.

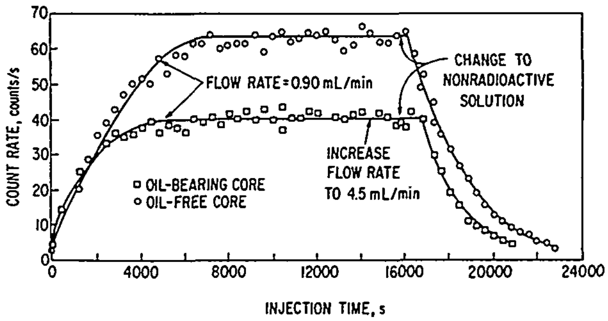


Fig. 5-34. Gamma Signals from Cores Injected with Radioactive ^{23}Na-Bearing Solutions

PERSONNEL

The glass studies were performed under the leadership of John Bates. Other members of the group included Teofilo Abrajano, Don Fischer, Tom Gerding, Les Jardine, Jim Maser, Bill Mecham, Gerald Reedy, and Ewald Veleckis. Two postdocs, Charles Byers and Bill Ebert, also made substantial contributions, as did several members of the Analytical Chemistry Laboratory (ACL) and the Chemistry Division (CHM).

Martin Seitz led the other work, which was performed by Rex Couture, Tom Gerding, Neil Sturchio, George Vandegrift, and Don Vissers. Again, several members of the ACL and CHM were involved significantly in the effort.

Applied Physical Research

In the early 1980s, the Applied Physical Research Program was concerned mainly with the physical and thermodynamic properties of oxide reactor fuels. By 1984, a sufficient amount of information had been accumulated in handbooks and computer databases to permit useful modeling of reactor accidents. About that same time, it became apparent that metallic reactor fuels could achieve much higher burnups than previously thought possible by redesigning the fuel pins to accommodate the swelling of the fuel. This result was a major breakthrough that led to the IFR concept, which kindled a renewed interest in metallic fuels in the Applied Physical Research Program.

OXIDE REACTOR FUELS

Gas-Cooled Fast Reactor Fuel. In support of gas-cooled fast-reactor (GCFR) technology, a brief investigation was conducted on the transport and reaction of oxygen and fission products in mixed uranium-plutonium oxide fuels. Although the GCFRs are similar to LMFBRs in that they both use oxide fuels, they differ in that the GCFR fuel pins are vented, the cladding is roughened, helium is used as the coolant, and there is direct contact between the coolant and the steam generator. Large axial temperature gradients that occur within the GCFR fuel pins lead to complex chemical and transport phenomena, which are related primarily to the chemistry of oxygen and cesium in the fuel pins. Under these conditions, solid-state thermomigration results in redistribution of oxygen (as well as actinides) in the fuel.

A mathematical model used a defect structure for UO_2-PuO_2 fuel involving oxygen vacancies and electronic disorder. The model relates a thermodynamic factor, $1 + \delta \ln\gamma_V / \delta \ln C_V$ (where γ_V is the oxygen-vacancy activity coefficient, and C_V is the vacancy concentration), to the oxygen potential of the fuel. Extensive data were available and accurate models already existed for the oxygen potentials, so only one quantity, the heat of transport of oxygen vacancies, Q_V, was required to obtain profiles of the steady-state oxygen redistribution under a given set of reactor operating conditions. The value of Q_V depends on the stoichiometry of the system. Experimental data showed that the value of Q (the heat of transport) decreases to zero as the mean valence of the plutonium goes from 4.0 to 3.0, which is consistent with the model.

High-Temperature Physical Properties. In modeling reactor accidents, one needs information about the thermophysical properties of reactor materials, such as fuels, coolants, and structural materials, from room temperature to very high temperatures (about 5700°C). The purpose of this work was to provide reliable values of these properties for reactor safety analysts. Available experimental data were assessed and calculations were made by using thermodynamic relationships as well as approximation and extrapolation techniques when necessary. Uncertainties in the recommended values were also estimated from experimental deviations, data-fitting errors, and approximations or extrapolations.

Recommended values for the properties of sodium were documented by Joanne Fink and Len Leibowitz, and Joanne published the computer codes used in the calculations in a sister document. Both documents were sent to the United Kingdom for comparison with recommended values from scientists in the United Kingdom, France, and the Federal Republic of Germany. A magnetic tape of the property values and the computer codes was sent to a database at Oak Ridge, which is entitled Safety Analysis Computerized Reactor Data (SACRD).

Equations used to fit experimental data on the enthalpy and heat capacity of UO_2 were evaluated by Fink and Leibowitz, taking into account factors such as contributions from phonons and thermal expansion and an anomalous electronic contribution. The best fit was obtained with a two-term, nonlinear equation below the transition temperature (2397°C), and a linear equation above that temperature. The two terms of the nonlinear equation represent contributions from the photons and electrons. Previous assessments of the thermal conductivity of UO_2 had resulted in a three-term nonlinear equation representing contributions from phonons, electrons, and a conduction decrease due to dislocations. A statistical study showed that the data did not justify the inclusion of the dislocation term. A two-equation formulation fit both the thermal conductivity and the thermal diffusivity data better, and it was consistent with the theoretical basis of the equations used for enthalpy and heat capacity.

Enthalpy measurements were performed on thoria-urania (ThO_2-UO_2) fuels for the Westinghouse Electric Corporation's Bettis Atomic Power Laboratory. The equipment, which was capable of operation up to about 3200°C, was an induction-heated drop calorimeter with a platinum crucible. This type of calorimeter was described earlier. Enthalpy measurements were made on ThO_2 between 2227 and 2948°C, and on 70 mol% ThO_2-30 mol% UO_2 between about 2000 and 2900°C. As of 1981, the enthalpies and heat capacities of UO_2, PuO_2, ThO_2, $(U,Pu)O_2$, and $(Th,U)O_2$, as well as $(Th\text{-}U)O_2$ containing 30, 15, and 8 wt% UO_2, had been determined by CMT workers.

Thermodynamic functions are needed for vapor species of the fuel in the analysis of hypothetical reactor accidents. Experimental studies were conducted in which the matrix-isolation, Fourier-transform infrared spectroscopic techniques mentioned earlier and calculational methods were used to estimate data that were not experimentally available. These studies yielded improved values for the thermodynamic functions used in the calculation of vapor pressures. Preliminary results indicated that the vapor composition was very sensitive to both the temperature and the composition of the condensed phase, whereas the total pressure was relatively insensitive to both. Further investigations were conducted on vapor species in equilibrium with hypostoichiometric (oxygen-deficient) UO_2. The vapor in equilibrium with UO_{2-x} was a complex mixture consisting of O, O_2, U, UO, UO_2, and UO_3 molecules. Figure 5-35 shows the composition of vapor in equilibrium with $UO_{1.96}$ as a function of temperature.

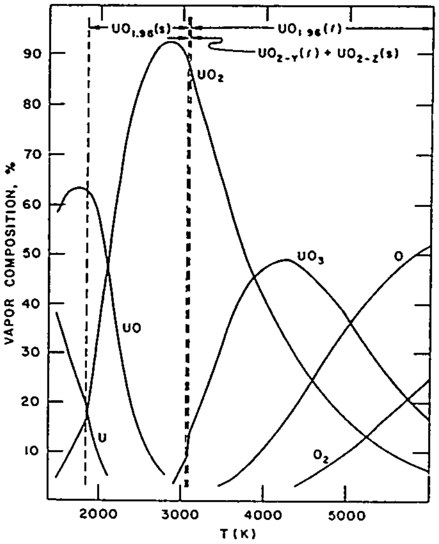


Fig. 5-35. Vapor Composition in Equilibrium with $UO_{1.96}$

Thermal Conductivity of UO_2. The thermal conductivity of reactor fuel is one of the more important pieces of information needed in reactor safety analysis. Investigators at three other laboratories had published values for the thermal conductivity of UO_2 at its melting point. These results were evaluated carefully with a proprietary heat-transfer computer code, and the discrepancies were largely resolved by identifying errors in the workers' analyses of their results. This study produced a value of 5.6 W/m·K. There was still some uncertainty in the value, but no measurements were made by CMT workers because further studies were in progress at other laboratories.

METALLIC REACTOR FUELS

A review was conducted on the available thermodynamic and transport properties of U-Zr and U-Pu-Zr alloys, which had been selected as potential blanket and driver fuels in the IFR. The existing data were found to cover only a relatively small part of the composition and temperature ranges of interest. To understand fuel behavior under both normal and accident conditions, a wide composition range is needed because zones of widely different composition are generated within the fuel by irradiation and thermal gradients.

Thermal Conductivity. Equipment was set up to measure the thermal conductivity of metal fuels by a comparative (axial rod) method, which had a precision of about 5%. In this method, a sample stack was prepared with the alloy of interest placed between two samples of a reference material of known thermal conductivity. Two thermocouples were placed a known distance apart in each of the reference materials, and heaters were used to establish a thermal gradient across the stack. The heat flux through the test sample could then be derived from the measured heat fluxes through the reference materials. To test the method, the thermal conductivity of a National Bureau of Standards (NBS) stainless steel standard was measured at temperatures from 325 to 825°C. Inconel was used as the reference material. The results indicated an accuracy of about 2%. Because stainless steel and Inconel interact with the IFR alloys, the thermal conductivity of tantalum was measured, and it was then used as the reference material to determine the conductivity of a U-11.36 wt% Zr alloy. The results agreed with estimated values based on literature data.

Conductivity measurements were then made on a single U-11.4 wt% Zr sample at 50 temperatures between about 300 and 900°C. The data were fitted to a second-degree polynomial equation: $\lambda = -1.763 + 4.871 \times 10^{-2}T - 1.330 \times 10^{-5}T^2$, where λ is the thermal conductivity in W m^{-1} K^{-1}, and T is the temperature in degrees Kelvin. A relatively large scatter in the data suggested that insufficiently long equilibration times were used for stabilization of numerous transition phases at the higher temperatures, but the data were in general agreement with results from earlier studies.

Next were thermal conductivity measurements on U-8.4 wt% Zr and two cladding alloys, D9 (an austenitic-type steel similar to Type 316 stainless steel) and HT9 (a ferritic-type steel similar to the 400-series steels). Some difficulty in obtaining reproducible results was experienced with the HT9 because of a slow phase transition. The variation in thermal conductivity, however, was fairly small over the temperature range of the measurements. In general, the thermal conductivity data for the cladding materials were in reasonable agreement with the literature values for steels of comparable compositions.

Thermal Expansion. Linear expansion measurements were conducted on IFR fuel alloys, using a dilatometer in a helium-atmosphere glove box. Two alloys were investigated in the initial experiments: U-8.4 wt% Zr and U-20 wt% Pu-1.3 wt% Zr. In both cases, the results were in reasonable accord with literature data, although some phase transitions were observed in greater detail. Measurements were then made on two additional fuel alloys (U-19 wt% Pu-10 wt% Zr and U-26 wt% Pu-10 wt% Zr) and the two cladding alloys (D9 and HT9). In the tests with U-20 wt% Pu-1.3 wt% Zr alloy, the thermal expansion values on heating differed significantly from those on cooling. A separate differential thermal analysis (DTA) indicated that the difference was probably due to a delayed solid-state phase transition at 347°C.

Thermal expansion of the cladding alloy, HT9, was measured at temperatures up to about 900°C. Data from the heating and cooling cycles were in agreement, and a phase transition was found at about 800°C. The D9 alloy did not show such a transition.

Fuel-Cladding Interactions. Previous studies had indicated that plutonium-rich layers can segregate on the surfaces of U-Pu-Zr fuel alloys when they are exposed to cladding, NaK, or a helium atmosphere. This behavior was ascribed to the availability of nitrogen at the alloy surface. Therefore, tests were performed in which selected IFR alloys were heated in nitrogen-helium mixtures that simulated the nitrogen activity estimated for the cladding. A thermogravimetric analysis (TGA) technique was used to follow the sample weight during the reaction. In a typical test, exposure of the U-20 wt% Pu-1.3 wt% Zr alloy to a flowing stream of 50 ppm nitrogen in helium for 12 hr at 700°C produced a distinguishable 10-µm-thick surface layer. Scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) showed that the layer had undergone major compositional changes involving a considerable enrichment of zirconium and a large depletion of uranium. This discovery suggested that the reaction products of nitrogen with zirconium and plutonium were more stable than those with uranium, which resulted in migration of zirconium and plutonium to the surface.

Because low-melting eutectics occur in the U-Fe and Pu-Fe systems, there was concern that cladding integrity might be compromised by the formation of liquid phases during irradiation of the fuel. Experiments were performed in which mixtures of the cladding alloy, HT9, and either a binary or a ternary fuel alloy (U-Pu or U-Pu-Zr) were heated in a DTA apparatus at 10°C per minute to about 1550°C in a yttria crucible, held for two hours, and then cooled. No unusual effects were observed until the binary fuel reached a temperature of 1155°C and the ternary fuel reached 1105°C, where large exothermal peaks occurred, indicating an energetic reaction. Scanning electron microscope examination of the residues from these tests indicated that the iron in the cladding had reacted with zirconium in the fuel to produce Fe_2Zr or Fe_3Zr. The DTA results showed that the zirconium did not change the eutectic temperature. Improved compatibility of U-Pu-Zr fuels over U-Pu fuels appeared to result from the presence of zirconium to react with iron, making the iron less available for melting. Zirconium appears to offer an additional benefit because of its strong affinity for elements such as carbon, oxygen, and iron, which form surface layers and thereby retard iron diffusion into the fuel.

The DTA results indicated eutectic freezing temperatures for the U-Fe and U-Fe-Pu systems that were somewhat lower than those obtained from phase diagrams or calculated. The difference was about 25°C for the binary fuel and 35°C for the ternary fuel. At the end of the 1980s, work was just starting on a more detailed study of the U-Fe system.

Phase Studies. A review of previous data on the U-Pu-Zr system had revealed large uncertainties in the solidus and liquidus temperatures, estimated to be about ±125 and ±75°C, and other inconsistencies in the ternary phase diagrams. Calculations of a ternary phase diagram require thermodynamic functions for all phases existing in the three binary subsystems. An analysis was completed on the U-Zr system. In the U-Pu system, however, the published solidus-liquidus values were inconsistent with the accepted enthalpy of fusion of uranium. The U-Pu system is complex because of the large number of phase transitions in the constituent elements. Further work was in progress on the development of an approach for a thermodynamic analysis that could accommodate the numerous phase transitions.

Some experimental work was done on a U-26 wt% Pu-10 wt% Zr alloy, a typical IFR fuel composition. Differential thermal analysis techniques were utilized. The results of this work provided guidance in evaluating a conflict in the literature data between the U-Pu phase diagram and the enthalpy of fusion of uranium. It appeared that the U-Pu phase diagram should be redetermined. The calculated diagram for U-Zr was in good general agreement with literature data, although there were some minor differences, which were resolved. By 1989, a more reliable ternary U-Pu-Zr phase diagram based on experimental data and calculations was nearing completion.

FISSION-PRODUCT BEHAVIOR

Fission-Gas Behavior in LWR Fuels. In a light water reactor (LWR), gaseous fission products, krypton and xenon, are released during the irradiation, with the result that internal pressure develops with burnup. Escape of these gases into the gap between the fuel and the cladding decreases the heat transfer because the thermal conductivities of these gases are lower than that of helium, which was used to fill the gap initially. The electric utilities, for economic reasons, wished to increase the burnup by about a factor of two. At the time, a great deal of information was available on fission-product gas release from UO_2 fuels, but it was not generally applicable to commercial LWR fuels. The Electric Power Research Institute (EPRI) sponsored a Multiple Cycle Plutonium Utilization (MCPU) program under which a detailed post-irradiation study of LWR fuel rods was initiated to determine the behavior of fission products under prototypical operating conditions. The study was aimed originally toward mixed oxide (UO_2-PuO_2) fuels, but it was reoriented toward UO_2 fuels alone because of federal restraints on fuel reprocessing and use of plutonium in commercial reactors.

The quantities of released fission gases and helium from irradiated fuel elements obtained from the Consumers Power Big Rock Reactor were measured. Fission-gas release was about 5-8% from three of the five fuel rods, but only about 0.2-0.5% from the other two. This discrepancy was difficult to rationalize but may have resulted from differences in the peak power and the temperatures within the rods. The relationships among power density, thermal conductivity as the gases are released, and the temperature are complex. Because of these factors, modeling of the system to predict fission-gas release is difficult. The investigators concluded that a statistical modeling approach might be more appropriate.

Model Development. The potential public risk associated with an accident at a commercial nuclear power plant results from the release of radioactive fission products produced in the fuel during the reactor operation. Under normal circumstances, the fission products remain within the fuel. Under accident conditions, however, some of the fission products may be released from the fuel and find their way into the environment. The amount of a specific fission product released to the environment is called the "source term" for that species.

A program was initiated to identify and characterize the radioactive fission products that might be released to the environment by an LWR under a variety of accident conditions. The program consisted of four components:

1. Assessment of thermochemical data for compounds formed from fission products, fuel, cladding, and structural materials.
2. Development of a core chemistry model to predict the behavior of fission products in the fuel, cladding, coolant system, and containment building.
3. Measurement of additional thermochemical data needed to complete the model development.
4. Development of a transport model to predict fission-product release rates.

The initial assessment indicated that pertinent thermodynamic data were lacking for the compounds Cs_2Te, $ZrTe_2$, and Cs_2ZrO_3, and specimens were prepared for enthalpy of formation and heat capacity measurements.

A core chemistry (fuel and fission product) computer model was developed to calculate equilibrium vapor pressures of fission-product gases and condensed (liquid and solid) phases formed by interaction of the fission products with one another, with oxygen in the fuel, and with uranium. The main emphasis was on the partial pressures of the more volatile fission products of Xe, Kr, I, Cs, Te, Mo, Sr, Ba, and Ru.

A scaling model, based on information from the core chemistry model, was developed to evaluate the movement of fission products from the fuel through the cladding, reactor vessel/coolant system, and containment building. The scaling model showed good agreement with experimental measurements.

Further experimental investigations showed that the fractional release rate of the fission gases was proportional to that of the other volatile fission products. The mechanism of fission-gas release, however, was not well understood but was believed to involve migration of the gas bubbles within the fuel.

Release of Fission Products from Breached LWR Fuel Pins. An experimental study was conducted on the release rate and chemical form of fission products from an irradiated LWR fuel pin into which a defect was introduced. A 10-cm-long section of the fuel pin, sealed at both ends, was inductively heated in a vacuum, and the gaseous species escaping through a hole drilled in the cladding were identified and measured by means of a quadrupole mass spectrometer. In the mass spectrometer, the ion current is related to the partial pressure of a species by the equation, $p = k\,(IT)$, where p is the partial pressure, I is the ion current, T is the temperature, and k is a constant. The defected pin could be regarded as a Knudsen cell, and the data were analyzed accordingly. Values of k were determined for gaseous CsI, I_2, Te_2, Kr, and Xe.

To develop the methodology for the work with irradiated fuel pins, a simulated pin containing UO_2 and inactive fission-product elements was prepared. A 1-mm-dia hole was drilled in the cladding, and the pin was heated to 600-900°C in a vacuum. Both CsI and Cs were found in the emitted gas, but no tellurium was evident. Further tests suggested that the tellurium had reacted with zirconium to form solid $ZrTe_2$. The rate of cesium release decreased with time, probably due to the development of a CsI-depleted layer on the top of the sample, but all of the cesium eventually escaped from the sample.

After extensive testing and calibration, the equipment was moved into a shielded cave facility. As a final test, a mockup fuel-pin section was made and filled with a powdered mixture of UO_2 and inactive fission-product compounds. Below 1290°C , the only species found were Cs and CsI. At 1290°C , there was evidence of SnTe, probably from a reaction of tin in the Zircaloy cladding with $ZrTe_2$. On continued heating up to 1590°C, Cs, Te, and I were observed.

An irradiated fuel sample was then heated stepwise from 450 to 1500°C over a 28.5-hr period. Over this temperature range, Xe, Kr, Cs, and Te were found. The cesium came off first, followed by the tellurium. The release rates of Xe and Kr were about the same and were relatively complex, with different activation energies in two temperature regimes and a dependence on the previous history of the specimen. A second test made with another sample produced somewhat similar results; krypton and xenon were released at all temperatures. Cesium was first noted at 990°C, tellurium began to appear at 1160°C, and elemental iodine was observed at 1260°C.

In a reactor accident situation, rupture of the cladding would most likely expose the fuel to oxygen. An unclad, irradiated fuel-pin section was heated at temperatures up to about 1140°C in a nickel Knudsen diffusion cell equipped with an outside manifold to permit controlled additions of oxygen. No effect of oxygen addition on the xenon release rate was observed in six temperature cycles, but on the seventh cycle it increased about 100-fold. When the oxygen flow was stopped, the xenon release rate returned to its original value. The lack of an effect in the first six cycles was attributed to a reaction of the oxygen with the nickel cell until a layer of nickel oxide was formed. After that point, the release of xenon was proportional to the amount of additional oxygen retained in the cell.

The behavior of fission-product iodine was studied by modifying the diffusion cell so that condensable gaseous species could be collected on a cold plate. Condensed specimens were collected from fuel samples that had been heated to 914, 1290, and 1395°C. Only the first specimen contained a significant amount of iodine, which was present as iodide. This was a significant result in that it indicated that the release rates of cesium and iodine were not the same, as had been assumed previously in degraded core accident analyses.

Downstream Behavior of Volatile Fission Products. After fission products are released from a defected fuel pin, they are likely to interact with a steam-hydrogen mixture flowing upward in the reactor vessel. The apparatus, shown schematically in Fig. 5-36, was constructed to mix gaseous, nonradioactive fission-product species with a flowing gas stream containing various proportions of air, steam, hydrogen, and/or aerosol particles. As the temperature of the flowing gas stream decreased, the fission products were expected to condense as aerosol particles and deposit on the duct wall. Chemical reactions of the fission-product species with the gas-stream components were also a possibility. The major component of the experimental unit used in these studies was a 3.7-m-long stainless steel pipe (duct). Volatile fission products and superheated steam entered the duct at temperatures up to 1000°C, pressures up to 600 kPa, and flow rates up to 60 kg/h. The tube was fitted with liner sections which could be removed for analysis of the deposits.

Among the possible volatile fission products present in a reactor accident, cesium, tellurium, and iodine were selected for study because of their harmful biological effects if released to the air. In the presence of steam, the cesium and iodine would be expected to

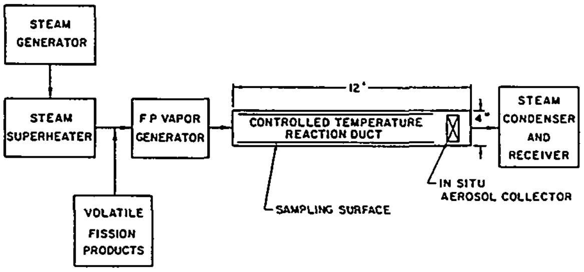


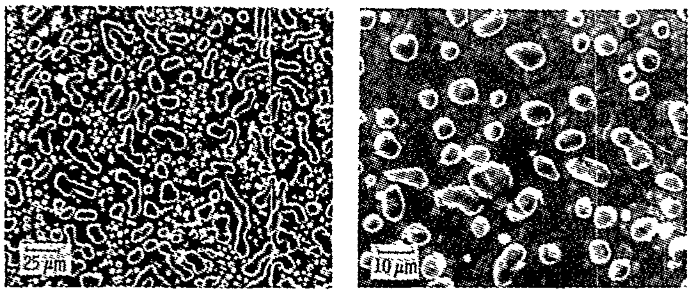
Fig. 5-36. Experimental Setup for Study of Downstream Behavior of Volatile Fission Products

react to form CsI, which is volatile at the high temperature, but would condense as it reached the cooler downstream part of the duct. Condensation of the CsI began where the steam temperature and the duct wall temperatures had decreased to about 700°C and increased with a further decrease in temperature downstream. Scanning electron microscopy indicated that the CsI had condensed as liquid particles or drops.

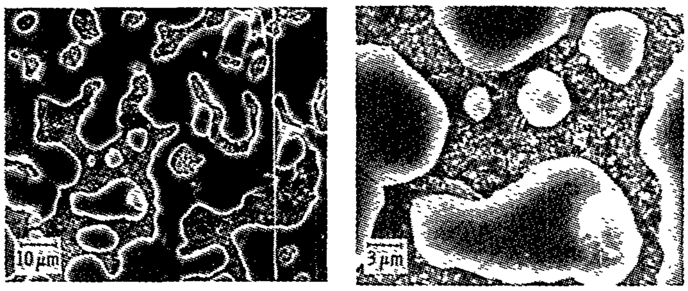
In 1985, five experimental runs were made—two with CsI, one with CsOH, one with CsI-CsOH, and one with Te-CsI-CsOH. During this work, scanning electron microscopy was used to view the deposits; the results are illustrated in Fig. 5-37. With CsI and CsOH alone, deposition occurred where the wall temperature had decreased to 680 and 670°C, respectively. With the CsOH-CsI mixture (molar ratio 8.4), the CsOH started to deposit at the same location as CsOH alone, but the CsI deposited farther downstream. This behavior was attributed to an equilibrium reaction

$$\mathrm{CsOH} + \mathrm{CsI} \leftrightarrow \mathrm{CsOH{\cdot}CsI}$$

The idea was that the large excess of CsOH molecules prevented CsI condensation until the CsOH concentration had been decreased by condensation, thereby freeing the CsI. In the case of the Te-CsI-CsOH mixture, all three elements, Cs, I, and Te, were found at the downstream end of the duct. In two other experiments, one with CsI and the other with CsOH, aerosol particles formed in the gas stream were collected on stainless steel wires and strips, which were examined by scanning electron microscopy to determine the particle-size distribution and calculate the collection efficiency.



(a) Horizontal Coupon (b) Horizontal Coupon



(c) Vertical Coupon (d) Vertical Coupon

Fig. 5-37. Scanning Electron Microscopy of CsI Deposition in Transport Duct

Attention was then directed toward the revaporization of material from deposition sites and movement further downstream that could be important in loss-of-coolant accidents. Revolatilization experiments were conducted with the same duct arrangement. The results suggested that the quantity of volatile fission products converted to aerosols depends on the cooling rate of the carrier gas. The deposits could heat up by radioactive decay, and a flow of gas over the heated deposits could revaporize the materials, possibly leading to their escape into the containment vessel.

A study was made of the interactions of various fission products with one another, with steam and hydrogen, and with materials of construction. The system is complex. For example, the behavior of iodine depends on its reactions with cesium and steam, and the behavior of tellurium depends on its reactions with cesium.

A separate follow-on investigation was conducted on the CsI-CsOH system. A quadrupole mass spectrometer was used to measure partial pressures of vapor species over liquid CsOH, CsI, and solutions of the two salts in a silver Knudsen cell over various temperature ranges between 349 and 762°C. The partial pressures of CsOH, $Cs_2(OH)_2$, CsI, Cs_2I_2 were determined. The existence of the compound CsI·CsOH was shown by derivation from the experimental results.

In 1984, separate, but similar experiments were performed in which a mixture of nonradioactive compounds and metals composed of CsI, CsOH, TeO_2, SrO, Ag, In, Cd, Sn, and Mn was loaded into a stainless steel boat, which was then placed inside a stainless steel pipe. A steam-hydrogen mixture was passed over the mixture as the temperature was increased rapidly and then held for one hour at 500, 750, and 1000°C. The tube was then disassembled, and chemical analyses were performed on the residue in the boat and the downstream deposits. At all three temperatures, I, Cs, Te, and Cd had been transported from the boat; in this case, cadmium was transported only at the highest temperature. The quantities of cadmium transported were consistent with calculated values when it was assumed that the pure metals had formed a liquid alloy. The mode of transport of iodine was not known, but it was probably through formation of the CsI·CsOH species mentioned earlier. The behavior of tellurium was not completely understood, but was thought to have been related to interactions with the indium.

Fission-Product Release from Core-Concrete Interactions. The objective of this effort, which began in 1985, was to predict the release of certain fission products that would occur if the molten core mixture penetrated the bottom of the reactor vessel in a severe accident. Three important fission products, La, Ba, and Sr, whose oxides can form solid solutions with the UO_2 fuel material, were of particular interest. In a laboratory-scale simulation of a reactor accident, UO_2 fuel granules containing La_2O_3, BaO, and SrO, separated from concrete by stainless steel and zirconium chips, were heated to about 2110°C for 132 min in a helium stream saturated with water. This charge was supported on a perforated tungsten plate. Upon completion of the run, a tungsten condenser tube was removed, and the deposits were dissolved in nitric acid and analyzed for La, Sr, Ba, Fe, Cr, Ni, Mn, Ca, and Mg. The amounts of these species that were vaporized ranged from 0.01 to about 0.15%, except for manganese, for which the value was 33%. This high value was attributed to the relatively low boiling point of the metal (2041°C). The behavior of the other species was in reasonable agreement with values calculated from existing thermodynamic data. The following year, five more experiments were completed. For the elements La, Sr, and Ba, the amounts released were in the order Ba>Sr>La, and most of the loss was by vaporization, with particulate entrainment making only a minor contribution (<10%). At this stage of the work, the investigators summarized their conclusions as follows:

1. Core-concrete melts containing metals give lower oxygen-potential values than do core-concrete melts containing no metals.
2. The release of stainless steel components follows the vaporization behavior of the elements in the steel.
3. The trend in the release of Ba and Sr is in accord with thermodynamic calculations.

By 1987, the experimental conditions had been modified somewhat. The materials tested were stainless steel, concrete (basaltic or limestone), and UO_2 doped with La_2O_3, SrO, BaO, and ZrO_2. The materials, alone or as mixtures, were vaporized from a ZrO_2 crucible into a He-6% H_2 gas stream to which up to 600 ppm water was added to maintain the desired partial molar free energy of oxygen in the desired range (-420 to -550 kJ). The fraction of the sample that had been vaporized was determined by weight change and by chemical analysis of the condensates. The experimental results were compared with the SOLGASMIX computer code. The results were difficult to interpret due to their complexity, but it was clear that the transport of stainless steel constituents, Fe, Cr, and Ni, was considerably lower than in runs with the steel alone.

Detailed post-test examinations using electron-probe microanalysis were done on the ZrO_2 crucible and its contents. The solidified mass of concrete, UO_2, and steel in the bottom third of the crucible appeared to have been at least partially liquid during the experiment, and the thickness of the crucible had been reduced by about 40% in that area. The steel phase, which was approximately spherical, was embedded in the concrete-UO_2 mixture, which probably accounted for the reduced transport rate of Fe, Cr, and Ni. The major phases in the mixture were UO_2 containing CaO and ZrO_2, and silicates and zirconates of calcium and magnesium. When molybdenum, rather than ZrO_2, was used as the crucible material, the transpiration results were nearly identical.

The status of information from this work after two more years of similar experimental and calculational studies is summarized briefly as follows:

1. The releases of Sr, Ba, La, and U in a severe reactor accident as described here will be less than 1% of their inventory. This result is as low, or lower than source-term values in the Reactor Safety Study sponsored by the U.S. Nuclear Regulatory Commission (NUREG-75/104). The aerosol release will be less than about 0.5% of the total core-concrete mass.
2. The release of refractory fission products is suppressed by shifts in the partial molar free energy of oxygen in the gas phase toward more positive values.
3. In a severe reactor accident, an oxide phase (concrete, UO_2, and ZrO_2) will lie over a metallic phase containing zirconium and stainless steel. The gas emanating from this concrete-core mixture will have a partial molar free energy of oxygen that is in equilibrium with the overlying oxide phase. The calculational procedure assumes that H_2O and CO_2 formed by decomposition of the concrete will first be reduced as they contact the metal phase and then reoxidized as they contact the oxide phase.
4. Accurate source-term information is not yet possible, given the existing thermodynamic database.

Fission-Product Chemistry in Source-Term Experiments. In 1984-85, the Source-Term Experiments Program (STEP) consisted of four reactor-accident simulations run in the Transient Reactor Test (TREAT) facility. The behavior of fission products released from irradiated UO_2 fuel rods (3-4.5 at.% burnup) overheated in flowing steam to the point of catastrophic failure of their Zircaloy cladding (about 2200°C) was investigated. Materials released from the fuel rods were collected on various coupons and wires in three types of aerosol-characterization devices. A CMT team consisting of Joanne Fink, Mike Roche, Chuck Seils, Dave Steidl, Carl Johnson, and Bob Ritzman was involved in identifying and characterizing the deposits and developing plausible mechanisms for their formation.

In the STEP-1 experiment, no CsI was found in the deposits, but droplet-shaped deposits containing nickel and iodine were observed at three locations. The deposits were not identified positively, but they appeared to be an amorphous form of nickel iodate. X-ray diffraction showed the presence of SnO_2, which apparently came from the Zircaloy cladding, which contained 1.5 wt% Sn. Molybdenum was found with Cs (and the Sn), which suggested the formation of Cs_2MoO_4, which is known to be a stable gas-phase molecule with a significant pressure over the fuel. Tellurium, usually along with cesium, was detected on a few isolated samples, but other laboratory data had shown that tellurium deposition occurs at a higher temperature than that of the collectors. In the STEP-3 and -4 experiments, the initial flow velocities and the peak temperatures were much lower. The predominant constituent in the STEP-3 aerosol deposits was Fe, and in STEP-4 it was Si, as opposed to STEP-1 and -2 where the main constituents were Cs, Mo, and Sn.

PERSONNEL

Carl Johnson was in charge of the Applied Physical Research Program in the 1980s. Others involved in this effort were Jack Arntzen, Paul Blackburn, Bob Blomquist, Martin Chasanov, Magdy Farahat, Darrell Fee, Joanne Fink, Dave Green, Bill Gunther, Irv Johnson, Len Leibowitz, Yung Liu, Art Pelton, Bob Ritzman, Mike Roche, Chuck Seils, Jack Settle, Bill Shinn, Bruce Spencer (RAS), Shiu-Wing Tam, Marvin Tetenbaum, and Ewald Veleckis.

Basic Research

The CMT basic research programs in the 1980s continued much as before. In 1982, the programs on environmental chemistry and on thermodynamics and electrochemistry were incorporated formally into the Materials Science and Technology Division (MST), which had been formed at that time to show the Laboratory's commitment to materials research. These programs, however, remained in CMT administratively and physically. Fred Cafasso led this work through the early 1980s, Vic Maroni after that.

HOMOGENEOUS CATALYSIS

Research in this area, which began in the 1970s and continued through the 1980s, involved the use of *in situ* catalysts to promote desired chemical reactions in organic systems. In 1980, work was in progress on the use of a cobalt carbonyl catalyst for (1) the catalytic hydrogenation of carbon monoxide to form methanol and other products and (2) homologation of methanol to form ethanol, which is commercially important as a solvent, a chemical feedstock, and a fuel extender. Ethanol is currently produced from ethylene obtained from petroleum and by fermentation of feed grains. The research to date, which had proved highly successful, was not based on unprecedented chemical reactions, but rather on unprecedented combinations of known reactions.

Hydrogenation of Carbon Monoxide. The primary reaction products from the hydrogenation of CO were methanol, methyl formate, and ethylene glycol. Although these were the only products formed under special conditions, several others were usually formed by branching reactions. Variations of the ratios of primary and other reactions were determined at different carbon monoxide and hydrogen pressures. The amount of methanol in the product ranged from about 43 to 90%, depending on the conditions.

Further studies of catalytic carbon monoxide hydrogenation were based on a new concept and observation. Methanol can be formed by the disproportionation of formate ion. By this reaction, methanol can be formed from water and carbon monoxide:

$$3\,CO + 2\,H_2O \rightarrow CH_3OH + 2\,CO_2$$

This reaction is highly desirable in terms of raw material costs because it uses water, rather than elemental hydrogen, as the hydrogen source. It is also thermodynamically favored over the commercial process, which uses hydrogen, by a free energy change of -19.5 *vs.* -5.9 kcal/mol.

$$CO + 2\,H_2 \rightarrow CH_3OH$$

The products of the reaction with water were not always limited to methanol. Acetone and other organic materials were also obtained in some cases.

Although the larger negative free energy change for the water reaction is highly desirable, the reaction must also have an acceptably high rate, which requires the use of an effective catalyst. The reaction is promoted by a variety of metal complexes containing oxide or oxo ligands, *e.g.*, PbO, PbO_2, $Pb(O_2CH)_2$, and $PbTiO_3$. The reaction occurs at 200-350°C when these materials are slurried or dissolved in molten formate salts. Not all of these catalyst materials are stable in the presence of the CO and H_2O; for example, PbO is rapidly reduced to metallic lead. A search was conducted for lead-oxide-like compounds in which the lead is coordinated strongly to oxo ligands. Materials of this type include $PbTiO_3$, $PbMoO_4$, $PbWO_4$, and PbV_2O_6. A flow reactor containing a slurry of $PbTiO_2$ in molten KO_2CH was operated for 19 days at CO/steam pressures from 1.7 to 11.2 atm with no loss of catalytic activity or lead formation. With the $PbTiO_2$ catalyst, the product was about two-thirds methanol, one-third ethanol, and a small amount of propanol. These higher alcohols are desirable if the product is to be used as a fuel extender. A mechanism was developed for the catalytic reactions involved in the formation of the alcohols.

A research study was then focused on the mechanism involved in the disproportionation of formate ion to produce methanol:

$$4\,O_2CH^- \rightarrow CH_3OH + CO + 2\,CO_3^{2-}$$

This reaction occurred at a temperatures around 230°C in slurries of lead compounds such as the oxide, titanate, or phthalocyanine in potassium formate salts. The reaction mechanism appeared to involve the intermediate species, formaldehyde and methyl formate. Details of the mechanism were explored in several separate experiments.

A mechanism was identified for the formation of methanol from a soluble organometallic formate. The mechanism includes a pre-equilibrium process in which trimethylsilyl formate was equilibrated with hexamethyldisiloxane, carbon dioxide, and methyl formate at 250°C. Methanol was then produced by decarboxylation of methyl formate. Isotope labeling studies, using $(CH_3)_3SiO_2CD$, showed that the methanol and methyl formate came solely from formate on the silicon, and not from the appended methyl groups. The decarboxylation reaction turned out to be the rate-limiting step. Zinc phthalocyanine was identified as a catalyst for the formate disproportionation and a related carbon monoxide hydrogenation.

This research continued along the same lines in 1986, although it was described a bit differently as new catalytic chemistry involving small molecules such as CO, CO_2, and O_2. It had been hypothesized that the mechanisms involved in the hydrogenation of carbon monoxide described here bore some significant similarities to the use of a metal oxide catalyst system (supported CuO-ZnO) in the commercial production of methanol, and that the mechanisms in this study might lead to improvements in the commercial process. A rather detailed mechanism was proposed for the catalytic effect of hexamethyldisiloxane, and activation of hydrogen by the oxide was identified as the rate-determining step. Based on the premise that the activation step involves nucleophilic attack on the hydrogen molecule, nucleophilic siloxide catalysts, exemplified by $NaOSi(CH_3)_3$, were tested and found to increase markedly both the rates of hydrogen activation and carbon monoxide hydrogenation.

Ethanol Synthesis. Homogeneous catalytic systems for cobalt-catalyzed methanol homologation to ethanol by carbon monoxide and hydrogen had been reported extensively in the literature. The economic viability of such processes was in doubt, however, because of problems with inadequate conversion, selectivity, and catalyst recovery. The investigators in CMT discovered a new catalyst, iron pentacarbonyl, $Fe(CO)_5$, which catalyzed the homologation of methanol to ethanol in the presence of Syngas and a tertiary amine at temperatures above 180°C, through the reaction

$$CH_3OH + 2\,CO + H_2 \rightarrow CH_3CH_2OH + CO_2$$

The only significant side-reaction product was methane. This reaction uses hydrogen efficiently in that carbon dioxide, rather than water, is the oxygenated by-product. The roles of the iron carbonyl, $Fe(CO)_5$, and tertiary methyl amine, $N(CH_3)_3$, are included in a detailed mechanism that was worked out for the above reaction. A conversion rate of 13% per hour with 70% selectivity was achieved in a batch reactor.

At this juncture, the researchers found that carbonyl complexes of metals other than cobalt were effective catalysts when used with the amine. For example, the manganese compound, $Mn_2(CO)_{10}$, was very similar to iron in its effectiveness. Further work showed that $RhCl_3$, $Mn_2(CO)_{10}$, and $Ru_3(CO)_{12}$, separate or combined with $Fe(CO)_5$, were all effective catalysts. For the $Fe(CO)_5$ and $Mn_2(CO)_{10}$ systems, a bimolecular methyl transfer from a tetramethylammonium cation to the transition metal carbonyl anion appeared to be the rate-limiting step.

An experimental study was made of the kinetics of the several individual reactions which, when added up, correspond to the one shown above. Kinetics of the individual reactions were determined by measuring the rate of disappearance of pertinent species by reagent-specific analytical methods.

As the studies progressed, additional transition metal complexes were found to be active catalysts for selective homologation of methanol in methanolamine solutions *i.e.*, $RhCl_3{\cdot}3H_2O$, RhI_3, $Ru_3(CO)_{12}$, and $Cr(CO)_6$. These compounds were tested individually as catalysts, and also as co-catalysts with $Fe(CO)_5$. As individual catalysts, RhI_3 had the highest catalytic activity; $RhCl_3{\cdot}3H_2O$ was less active, but more selective for ethanol production. The $Ru_3(CO)_{12}$ was similar to $Fe(CO)_5$ in its catalytic activity as was $Mn_2(CO)_{10}$, but the selectivity for methanol production was better with the manganese compound. The $Cr(CO)_6$ showed no catalytic activity under these conditions. In the tests of mixed catalysts, the $Mn_2(CO)_{10}$-$Fe(CO)_5$ combination was the most promising. A methanol conversion rate of 14% per hour at 220°C was achieved.

The thrust of these studies was then turned toward replacing the tertiary amines with inorganic basic compounds that are less expensive, more stable, and more easily separated from the product. Alkali metal formates, *e.g.*, KO_2CH, function as an inorganic base and also as a methyl carrier. The only metal carbonyl complex that was found to be active in the presence of KO_2CH was $Mn_2(CO)_{10}$. The KO_2CH-$Mn_2(CO)_{10}$ system was reported to work well. This completed the homologation studies, which were successful in achieving their objective.

Catalytic Oxidation. This area of work, which was started in 1984, involved the development of catalysts for controlled air oxidations of substrates. Substrate oxidations for which the new strategies were being sought were (1) oxidation of methane to methanol or formaldehyde, (2) oxidation of higher alkanes to alcohols, aldehydes, or carboxylic acids, (3) oxidation of higher olefins to epoxides or, in the presence of water, to glycols, and (4) oxidation of methanol to formaldehyde.

A study was directed toward the use of organic bases, such as an amine or sulfide (designated here as "B"), to bind oxygen reversibly. This reaction forms an organic oxide adduct (B-O), which may be an amine oxide or a sulfoxide:

$$2\,B + O_2 \overset{\text{(catalyst)}}{\leftrightarrow} 2\,B\text{-}O$$

One potential application of this idea is the recovery of pure oxygen from air by cycling this equilibrium reaction back and forth through pressure and temperature changes. A thermodynamic estimate indicated that a B-O bond enthalpy of about 68 kcal/mol would be needed to achieve the desired result. A collaboration between the CMT researchers and the National Institute for Petroleum Energy Research resulted in a value of 70 kcal/mol for the N-O bond enthalpy in pyridine-N-oxide and a value close to that for trimethylamine-N-oxide. Autoclave experiments, however, showed that under conditions where oxidation was rapid and selective, the equilibrium constant for the reaction with molecular oxygen was too large to demonstrate reversibility.

Another application of interest was the use of organic base oxygen carriers with catalysts to control the aerobic oxidation of certain substrates. The concept was demonstrated by experiments in which cyclohexene was converted to cyclohexanediol by trimethylamine oxidation and by osmium tetroxide-catalyzed transfer of oxygen from trimethylamine-N-oxide. These preliminary results were highly promising.

On further investigation, mechanistic studies were conducted on the oxidation of tertiary amines containing α-hydrogen atoms. A rate-limiting electron transfer from the amine to the oxygen molecule, including the sacrificial loss of an α-proton, appeared to be a characteristic of this type of system. Future work was directed to amine oxidations with amines that do not contain α-protons or that contain α-protons not susceptible to abstraction.

Soluble Oxide Chemistry. By 1987, the work described so far had undergone some changes of emphasis and evolved into a situation where it could be categorized better as two topics: (1) soluble oxide chemistry and (2) phthalocyanine chemistry. Basic research on the nucleophilic activation of hydrogen had shown that alkali metal formates, hydroxides, and carbonates catalyze the water-gas shift reaction in triethylene glycol solution:

$$CO + H_2O \overset{\text{(catalyst)}}{\leftrightarrow} CO_2 + H_2$$

These were the first examples of homogeneous catalysts for this reaction, which is catalyzed by solid transition metal oxides in the existing commercial process. Homogeneous catalysts of this type might be expected to be more tolerant of impurities such as sulfur than are the solid oxides.

Attention was directed toward soluble oxide catalysts that promote hydrogenation and water-gas shifting by catalytic mechanisms that are different from those of other homogeneous catalysts and appear to be more relevant to suspected metal oxide surface chemistry. A study of the effect of formate on the rate of the water-gas shift reaction indicated that hydrogen activation occurs at the oxygen center of a formate or hydroxide, and a metal center is not needed.

The lack of sufficiently robust solubilizing ligands had limited the application of homogeneous metal oxide complexes in synthetic gas catalysis. The tristrimethylsilylmethyl ligand, a relatively new species at the time, had been used in other syntheses, and appeared to have good thermal stability. Synthetic procedures were developed for the preparation of tristrimethylsilylmethyl zinc formate and the corresponding hydroxide complex, both of which have solubilities in excess of 0.1 *M* in hydrocarbons. The initial studies were focused on soluble complexes of zinc because zinc oxide is an important component of catalysts used in the commercial production of methanol. The results of this research were highly significant in that they opened the door to a possibility that a variety of polar metal oxide and hydroxide complexes could be used in organic solvents at high temperatures and gas pressures.

Phthalocyanine Chemistry. Interest in metallophthalocyanines was sparked by the observation that ZnPc (Pc = phthalocyanine) catalyzed many reactions, even at the low concentrations (about 10^{-5} *M*) achievable with its limited solubility. It had been shown to catalyze the disproportionation of trimethylsilylformate and the addition of carbon dioxide to metal hydrides. Phthalocyanines are also highly stable. A sample of ZnPc heated for two weeks in a mixture of H_2 and CO_2 (300 atm) at 250°C showed no evidence of decomposition.

The investigators discovered that ring carbons in phthalocyanines can be metallated efficiently with metals such as lithium and magnesium, which opened up the possibility of introducing a variety of structural features into phthalocyanines. One motivation for such a substitution was to increase the solubility of the phthalocyanine, thereby increasing its effectiveness as a catalyst. Success was achieved when trialkylsilyl groups were incorporated into phthalocyanine rings to produce a mixture of trimethylsilyl-substituted phthalocyanines, *i.e.*, $H_2Pc(SiMe_3)_x$, where Pc is phthalocyanine, Me is the methyl group, and x is 2, 3, or 4. Nuclear magnetic resonance (NMR) spectra were determined to provide structural information on the molecule.

Although the trimethylsilyl complexes showed promise, their thermal stability was limited to temperatures below about 150°C. Therefore, the emphasis was shifted to alkyl-substituted phthalocyanines, which have higher thermal stabilities. A synthetic procedure that was developed for very stable metallophthalocyanines was used to produce the following complexes:

$Co(R_8Pc)$,
$Rh(R_8Pc)(CO)Cl$,
$Rh(R_8Pc)(PBu_3)Cl$,

$Rh(P_8Pc)(PhCN)Cl$, and
$Rh(R_8Pc)(PBu_3)\text{-}Cl\text{-}Rh(R_8Pc)Cl$,

where $R = C_5H_{11}$, Pc = phthalocyanine, and $Bu = C_4H_9$.

High-Pressure NMR Studies. In 1986, work began on the design and construction of a high-pressure, multinuclear NMR probe suitable for *in situ* kinetic studies. The existing apparatus was not capable of handling the extreme pressures required (*e.g.*, 300 atm) and the corrosivity of some of the materials under investigation. The following year was devoted to working out the design details. The new nuclear resonance detector (shown in Fig. 5-38) was developed in the shape of an elongated toroid. This design provided greatly improved sensitivity for ^{13}C and other insensitive nuclei associated with organometallic systems, and because of its confined magnetic field, the detector was ideal for use in high-pressure metal probes. This equipment was a major asset in expanding the scope of the research effort.

In 1989, investigations were started in which real-time kinetic and spectroscopic techniques at high temperatures and pressures were used to determine the chemistry of small molecules derived from coal, natural gas, and petroleum. Maximum concentrations of reactive gases were achieved by making use of their complete miscibility with supercritical fluids. A detailed NMR study, using the new probe, was initiated on the hydrogenation of cobalt octacarbonyl

$$Co_2(CO)_8 + H_2 \leftrightarrow 2\ HCo(CO)_4$$

Data were generated on enthalpies, entropies, and rate constants of the system.

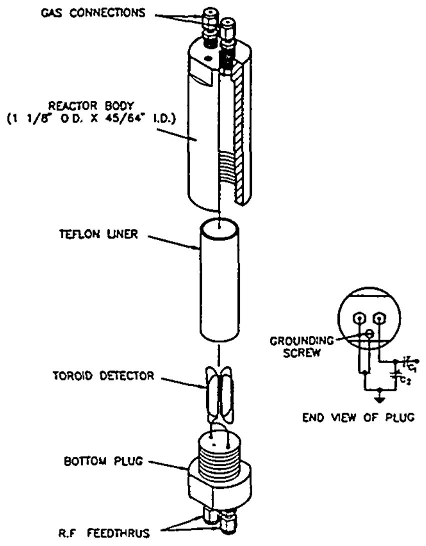


Fig. 5-38. High-Pressure Nuclear Magnetic Resonance Probe

Personnel. This area of research was initiated originally by Hal Feder, who kept in close touch with the work while at CMT and then during his retirement up to the date of his death in January 1998. Jerry Rathke is the Group Leader of this effort; others in the group in the 1980s were Ira Bloom (a postdoc at the time), Michael Chen, John Heiberger, Bob Klingler, and Theodore Krause, plus several postdocs and other temporary people. Larry Curtiss, although not a member of the group, contributed to a special aspect of the research.

THERMODYNAMICS

Molten Salt Systems. An effort was underway to develop fundamental solution theories to understand better the properties of solutions, to expand the ability to predict solution properties, *a priori*, and to facilitate the use of theories in technological applications. The derivation of thermodynamic properties of multicomponent ionic reciprocal molten salt systems by use of the conformal ionic solution (CIS) theory was mentioned in the previous chapter. The applicability of this theory was demonstrated by computations of the ternary phase diagrams of AlF_3-CaF_2-NaF, AlF_3-CaF_2-LiF, and CaF_2-LiF-NaF that are consistent with thermodynamic information.

The coordination cluster (CCT) theory is a statistical mechanical theory involving the activity coefficients of dilute solvents in multicomponent systems. The CCT theory was used not only for molten salt mixtures, but also for metallurgical slags and aqueous solutions. For the molten salts, it provided a rationalization of the energetics of association of cations and anions in dilute solutions. The CCT theory was extended to perform calculations for a multicomponent solvent based solely on data from the subsidiary binary systems.

Molecular dynamic studies of $MX-AX_3$ molten salts (where X is a halogen, M is an alkali metal, and A is a trivalent metal) at 500 K (227°C) allowed the six radial distribution functions and the near-neighbor and next-nearest neighbor coordination number to be deduced. The long-range order (up to 9.2 Å), due to X^- sharing, may exist in melts with large radius ratios. Theoretical and experimental studies of the complexing of S^{2-} and O^{2-} ions by Al^{3+} in LiCl-KCl melts suggested that large screening occurs in the formation of AlO^+ and AlS^+, and that the coulomb complexing model, which was used to treat this phenomenon, had a potential for predicting the effects of solvent and solute radii on complex formation.

Further studies of the energetics of bonding and association of Al^{3+} with divalent ions in molten salts were performed in which *ab initio* quantum mechanical calculations were made on the reactions of gaseous polyatomic molecules containing Al-F and Al-Cl bonds with oxygen- or sulfur-containing species. Evidence was found for the stability of Al-O and Al-S bonds in molten halides, which meant that it might be possible to create simple ionic pair potentials from which those bonds in a molten salt could be simulated by a molecular dynamics calculation.

Additional *ab initio* quantum mechanical calculations were made to study Al_2F_7 species, which were expected to occur in ordered AlF_3 melts. The calculations indicated a single Al-F-Al bridge that is bent in the presence of lithium ion. The bent bridge structure was in agreement with experimental observations on fluoride melts. Structural details were obtained by molecular dynamics calculations of melts that simulated $NaCl-AlCl_3$ and $KF-YF_3$ mixtures. Studies of melts simulating $KF-YF_3$ revealed a new type of intermediate-to-long-range order, a triangular triplet of Y^{3+} ions, and very few free YF_6^{3-} species at the K_3YF_6 composition.

In a separate study, emf measurements from an $Al/AlCl_3$-NaCl(s)//NaCl-$AlCl_3$/Al cell were used to obtain total excess free energies of mixing per mole. The results showed an unusual degree of ordering near the 50-50 $NaCl-AlCl_3$ composition. Near these compositions, the activity coefficients of many halide solutes increase drastically, with a resulting decrease in their solubilities.

Molecular orbital calculations were continued, in which vibrational frequencies were predicted for comparison with observed infrared and Raman spectra. The results showed that frequencies for $AlCl_4^-$ ions in melts were similar to those for the gas-phase ion. These studies led to a continuation of some earlier work on Mg_2O^{2+} and MgO in molten fluoride melts. In comparing the energetics of these two ions, consideration was given to reactions involving $Li_2Mg_2OF_4$ and Li_2MgOF_2. Structure and bond-energy determinations for these species indicated that coordination of the oxygen anion by either one or two magnesium ions in the LiF melt was of nearly equal stability in the LiF melt.

Further calculations were performed on the stabilities of MgO and Mg_2O^{2+} in four alkali halide melts (LiF, LiCl, NaF, and NaCl), and the results were consistent with experimental data from the literature. Vibrational frequencies were predicted for complexes of magnesium oxide (F_2MgO^{2-}, Cl_2MgO^{2-}, F_4MgO^{2-}, and F_3MgO^{3-}) and aluminum oxide (F_3AlO^{2-} and Cl_3AlO^{2-}). Vibrational frequencies were also calculated for the five- and six-coordinated Al^{3+} ions in a fluoride melt (AlF_5^{2-} and AlF_6^{3-}). Of the six calculated vibrational frequencies, the three that had been observed experimentally agreed with the calculations. Calculations for one sulfide ion complex, S_3^-, were also in agreement with frequencies obtained by Raman spectra.

Molecular dynamics calculations were performed on MAX_4 melts (M is an alkali metal, A is a trivalent metal, and X is a halogen), in which the X^- anions are polarizable. Such melts are analogous to the chloroaluminates. With polarization of the anions, A_2X_6 molecules as well as the AX_4^- ions are present. This result is in contrast with the observation of AX_4^-, $A_2X_7^-$, and $A_3X_{10}^-$ anions in an ionic melt with nonpolarizable anions. All the species postulated to exist in chloroaluminate melts were observed in the calculations, but their relative stabilities differed from those in real melts.

In 1988, a semiempirical quantum mechanical method, called Modified Neglect of Differential Overlap, was used to investigate the structures of $Al_2X_7^-$ and $Al_3X_{10}^-$ ions. The $Al_2Br_7^-$ anionic species was found to have a bent bridge structure similar to that found previously for $Al_2Cl_7^-$ ion in the *ab initio* studies. For the $Al_3X_{10}^-$ species, chain structures were favored over ring structures with bent bridges for the chlorides and bromides, and linear bridges were retained in the fluorides.

The solubility of $CoCl_2$ in NaCl-$AlCl_3$ melts exhibited a sharp minimum at the most ordered composition of equimolar NaCl and $AlCl_3$. The concentration dependence of solubilities was accurately described by the coordination cluster theory and the solubility product principle. The results provided the information necessary to predict solubilities in all other acid chloroaluminates.

Neutron-diffraction measurements were made on a series of trivalent halides at temperatures slightly above their melting points. The cation-anion coordination numbers were 4.0 for $AlBr_3$, 3.8 for $GaBr_3$, and 3.7 for GaI_3. This finding indicated that $AlBr_3$ melts consist of Al_2Br_6 molecules, but the two gallium salts were about 70-80% dimerized. The $NdCl_3$ structure factor was used to obtain a model structure by the Reverse Monte Carlo method. The resultant structure bore a close similarity to a randomized structure of solid $NdCl_3$ for features up to about 6 Å and no remnant of the solid structure at about 8 Å.

These studies were a valuable contribution in gaining an understanding of the thermodynamics and structural characteristics of molten salt systems. They provided data that were useful not only in adding to the general basic information on molten salts in the literature, but also in selecting and optimizing molten salt systems that were being used in the Division's applied programs.

Alloys. Activity coefficients for dilute solutions (about 0.1 mol%) of lithium in Bi-Pb, Pb-Mg, Bi-Tl, and Bi-Al alloys were determined as a function of solvent composition and temperature to test the range of validity of the coordination cluster theory (CCT). The most extreme case of non-ideality was the Li-Bi-Al system, where the Bi-Al solvent exhibits a miscibility gap and a large positive deviation from ideality. In all the cases, the calculations derived from the CCT were in agreement with precisely measured emf data.

The scope of this study was extended to include sodium, as well as lithium, as the solute in Bi and Sn solvents. Limiting excess potentials of the alkali metals were obtained from Nernstian emf plots at very low concentrations. Data from these experiments and the literature were used to evaluate the limiting slopes of ten binary systems involving lithium or sodium. The limiting slopes are related to correlation functions that provide information on the distribution of atoms around the solute. Electrical resistivity measurements were also made on the Na-Bi system over a temperature range of 400 to 500°C within which several liquid and solid phases exist in the phase diagram. A peak in the resistivity occurred at 20 at.% Pb, which suggested a boundary between localized and nonlocalized states.

Electromotive force studies were made on the Na-Sb system, which differed from most of the alloys studied previously in that it is a semiconductor near the composition of 50 at.% sodium. Moreover, it was believed that the antimony atoms tend to form "covalent" bonds. Activity coefficients were measured by means of a β''-Al_2O_3 solid electrolyte, which conducts sodium ions. The initial results indicated a large deviation from ideality. In addition, two inflections were observed in plots of the concentration dependence of the logarithm of the activity coefficients of sodium. These inflections appeared to relate to valence states of -3 and -1 for the antimony. The limiting slope of the activity coefficient for very dilute solutions of Na in Sb was very small and positive, which parallels the behavior of other "covalently" bonded systems.

These studies continued with measurements of the thermodynamic properties of liquid sodium-lead alloys at temperatures of 380-450°C. Coulometric titrations were used to measure the sodium activity as a function of temperature and alloy composition. Information derived from the resulting data included excess Gibbs free energies of mixing, excess stabilities and concentration fluctuation functions, and entropies of mixing. Plots of the logarithm of the sodium activity *vs.* the sodium concentration showed two peaks corresponding to NaPb and Na_4Pb.

In the 1985 CMT Annual Report, the investigators who had been working on the above alloy systems made the following statement: "Despite the recent strong interest in alloys undergoing a metal-to-nonmetal (MNM) transition, our basic understanding of these solutions remains rather primitive." There was no comprehensive theoretical treatment in which the various electronic, magnetic, electrical, and thermodynamic properties of these alloys were included. The current effort had been focused on the activity coefficients of alkali metals (Li, Na, and K) alloyed with metals having very different electronegativities (Pb, Sb, and Bi). Such alloys were considered to be "liquid semiconductors." A goal of the work was to determine whether the continuous change from metallic to semiconductor-like behavior, alloy ordering and structure, and transitions between ionic and covalent-like solutions could be related to thermodynamic properties.

All the emf measurements to date had employed β-Al_2O_3 or β''-Al_2O_3 solid electrolyte except for the system Li-Bi, where molten LiCl-KCl was used. For the first time, the potassium form of β-Al_2O_3 was used successfully. The K-Pb alloy showed unexpected behavior in that the MNM transition occurred at a potassium concentration of 50 at.% and not at a composition corresponding to the ratio of the chemical valences (80 at.% potassium). Coulometric titrations were performed on the K-Pb system by means of the potassium β-Al_2O_3 solid electrolyte, which could contain the volatile potassium at pressures up to 2 atm in the emf cell. Data on the emf *vs.* temperature at 300 to 600°C at constant compositions were accurate enough to obtain reliable data on the partial molar heat capacities. The concentration dependence of the heat capacities showed a large anomalous peak at about the equiatomic K-Pb composition. Enthalpies of the equiatomic alloy were obtained by calorimetric methods from the melting point at 589°C to 851°C. The heat capacity was very large at low temperatures, but decreased to values typical of "normal" liquids as the temperature was raised. This effect is consistent with order-disorder transitions and could be related to long-range ordering or to the formation of ordered clusters such as Pb_4.

In collaboration with personnel from the Materials Science Division and the Intense

Pulsed Neutron Source, neutron-diffraction experiments were undertaken on the equiatomic K-Pb liquid alloys. The results led to model calculations based on known structural units in the KPb crystal (nearly regular Pb_4 tetrahedra surrounded by K_4 tetrahedra oriented in the opposite direction). Results of the calculation were in excellent agreement with experimental data. Further investigation showed that all the equiatomic alkali metal-lead compounds had the same crystalline structure, known as a Zintl compound. This structure involves a Pb_4 tetrahedron interlocked with a larger M_4 tetrahedron, where M is an alkali metal other than lithium.

In other work, a hydrogen-titration method was used to measure the thermodynamic properties of hydrogen solutions in metals and alloys. Due to hydride formation, certain binary alloys (Ca-Al, Ca-Si, and Mg-Si) were of interest as potential media for hydrogen storage. Studies were initiated on the Ca-Al system, which has two intermetallic compounds, $CaAl_2$ and $CaAl_4$. Equilibrium hydrogen pressures over mixtures of these compounds were measured over a temperature range of about 400-650°C. The results showed that the Ca-Al system could serve as a "high-temperature" hydrogen-storage system with an absorptive capacity of 2.1 wt% H, which compares favorably with 1.9 wt% for FeTi and 1.4 wt% for $LaNi_5$, which are well-known "low-temperature" hydrogen-storage media.

The hydrogen-titration technique was extended to the Ca-Si system, which was complicated by uncertainties in the phase diagram. In addition to three well-established silicides, Ca_2Si, CaSi, and $CaSi_2$, evidence had been reported for two additional intermediate phases, an "E" phase and Ca_3Si_4. Hydrogen-titration isotherms for the calcium-rich portion of the phase diagram provided unambiguous evidence for the existence of the "E" phase, proof that the reaction of silicides with hydrogen is reversible, and corroboration of the validity of the theory underlying the HTM method by correct predictions for the stoichiometries of Ca_2Si and CaSi.

Personnel. In most of the basic programs, including this one, much of the work was collaborative with other ANL divisions or outside organizations such as universities. Much use was made of students, postdocs, visiting professors, and other temporary personnel. Milt Blander had the primary responsibility for most of this work. Other CMT members working in this area included Bob Blomquist, Ira Bloom, Yat Ching Chen, Larry Curtiss, Dave Frurip, Jerry Johnson, Jane Marr, Zoltan Nagy, Art Pelton, Marie-Louise Saboungi, Jack Settle, Marv Tetenbaum, Ewald Veleckis, and Bob Yonco.

THERMOCHEMISTRY

The thermochemistry studies were closely related to the thermodynamics work, but differed in that they generally involved calorimetric measurements to obtain basic thermochemical properties such as enthalpies, free energies, entropies, and heat capacities of specific substances with high accuracy and precision. (Because thermochemical data relate naturally to absolute temperature, all the temperatures in this section are expressed in degrees Kelvin. Energies are expressed in kilojoules, kJ.)

Zeolites. Work on zeolites was undertaken because these minerals are of considerable importance in various energy and environmental applications. Zeolites are involved in the extraction of geothermal energy, nuclear waste storage, isolation of radioisotopes, transport of radioactive species in groundwater, and numerous industrial applications such as water treatment. Although the chemical and physical properties of natural and synthetic zeolites had been studied extensively, almost no work had been done to obtain accurate, reliable data on their thermochemical properties.

Samples of five naturally occurring minerals—analcime, natrolite, mesolite, scolectite, and thompsonite—were obtained from Professor William Wise of the University of California at Santa Barbara. Enthalpies of formation for analcime of the composition $Na_{0.96}Al_{0.96}Si_{2.04}O_6 \cdot 1.02\ H_2O$ were determined by hydrofluoric acid reaction calorimetry, and the enthalpy functions to 625 K were measured by drop calorimetry. These data, together with results from low-temperature heat capacity measurements, provided the data for a complete table of the thermochemical properies of analcime between 0 and 625 K. The enthalpies of formation of dehydrated analcime and natrolite were also determined. There was a concern that, in a hot-dry-rock geothermal energy facility, native feldspar and water might react at low temperatures to produce analcime and quartz, a high-volume mixture that could plug the inlet and outlet bore holes through which the water must circulate. Based on the thermochemical values that were determined for analcime and literature data for the other substances involved in the reaction, the equilibrium temperature for the reaction is 380 K, which indicated that plugging should not be a problem.

There was concern, however, about a reaction of native albite with water to form voluminous analcime, which could cause borehole plugging. To evaluate that possibility, reliable thermochemical data were needed for albite, water, analcime, and aqueous quartz. Reasonably good data were available for all of these except albite.

Calorimetric measurements were made on several materials related to analcime (natrolite, scolecite, mesolite, and heulandite), and the resulting data were used to compute enthalpies, heat capacities, entropies, and free energies of formation. Information from this work indicated that the structure of water in these zeolites is close to that of ice. This finding contradicted results of earlier work which had indicated that the structure of zeolitic water in analcime is more characteristic of liquid water.

As experimental data became available on thermochemical values for various zeolites, it was possible to develop rudimentary methods for estimating thermochemical properties of materials that were too time-consuming or difficult to measure. Such estimates were made of the heat capacities and entropies of the hypothetical anhydrides of natrolite, mesolite, and scolecite, as well as the standard entropies of laumontite and Na-wairakite and the standard enthalpy of formation of gonnardite.

In 1984, an evaluation was made of all the earlier experimental results on zeolites and silicates. Recently determined thermodynamic functions for analcime showed that the values could not be used to predict stability ranges for naturally occurring combinations of analcime + quartz and analcime + natrolite because analcimes from various sources had different Si/Al ratios. These ratios were not necessarily the same as that of the analcime used in the calorimetric measurements. Estimates were therefore made on the effect of analcime composition on its Gibbs free energy of formation. A phase diagram that was constructed was fully compatible with natural occurrences and the experimentally determined stability of analcime.

A collaborative research effort was started with Professor Joseph Smith of the University of Chicago on the thermochemical properties of certain molecular sieves related to zeolites. Aluminophosphates were of interest as industrial absorbents, catalysts, and catalyst supports. Another molecular sieve, synthesized by the Union Carbide Corporation, was silicalite, which is essentially pure silica and can be considered to be the end member of a series of silica-rich zeolites. It is used for removal of organic contaminants from water. The standard molar enthalpy of formation of this material was determined to be -904.6 ± 1.1 kJ/mol, which indicates that its stability is comparable to that of α-quartz. Unlike α-quartz, silicalite can be dissolved readily in hydrofluoric acid, which makes it a convenient reference substitute for α-quartz in calorimetric studies. The following year (1985), low-temperature heat-capacity and high-temperature enthalpy measurements on silicalite provided the additional information needed to establish its thermodynamic properties at temperatures from 5 to 1500 K. In addition, this work showed that the material began to decompose at about 1300 K, contrary to previous reports in the literature.

Calorimetric data on hydrated and dehydrated mordenite, one of the few zeolites that can be dehydrated without altering the framework structure of the material, yielded data on the binding enthalpy of water.

In modeling studies of rock-water interactions, which are important to geothermal energy and to high-level nuclear waste repositories, reliable thermochemical data on zeolites are essential. The natural zeolites presented a problem in gathering valid thermochemical data because of the variability in their compositions. The variabilities are not only in the silicon-to-aluminum ratios, but also in differences in the substituted cations, *i.e.*, Ca^{2+} for $2Na^+$. Studies were initiated on the effect of Si/Al ratio on the standard molar enthalpies and entropies of formation. The mineral, faujasite, was used because it is one of the few zeolites that can be dehydrated without affecting the basic aluminosilicate structure. Faujasites having Si/Al ratios of 1.23 to 2.84 were investigated. The enthalpy of formation of gibbsite, $Al(OH)_3$, was also determined because it was needed as auxiliary data in deriving values for the zeolites.

In continuing studies, enthalpies of formation of four faujasites in the hydrated and dehydrated forms were measured. The binding energy of the water of hydration was highly variable, even within this family of structurally similar zeolites. Apparently, there was no way to predict with certainty the effect of water of hydration on the enthalpy of formation. Further study of the effect of Si/Al ratio indicated that a sufficient correlation exists between that ratio and the enthalpies of formation to predict the effect of only small changes in the ratio.

An effort was directed toward certain other minerals of importance to nuclear waste storage, particularly at the Nevada site. The thermochemical properties of clinoptilolite, dehydrated clinoptilolite, and tobermorite were determined.

Uranium Compounds. Among the numerous thermochemical studies of binary uranium fluorides reported in the literature, the enthalpy of formation of only one of them, UF_6, appeared to have been established with any degree of certainty. A cooperative program to establish firm enthalpy of formation values for UF_3, UF_4, α- and β-UF_5, and, if possible, U_2F_9 and U_4F_{17}, was initiated among the CMT thermochemistry group and other groups at the Netherlands Research Foundation (ECN) in Petten, Los Alamos National Laboratory, and the Chemistry Division at Argonne. In 1980, results were obtained for α- and β-UF_5, UF_4, and UF_3. Data obtained for UF_3 and UF_4 by solution calorimetric measurements at ECN and by fluorine bomb measurements at ANL were not in agreement.

In irradiated nuclear fuels, the noble metal fission products, ruthenium, rhodium, and palladium, form exceptionally stable intermetallic compounds with the uranium: URu_3, URh_3, and UPd_3. Thermochemical data were desired on these compounds both for evaluating their role in practical applications such as fuel reprocessing and in the testing of theories of chemical bonding. An experimental determination of the enthalpy of formation of UPd_3, which indicated that it is, indeed, very stable, lent credence to the Brewer-Engel theory of chemical bonding.

Several thermochemical cycles that had UO_2 in common were yielding data for various