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Chemical Technology Division Annual Progress Report

Period Ending March 31, 1979

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Preface

This progress report is a summary of the research and development efforts conducted in the Chemical Technology Division during the period April 1, 1978–March 31, 1979. Further information regarding work in the various programs can be obtained from the topical reports and journal articles cited in the references.

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1. Introduction and Divisional Overview

The Chemical Technology Division presently consists of about 400 staff members who occupy space in 12 buildings located at the ORNL, Y-12, and HFIR-TRU sites. Of these, approximately 240 are engineers or scientists and 105 are technicians or draftsmen; the remainder are secretaries or administrative personnel. These individuals comprise a versatile, mobile work force that may be deployed in various jobs, within the Division or throughout ORNL, as needs and priorities arise.

The Chemical Technology Division is involved in a large number of programs of a widely diverse nature, including nuclear and nonnuclear energy studies, basic and applied science and engineering, construction and operation of small and large pilot plants, operation of various production facilities, and work for several other governmental agencies including the U.S. Nuclear Regulatory Commission (NRC).

During the past year there were no major changes in the Division's programs, although significant redirection was experienced in some of them and shifts of emphasis were necessary in others. ORNL was named Lead Laboratory for Spent Fuel Reprocessing, and the Consolidated Fuel Recycle Program (CFRP) was established to manage all fuel reprocessing research and development in the United States. The scope of this program, the major portion of which is carried out in the Chemical Technology Division, includes the use of thorium in both breeders and light-water reactors (LWRs), as well as liquid-metal fast breeder reactor fuel reprocessing. Studies of the high-temperature gas-cooled reactor fuel cycle continue, although in a relatively minor position.

Work concerning nuclear waste management remains high on our list of priorities. We believe that the use of cement grouts for waste fixation is an important area for future development.

We have broadened the base of the process development aspect of our coal conversion programs, and new experimental efforts are yielding significant data. These efforts include investigations of the effects of chemical and physical properties of process streams on equipment design and new chemical approaches to liquefaction. Significant new efforts have been initiated in engineering analysis and process simulation. In this area, we play a central role as the U.S. Department of Energy's (DOE's) principal contractor for systems engineering studies of coal liquefaction.

Energy-related programs of growing importance include studies of the application of biotechnology to pollution abatement, as well as other environmental monitoring and control studies.

Our chemical separations and chemical engineering research programs constantly serve as a source of new ideas and provide impetus and direction for the more applied programs. A good example is that of resource recovery, which is a relatively new area of study aimed at recovering and conserving scarce chemical resources. This is an area in which we propose to expand our effort significantly over the next few years.

We have continued to operate the facilities for transuranium-element processing and stable-isotope separations. The materials produced by these facilities are supplied to investigators for use in research projects at ORNL and elsewhere.

Under the "Work for Others" programs, we have carried out substantial reactor safety research and contributed to NRC programs involving safety analyses for the nuclear fuel cycle and related studies.

Some specific highlights of this report period include:

1. Preparing laboratory samples of FUETAP (formed under elevated temperature and pressure) concrete that have high retentiveness for cesium, strontium, and plutonium and also possess sufficient catalytic activity to recombine the hydrogen and oxygen produced by radiolysis.
2. Modifying the recovery of aluminum from fly ash via the Calsinter process, which was developed during the previous report period, by utilizing flue-gas desulfurization sludge as the

reagent in the sinter step prior to dissolution for recovery of the metal values.

3. Developing an internal gelation process that was subsequently used to prepare several hundred kilograms of UO_2 spheres for irradiation testing in the Halden and Big Rock Point Reactors.
4. Receiving an I·R-100 award, which was granted by *Industrial Research* for our development of a tapered fluidized-bed bioreactor.
5. Operating a small, continuous coal liquefaction test unit to measure rheological phenomena in coal slurry preheaters and physical properties of product streams.
6. Installing a small solvent extraction test system in a hot cell for use in the evaluation and demonstration, at full activity levels, of solvent extraction flowsheets for recovering fissile and fertile materials from irradiated reactor fuels.
7. Completing the installation and operation of an engineering-scale voloxidizer to be used in studies associated with the CFRP.
8. Preparing the conceptual design of a system for converting Consolidated Edison uranium (which is presently being stored as nitrate solution in Building 3019) to solid U_3O_8, and completing the construction of a seismic-proof facility for storing solid fissile materials.
9. Updating the physical security system of Building 3019 to comply with the most recent DOE specifications (e.g., by installing an in-house computer system for on-line, near-real-time accountability of fissile materials).
10. Demonstrating the removal of carcinogenic polynuclear aromatic hydrocarbons (PNAs) from coal conversion wastewater by using a combination of biological treatment, ozonation, and adsorption.
11. Developing a method for trapping volatile and gaseous ions by ion implantation in a continuously renewable substrate.
12. Addressing the problems of shipping and receiving radioactive spent fuels and wastes through the development of logistics programs and a data base of legislation which permits the mapping of routes for such shipments throughout the United States.
13. Developing a portable fluorescence monitor ("spill-spotter") for detecting surface contamination by PNAs.
14. Successfully attaining size-selective synergism for the solvent extraction of alkali ions by employing di(2-ethylhexyl)phosphoric acid in conjunction with selected crown ether compounds.
15. Analyzing recent data on direct acid leaching of several coal gasification ashes which indicate that relatively simple, inexpensive processes may provide high metal recoveries from these materials.
16. Demonstrating that multiple leaches with nitric acid will remove most of the radionuclides from uranium mill tailings and can reduce the residual ^{226}Ra to ~8 pCi/g (or about four times greater than the background level).
17. Establishing that electrofiltration in granular beds can be used effectively to remove micron-sized particles from nonaqueous liquids with very small pressure drops.
18. Completing reviews of the current state of the art of hot-gas purification, low-Btu gasification, heat recovery, and effluent control technologies.

2. Fission Energy

2.1 CONSOLIDATED FUEL REPROCESSING PROGRAM

Fuel cycle studies concerned with the development of reprocessing technology for all types of reactor fuels are not reported here, in compliance with regulations which stipulate that such information must be distributed only through limited, controlled lists.

Effective October 1, 1978, all U.S. research and development on fuel reprocessing was combined in one major program, the Consolidated Fuel Reprocessing Program (CFRP), under the direction of the Oak Ridge National Laboratory (ORNL). The purpose of this effort was to organize a single generic program which would address all fuel-reprocessing development efforts. During this period when the future of several proposed fuel cycles is so uncertain, the resources will be concentrated, to the extent possible, on problems that are associated with more than one of the cycles. As future directions are clarified, emphasis on more specific areas is anticipated.

The CFRP for FY 1980 is a combination of the major portions of four previous programs: (1) the Advanced Fuel Recycle Program at ORNL; (2) the Converter Fuel Reprocessing Program at Savannah River Laboratory; (3) the High-Temperature Gas-Cooled Reactor (HTGR) Fuel Recycle Program, primarily at the General Atomic Company and ORNL; and (4) the Pyrochemical and Dry Processing Methods Program at Argonne National Laboratory. Only the reprocessing phases of the HTGR Fuel Recycle Program were incorporated into the CFRP. Other prime Department of Energy (DOE) contractors, along with several subcontractors, are participating in the program. All work is now reported under the Consolidated Fuel Reprocessing Program in topical reports and in a series of quarterly progress reports, the most recent of which is the *Consolidated Fuel Reprocessing Program Quarterly Progress Report for Period Ending March 31, 1979,* ORNL/TM-6836.

2.2 HTGR TECHNOLOGY PROGRAM

The work relative to HTGR technology studies is not reported here, in compliance with regulations which stipulate that such information must be distributed solely under category UC-77—Gas-Cooled Reactor Technology. The results of our investigations have been reported in internal documents and in annual reports. The most recent publications are the *High-Temperature Gas-Cooled Reactor Base Technology Program Annual Progress Report for Period Ending December 31, 1977,* ORNL-5412 (July 1978) and *High-Temperature Gas-Cooled Reactor Base Technology Program Annual Progress Report for Period Ending December 31, 1978,* ORNL-5536 (June 1979).

2.3 FUEL FABRICATION STUDIES

In support of our national nuclear energy policy, the Consolidated Fuel Cycle Development Program is being supported by the Nuclear Power Development Division of DOE. The purpose of this program is to assess and develop nuclear fuel cycle technology which offers increased proliferation resistance of the fissile materials at all stages of the fuel cycle. The lead responsibility for fuel refabrication and development within the overall program has been assigned to Battelle Pacific Northwest Laboratories.

To achieve a proliferation-resistant fuel cycle, a technical approach employing various combinations of U, Th, and Pu has been proposed which includes coprocessed UO_2-PuO_2, highly radioactive (fission product–"spiked") plutonium-containing fuel, and denatured $^{233}UO_2$-ThO_2.

All handling of spiked fuel or ^{233}U fuel must be done remotely due to the very high level of gamma activity; therefore, development of fuel cycle technology which can be readily adapted to remote fabrication is of great interest to this program. Even conventional plutonium recycle will probably eventually require semiremote fabrication because of the buildup of active isotopes.

A promising technology in this regard is the gel-sphere-pac process, which was in fact originally developed with remote application in mind. Major responsibility for the development of the gel-sphere-pac refabrication option has been assigned to ORNL. It is a cooperative effort between the Chemical Technology Division and the Metals and Ceramics Division. The purposes of this part of the program are to develop the sphere-pac process and equipment necessary to serve as a basis for designing a reference commercial-scale facility and to establish an irradiation-test data base adequate for licensing sphere-pac fuel for use in commercial power reactors.

The gel-sphere-pac fuel concept is notable in that it can be directly applied to all proposed fuel compositions. In addition, it is particularly advantageous for remote operation because it converts U, Th, and Pu nitrate solutions to dense oxide spheres without powder preparation and handling or precise grinding, as required in the manufacturing of pellets. This results in lower radioactive dose rates to operating and maintenance personnel, easier equipment maintenance, better material accountability, and less scrap generation. The limited test fuel irradiation data that are presently available indicate that sphere-pac fuel performs at least as well as pellet fuel, and some data indicate superior performance.

On these bases, sphere-pac process development and irradiation testing are planned to receive major emphasis during 1990–95, when programs utilizing proliferation-resistant fuel cycles dealing with high-activity fuels will be employed. Sphere-pac fuel has been proposed as a backup to pellet fuel during the period 1985–90, when "clean" coprocessed UO_2-PuO_2 will be used.

The gel-sphere-pac process consists of preparing dense ceramic microspheres from solutions of Pu, U, and/or Th salts by chemical gelation techniques that are flexible and easily controlled. Fuel rods with a smear density of up to 87% can be manufactured by loading a blend of three sizes of spheres by low-energy vibration. For light-water reactor applications, the nominal sphere diameters required for high-density packing are 1200, 300, and 30 μm; somewhat smaller spheres are required for fast breeder reactor applications due to the difference in fuel rod diameters.

Preparation of UO_2 Spheres

Development of a process for the preparation of UO_2 spheres has been very successful during the past year. More than 200 kg of high-quality spheres ranging in diameter from 30 to 1500 μm have been produced for rod loading, thermal conductivity, and pneumatic transport studies. Two batches (total of 70 kg) of low-enrichment (2.5% and 11% ^{235}U) UO_2 spheres of three sizes—fines (15 to 45 μm), medium (300 μm), and coarse (1200 μm)—have been delivered to the Exxon Nuclear Company for irradiation testing in the Halden Reactor and in the Big Rock Point Reactor. The enriched spheres were well within chemical purity specifications for pellets. Experiments are also under way to use spheres in place of powder as feed for pellet pressing.

Flowsheet description. Internal gelation is used in the preparation of UO_2 spheres. An ammonia donor is mixed with a uranyl nitrate solution at a temperature near 0°C, and gelation of drops occurs rapidly in an immiscible liquid at >40°C. The gel spheres are then washed, dried, calcined, and sintered to dense spheres. The flowsheet developed at ORNL (a modification of that developed at KEMA[1]) is presented in Fig. 2.1.[2] Acid-deficient uranyl nitrate (ADUN) is prepared by dissolving UO_3 or U_3O_8 in a solution that is deficient in HNO_3. A high concentration is desired to obtain strong gel spheres and to produce drops with densities high enough to sink in the gelation medium. The ADUN-urea and hexamethylenetetramine (HMTA) solutions, which are stable at room temperature, are metered, chilled, and forced through a mixer at 0°C and through a nozzle to form drops which gel as they fall through trichloroethylene at temperatures in the range of 50 to 65°C. After the spheres are aged, which completes the gelation, they are washed thoroughly with dilute ammonium hydroxide to remove the neutralization products and excess HMTA so that drying can be done without excessive gassing, which would cause the spheres to crack. The gel spheres can be dried easily in open trays measuring at least 10 cm deep without cracking or distortion. The dry spheres are calcined at 450°C and sintered in hydrogen at 1600°C to yield strong UO_2 spheres. The sintered spheres have densities >99% of theoretical and therefore meet the ASTM/ANSI C 776-76 specification for reactor-grade UO_2 pellets. The yield of shape- and size-separated spheres of multikilogram batches is as high as 99% for large (1140- to 1210-μm) and

1. Keuring van Electrotechnische Materialen at Arnhem in the Netherlands.

2. P. A. Haas, J. M. Begovich, A. D. Ryon, and J. S. Vavruska, *Chemical Flowsheet for Internal Gelation to Prepare Urania Spheres*, ORNL TM-6850 (July 1979).

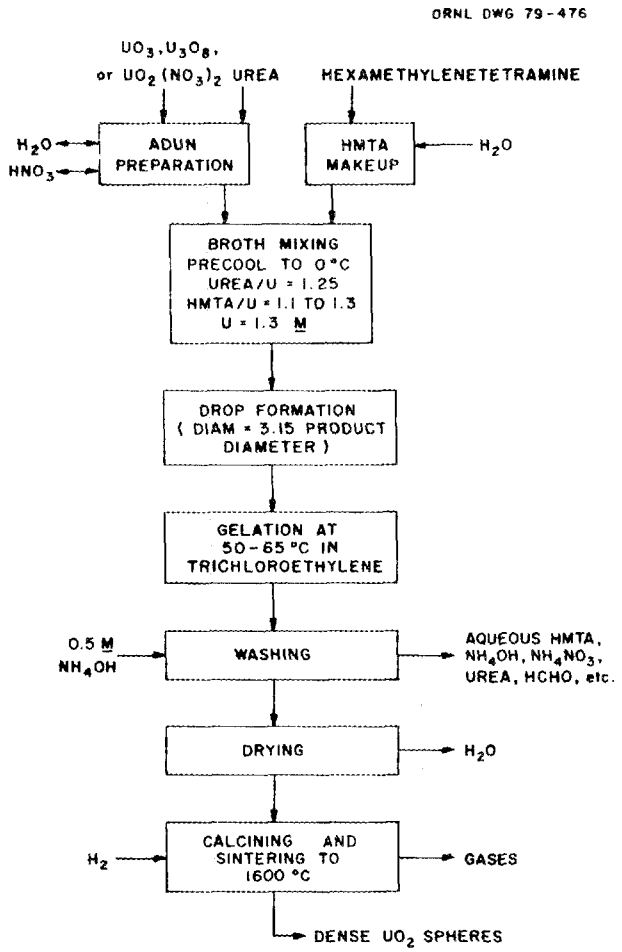

Fig. 2.1. Preparation of 200- to 1400-μm UO_2 spheres by internal gelation.

medium (280- to 320-μm) spheres and 95% for fines (15 to 45 μm). Using these size fractions, a LWR-type fuel rod (0.97 cm ID) can be loaded to a smear density of 87%.

Effects of variables. Several variables have been investigated to determine their importance and the ranges required for good sphere formation. The ratio of nitrate to uranium in the feed affects the solubility of uranium and should be adjusted to 1.5 to obtain the maximum solubility of 3.8 *M*. This is sufficient to allow mixing with a solution of HMTA to obtain the required density.

Urea is added to stabilize the mixture and prevent premature gelation before the drops are formed. The urea can be dissolved in either the ADUN or the HMTA solution. The addition of urea destroys any nitrite that may be present in the ADUN and avoids later gas formation, which would be destructive to the gel spheres. Excess nitrate in the uranium feed affects the gelation rate and requires that more HMTA be added. Partial preneutralization with ammonia can be effective but generally does not yield the best spheres. The ratio of HMTA to uranium can be varied over a narrow range (1.2 to 1.5) and used to compensate for changes in nitrate concentration and/or the temperature of the gelation liquid.

The sizes of the large (1200-μm) and medium (300-μm) spheres are determined by the precise metering of the ADUN and HMTA solutions, the known uranium content of the ADUN solution, and the frequency of the electronically vibrated nozzles. The best results have been obtained by placing a single-fluid nozzle above the gelation liquid to form medium spheres and by immersing the tip of the nozzle to form large spheres. The standard deviation of sphere diameter can be held to <3% for 1200-μm and 2% for 300-μm products. The fines fraction is prepared by the use of a turbulent-flow nozzle, which produces a range of sizes such that 75% are within 0.7 to 1.4 of the mean diameter. This yield can be increased to 95% by use of a special mixing nozzle.

Gelation temperature is an important variable. Gelation at 40 to 60°C produces good, strong gel spheres that are easily washed and dried. At temperatures >70°C, the gel properties change, particularly for fines (<100-μm drops); the fresh gel spheres are transparent, rather than opaque, and soften during washing to the point where they adhere to each other and form an unusable mass. The adherence of spheres to each other or to the surfaces of process equipment is greatly reduced by the addition of surfactants such as Span 80.

The effect of temperature depends on the type of organic liquid. Some organic liquids, such as 2-ethyl-1-hexanol, extract water readily from the drops, producing a desirable tough, firm surface which is particularly important for fines that have a large surface-to-volume ratio. Hydrocarbons have a low water-extraction capability and tend to produce soft surfaces which erode during washing. Trichloroethylene appears to be the best forming medium. For large drops (4000 μm), the density of trichloroethylene is close enough to that of the aqueous drops to cause slow fall without distortion and provide sufficient residence time for gelation. Its water-extraction capability is adequate to permit gelation of small spheres, and its boiling point is high enough (73°C for the water azeotrope) to provide acceptable gelation rates. In addition, trichloroethylene is sufficiently volatile to evaporate from the surfaces of the

gel spheres before they are washed. Other gelation media such as 2-ethyl-1-hexanol, silicone oil, and mineral oil require an additional rinse with a volatile solvent before washing.

Aging of the gel spheres in the hot gelation medium is necessary in order to avoid catastrophic cracking during subsequent processing. A period of 20 min appears sufficient for the large spheres, which are most seriously affected. Washing of the gel spheres with dilute ammonium hydroxide completes the precipitation of the uranium and leaches out the products of neutralization and excess HMTA. The ammonium nitrate must be removed to prevent cracking during drying. Greater than 95% of the nitrate can be removed with six volumes of wash solution per volume of gel spheres. For large gel spheres (4000 μm), the wash-solution flow rate through a bed of spheres is controlled to provide a total washing time of at least 2 hr. Fines are washed as a cake on a porous metal filter using a vacuum to pull the wash through the spheres.

Drying is relatively simple if the preceding steps of feed preparation, forming, and washing are done correctly. However, defects or stresses in the wet gel frequently do not become visible until the spheres have been dried. Well-formed spheres can be dried by passing air heated to temperatures of 20 to 80°C through them where drying occurs at the dew point (14 to 20°C). They can also be dried in trays up to 10 cm deep in an oven at 220 to 240°C where most of the water is evaporated at 100°C. Attempts to maintain a steam atmosphere over the spheres by using a covered tray can actually be detrimental because of the condensation that occurs. This results in soaking the spheres, which causes gross distortion. Spheres of all sizes can be routinely dried in a circulating air oven at 230°C on a 24-hr cycle.

A procedure for calcining and sintering has been developed by members of the Metals and Ceramics Division in which strong, dense UO_2 spheres are produced without additional cracking or distortion. Generally, if the spheres survive drying, they can be sintered successfully. Calcining is done in trays ~2.54 cm deep with 4% hydrogen–argon sweep gas starting at room temperature and increasing at a rate of 100°C/hr to 450°C and holding for 1 hr. This removes residual water and organic material with no significant shrinkage. Sintering is done in pure hydrogen by heating to 1600°C in 3 hr, maintaining this temperature for 4 hr, and cooling by natural heat loss (~3 hr).

Preparation of $(Th,U)O_2$ Spheres

Research and development tests on methods of preparing $(Th,U)O_2$ spheres have made use of chemical gelation processes. Both external gelation using ammonia gas and internal gelation using HMTA (as was the case for UO_2 spheres) were tested. An external gelation process reported by KFA[3] for preparation of medium-size spheres (350 μm) containing 15% uranium was demonstrated by a guest scientist from KFA. The spheres were made from an aqueous sol that was prepared by partial neutralization of a mixed solution of thorium and uranium nitrate with ammonia gas at ~100°C. The sol was formed into drops by a vibrated nozzle, and gelation was effected by ammonia gas. Gelation was completed, and the ammonium nitrate was leached by washing the gel spheres in dilute ammonium hydroxide. The soft spheres were dried in a monolayer to minimize distortion. The spheres were then sintered to high density in 4% hydrogen–argon at 1450°C. Attempts to make large spheres (>600 μm) by external gelation were not successful because of gross distortion and cracking during forming and drying. Other attempts to make spheres containing 20 to 25% uranium were also unsuccessful because sols containing greater than 15% uranium were unstable, and a uranium-rich precipitate was formed.

Research has been directed toward the use of internal gelation because of these difficulties. Scouting tests to explore the important variables have shown that medium-size spheres (500 μm) with high densities can be prepared. However, considerable cracking and distortion are common. Gelation is very sensitive to the ratio of HMTA to nitrate that has not been preneutralized with ammonium hydroxide.

Several methods of preparing feed have been tested. It appears that the mole ratio of unneutralized nitrate to Th + U must be ≤ 3. This can be accomplished by dissolving UO_3 in a thorium nitrate solution, by partial neutralization of the mixed thorium-uranium nitrate solution with ammonia or ammonium hydroxide, or by removing nitrate from the mixed thorium-uranium nitrate solution via extraction with an amine. The best results have been obtained by the partial neutralization technique;

3. Kernforschungsanlage, Jülich, Federal Republic of Germany.

however, we have not yet attempted to make large spheres (>800 μm) or fines (30 μm). Medium-size spheres (500 μm) containing 15 to 35% uranium have been prepared from feed containing from 0.5 to 1 *M* total uranium plus thorium, with nitrate/Th + U ratios of 2.5 to 3 and with several organic-gel support media added to the broth.

Preparation of $(U,Pu)O_2$ Spheres

The preparation of $(U,Pu)O_2$ microspheres (Pu/U+Pu = 0.25) by an internal gelation process has been successfully demonstrated on a laboratory scale.

The initial feed for microsphere preparation is considered to be a coprocessed uranium-plutonium product stream from a fuel reprocessing plant. The feed is therefore a HNO_3 solution of $Pu(NO_3)_4$ and $UO_2(NO_3)_2$; under some potential reprocessing modes, it may be expected to contain significant concentrations of radioactive isotopes.

The feed preparation step is designed to produce highly concentrated metal solutions from these dilute feeds and remove essentially all free HNO_3. Stable feed solutions that can be used to form microspheres were prepared from a variety of components. These include pure uranium and pure plutonium feeds and mixed feeds that contained 12%, 25%, and 50% plutonium. Stable feeds containing Ce, Nd, Zr, Ru, or Co at concentrations as high as 5 wt %, as well as feeds containing various mixtures of these elements, were also prepared.

With two exceptions, all feed solutions were readily converted into uniformly sized microspheres. Excessive cracking occurred during sphere washing and drying steps for pure plutonia microspheres and microspheres that contained 5 wt % cobalt. (Cobalt-60 has been proposed as a "spiking" agent to reduce the likelihood of theft of plutonium.)

Sintered densities ≥95% of the theoretical density were obtained for most of the products that were prepared. Product yields varied with system variables and microsphere composition, but yields of 95 to 100% were common. Studies to date therefore demonstrate that the preparation of $(U,Pu)O_2$ microspheres by internal gelation procedures is a feasible option for continued process development, and that internal gelation may be uniquely suitable for the preparation of large microspheres (diam ≥1 mm) from dilute acid solutions of uranium and plutonium.

Experimental Facilities

An interim engineering facility[4] for the preparation of dry UO_2 spheres has been installed. Included in this facility is equipment for feed preparation, continuous sphere formation (coarse and fine), recycle of organic gelation medium, batch washing, and drying. The capacity is 1 kg UO_2/hr. The facility has been used to dissolve enriched and depleted U_3O_8 and to prepare three sizes of spheres that are required for sphere-pac and irradiation tests.

An integrated engineering facility capable of handling uranium and thorium (but not plutonium) will be built in which the major steps for feed preparation, sphere formation, continuous washing and drying, calcining, and sintering can be accomplished. During the past year, major modifications to the site of this facility have been completed. An office addition is ~50% complete, and the installation of process facilities has been started.

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4. D. R. Williams et al., *Design and Operating Procedures for an Interim Engineering Facility for Preparing Kilogram Quantities of UO_2 Spheres by Internal Gelation*, ORNL/TM-6650 (in preparation).

3. Coal Conversion and Utilization

During this report period, research and development (R&D) activities supporting coal conversion and utilization continued in three broad areas within the Chemical Technology Division—coal conversion process development, coal conversion engineering studies and program analysis, and environmental control technology for coal conversion processes as part of the Laboratory's growing responsibilities for DOE's Office of Fossil Energy. Related R&D activities of a more basic nature are reported separately in Sect. 5.

3.1 COAL CONVERSION PROCESS DEVELOPMENT

During this report period, progress was accomplished in the following activities related to coal conversion process development: (1) measurement of the physical properties of coal-derived liquids, (2) studies of heat transfer and fluid-dynamic phenomena in slurry preheaters, (3) studies of chemical reactions which may serve as potential alternatives to conventional thermolysis and hydrogenolysis reactions for producing liquids from coal, and (4) engineering studies of the pyrolysis of large coal particles in support of underground coal gasification (UCG) process development.

Measurement of Physical Properties of Coal Liquids

Knowledge of the physical properties (e.g., viscosity, density, thermal conductivity, and heat capacity) of coal liquids under process conditions is essential for the proper design of heat transfer equipment, preheaters, reactors, separation units, and process piping systems in liquefaction processes. Because of the high-hydrogen-pressure, high-temperature conditions present in slurry hydroliquefaction schemes, physical properties may be strongly influenced by the effect of dissolved hydrogen and/or by the effects of ongoing liquefaction-hydrogenation reactions. Therefore, flowing stream measurements are essential, and the test fluid must be quenched, sampled, and chemically characterized to provide a basis for correlating physical properties with the chemical composition and physical conditions.

Instruments for measuring the viscosity, density, heat capacity, and thermal conductivity of flowing streams of coal liquids at process conditions are incorporated into the Coal Liquids Flow System (CLFS) and are shown in Fig. 3.1. The CLFS is a bench-scale, continuous-flow, high-hydrogen-pressure, high-temperature system that is capable of processing both coal-solvent slurries and solids-free

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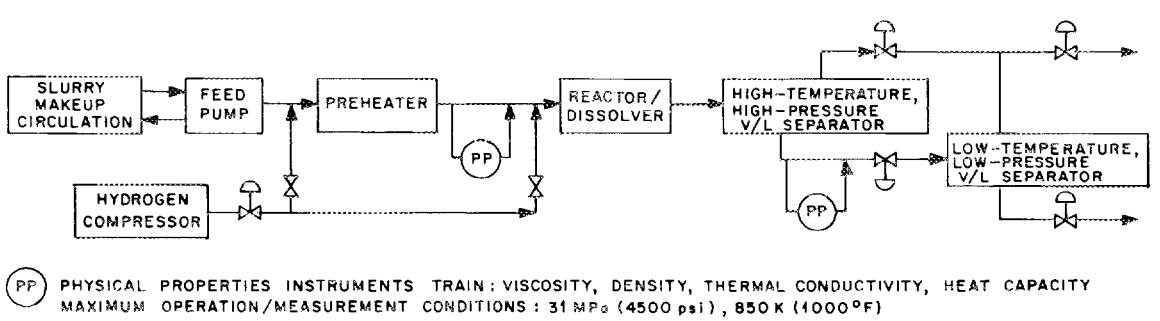

Fig. 3.1. Schematic flow diagram of the Coal Liquids Flow System.

coal-derived liquids at pressures and temperatures of up to 31 MPa and 810 K, respectively, and measuring their physical properties under these processing conditions. The unit can simulate coal-solvent slurry preheating and liquefaction conditions prior to physical property measurements. The maximum liquid throughput of this system is 4 liters/hr. The analytical techniques employed for measuring the physical properties are as follows: viscosity—falling-ring and pipeline viscometers; density—gamma-ray absorption; thermal conductivity—transient heated-wire technique; and heat capacity—flow calorimetry.

During this reporting period, construction of the CLFS was completed and operations were initiated. The operations had two objectives: (1) to obtain rheological characterizations on coal-solvent slurry [35 wt %, Illinois No. 6 coal (−170 mesh)/Wilsonville recycle solvent] at elevated temperatures and pressures, and (2) to successfully operate the system with high-temperature and high-pressure flowing hydrogen and slurry in a combined-phase preheating mode. Significant results are summarized below. Additional details of these results have been reported elsewhere.[1-4]

Rheological characterizations, using the pipeline viscometer, were made on a 35 wt % slurry at temperatures of up to 550 K and overpressures of up to 13.9 MPa. The rheograms (plot of shear stress vs shear rate) obtained show that the slurry is essentially Newtonian at low temperatures (<400 K) and becomes increasingly pseudoplastic as the temperature increases to 550 K. Some data were collected at 700 K; although they were insufficient for complete rheological characterization, they indicate highly pseudoplastic behavior over the small span of shear rates investigated. Rheograms are included in the following section on coal slurry preheaters.

High-temperature operability of flowing slurry and hydrogen in the combined-phase preheating mode was successfully demonstrated. The most severe conditions attained were preheater discharge temperatures of 700 to 710 K, a system pressure of 13.9 MPa, a hydrogen rate of 0.91 scmh [m^3(STP)/hr], and a slurry rate of 3.6 kg/hr. During these combined-phase preheating operations with hydrogen, the differential pressure across the pipeline viscometer was recorded immediately downstream from the preheater. Although these data cannot be interpreted for rheological characterization of the liquid phase, they are useful for qualitative observation of the overall changes in slurry viscosity during the preheating operation. As the discharge temperature of the preheater was increased, the differential pressure measured across the viscometer remained essentially constant from 400 to 565°C (Fig. 3.2). Above this temperature, the differential pressure increased sevenfold as the preheater discharge temperature went from 565 to 633 K. These observations were made at constant slurry and hydrogen mass flow rates. The increase in differential pressure results from the increased viscosity of the slurry as it undergoes the postulated formation of a gel stage during the preheating operation. Differential pressure appears to reach a maximum at 633 K. Differential pressure measurements during a subsequent run at 700 to 710 K imply a significant viscosity decrease as the temperature increases beyond the gel region; at 700 to 710 K, the differential pressure was less than half that observed at 630 K, even though the slurry mass flow rate was 3.7 times greater than that for the higher temperature measurement. Flow in the pipeline viscometer during these measurements was probably in the slug-flow regime, based on mockup studies.

Coal Slurry Preheater Studies

In coal liquefaction processes such as the Solvent Refined Coal (SRC) process, fired preheaters are used to heat the coal slurry–hydrogen gas mixture to a temperature of ~700 K at pressures of up to 14 MPa. During preheating, coal dissolution and chemical reactions occur which change the properties and flow characteristics of the slurry. These changes are not well understood and result in difficulties in the design and operation of preheaters.

The bench-scale CLFS that was described earlier was designed, constructed, and made operational during this report period. Included in the CLFS is a 0.28-cm-ID electrically heated preheater test section measuring 11.9 m long. The extreme operating conditions of the preheater and CLFS are 31.7 MPa and 810 K. The preheater is designed to study the rheological behavior and heat transfer characteristics

1. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for Period Ending June 1978*, ORNL-5444 (November 1978).
2. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for Period Ending September 1978*, ORNL-5487 (January 1979).
3. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for Period Ending December 1978*, ORNL-5520 (April 1979).
4. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for Period Ending March 1979*, ORNL-5550 (in preparation).

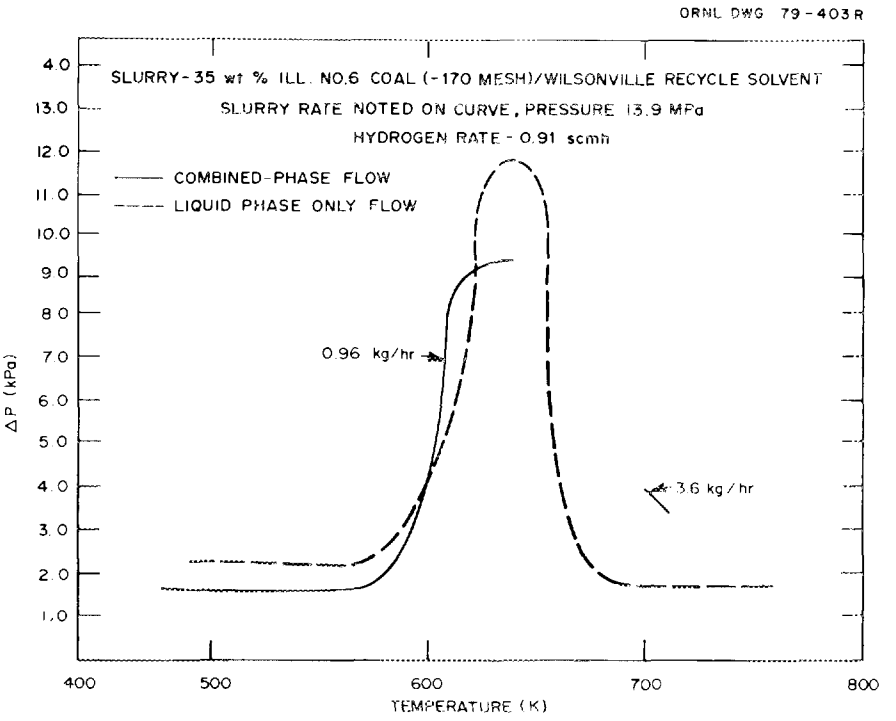

Fig. 3.2. Pipeline viscometer differential pressure versus preheater discharge temperature.

of the coal slurries and can be operated in combined-phase hydrogen-slurry flow or in slurry-phase flow with no gas overpressure. The preheater is instrumented with multiple thermocouples to measure inlet and outlet temperatures and wall temperatures along the length of the unit. A pipeline viscometer is located at the outlet of the preheater; the entire preheater stream passes through the viscometer, thus enabling rheological measurements to be taken in-line and at process flow conditions.

Checkout operations with the CLFS began in December 1978. Since then, rheological characterizations of slurry behavior, in the absence of hydrogen-gas overpressure, have been made for several operating temperatures. Three additional tests were conducted to check out the system operability with combined-phase hydrogen-slurry flow at 700 K and 14 MPa. A brief description of both the data-reduction procedure used and the results obtained from these tests is given below. A more complete discussion of these results has been reported elsewhere.[1-4]

Rheological characterizations of the slurry are made with the pipeline viscometer. The pressure drop across the viscometer and the slurry flow rate through it are used to construct flow curves, plots of shear stress (τ_w) vs $8V/D$, where V is the slurry velocity and D is the internal diameter of the viscometer. The flow curves are then used, in a procedure described by Govier and Aziz,[5] to make rheograms (plots of τ_w versus shear rate $\dot{S}_w$). Figure 3.3 shows the rheogram plots of a 35 wt % Illinois No. 6 coal/Wilsonville recycle solvent slurry at three different temperatures. These initial results indicate that the slurry behaves as a Newtonian fluid up to 400 K. At higher temperatures, however, the slurry begins to depart from Newtonian behavior and becomes increasingly pseudoplastic. Limited data were obtained at 700 K, but the same trend toward strong pseudoplastic behavior was observed. From Fig. 3.3, the apparent viscosity ($\tau_w/\dot{S}_w$) is seen to decrease as the temperature is increased for shear rates above 200 sec^{-1}. However, the apparent viscosity is expected to increase more sharply near 600 K as the slurry gels and reacts. Tests are scheduled to verify this and to further characterize slurry behavior at temperatures up to 700 K.

5. G. W. Govier and K. Aziz, *The Flow of Complex Mixtures in Pipes*, Van Nostrand, New York, 1972.

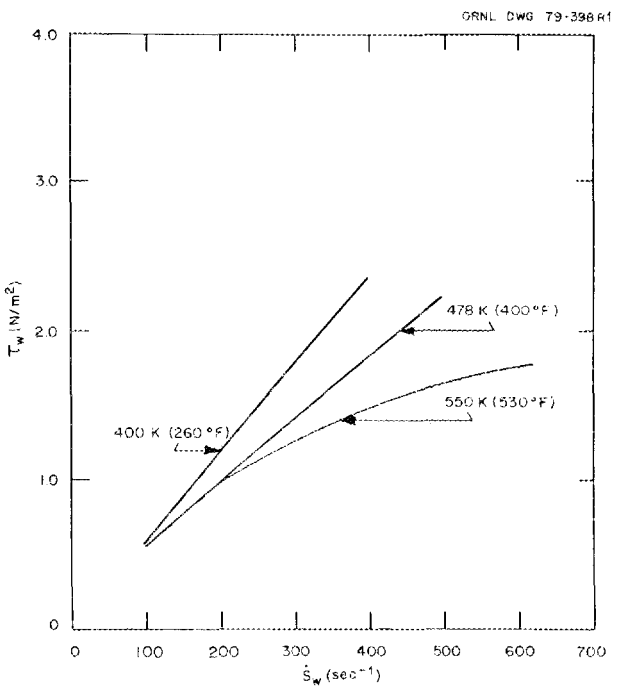

Fig. 3.3. Rheograms of 35 wt % coal slurry at temperatures of 400, 478, and 550 K.

System operability was demonstrated in tests with combined-phase hydrogen-slurry flow, and a few design improvements were made as a result. Additional tests are planned in combined-phase flow in order to obtain pressure drop data across the pipeline viscometer and full rheological data in a second pipeline viscometer located downstream from the high-temperature, high-pressure vapor-liquid separator in the CLFS.

Heat transfer data were taken during a few of the experiments. An analysis of both the data and possible correlations with operating parameters and with the rheological data is currently in progress and will be reported as developed.

New Liquefaction Techniques

This is the first report on a new project which was initiated during April 1978. The scope of the program encompasses research studies aimed at a better understanding of the chemical processes involved in coal liquefaction, improved methods of classical coal conversion, and entirely new methods for coal conversion. Two novel approaches to coal liquefaction have been studied. One technique utilized a family of new ionic hydrogenation reactions developed at ORNL; the other was an exploration of Heredy-Neuworth depolymerizations using phenols.

It was demonstrated that partial liquefaction of coal can be achieved by using $BF_3 \cdot H_2O$ in combination with a hydride donor by an ionic hydrogenation mechanism. Initial experiments using isopropanol, ethanol, and methanol as hydride donors were not promising. Although as much as 44% of the carbonaceous material in an Illinois No. 6 coal sample was converted at 300 K, incorporation of the expensive acid catalyst in the products rendered this approach ineffective, and efforts were concentrated on the more promising coal-phenol reactions.

Heredy-Neuworth depolymerizations of coal using phenol plus Lewis acid catalysts at a low temperature (460 K) required long reaction times (20 hr) and resulted in high-molecular-weight products. By increasing the reaction temperature to 700 K (slightly above the critical temperature of phenol), reaction times were reduced to a few minutes and considerably more low-molecular-weight material was produced. A most significant discovery was made: acid catalysts are *not* necessary for the depolymerization reactions of coals using phenols at these elevated temperatures. Conversion of 80% of the carbonaceous material in Wyodak coal was achieved at 730 K without a catalyst or molecular hydrogen. Initially, a mechanism was proposed that involved thermally induced rupture of covalent bonds in the coal to produce radicals which attack phenol in an aromatic substitution reaction. This mechanism is currently being questioned because of the lack of evidence of phenol incorporation into the products and because of the work done by M. L. Poutsma of ORNL's Chemistry Division with model compounds, which indicates that aromatic substitution does not occur under these conditions. We are now proposing a novel mechanism of hydrogen redistribution within the coal by phenol. The ratio of atomic hydrogen to carbon (H/C) shown in Fig. 3.4 increased steadily as conversion increased. At high conversions, the H/C ratio of the product (1.22) is considerably higher than that of the starting coal (0.86), while the H/C ratio of the unconverted residue is reduced to 0.6.

It is clear from these data that hydrogen is being moved from one place to another within the coal, and that this shift renders the hydrogen acceptors soluble. Most coals contain a sufficient amount of hydrogen to be in liquid form if the hydrogen were properly distributed. The data obtained here show that it is possible to redistribute the hydrogen in coal in order to produce large amounts of extractable material.

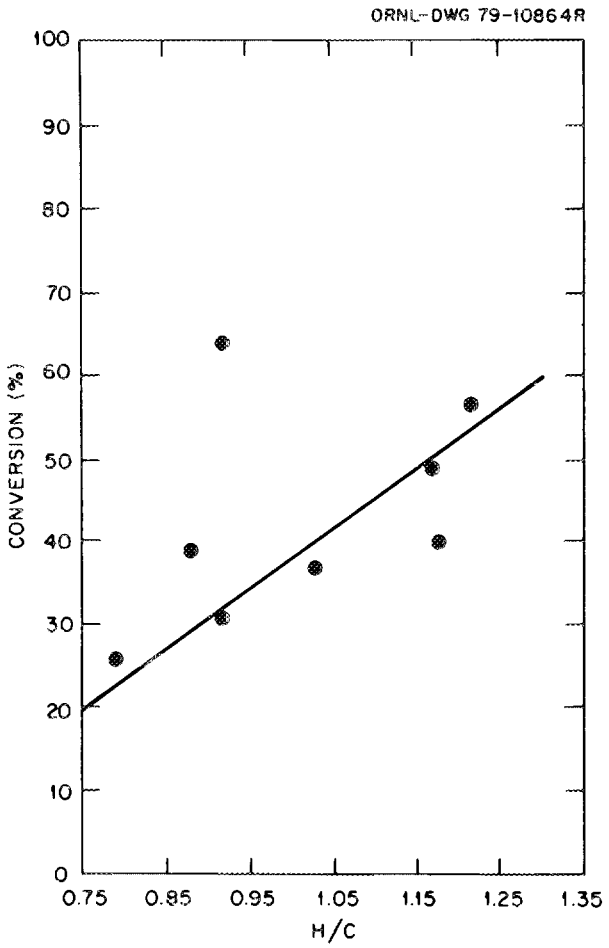

Fig. 3.4. Conversion to pyridine-extractable products of Wyodak coal with phenol versus the atomic hydrogen-to-carbon ratio of the extract.

Exploitation of this reaction may be an attractive method of obtaining heavy liquid fuels from coals.

The reaction of Bruceton (Pittsburgh) bituminous coal with phenol, showing the effect of rank when compared with earlier Wyodak subbituminous coal research, is currently being investigated.

Future experiments will examine alternative solvents. As our understanding of these phenomena improves, it appears that phenol may not be unique in its ability to effect this depolymerization. Scoping tests of dihydroxybenzenes such as resorcinol are planned, and the nitrogen-containing solvents such as pyridine may also be tested.

Engineering Support for In Situ Gasification Process Development

Chemical and physical properties have been determined for lignite, subbituminous coal, bituminous coal, and overburden samples from UCG field test sites. These results were obtained by controlled pyrolysis of instrumented blocks of lignite, coal, and overburden. Thermal data and product yields have been correlated, thus providing a basis for extrapolation from conventional pyrolysis data obtained on powdered samples to the pyrolysis steps in UCG.

Significant results obtained during the past year include:

1. correlation of block pyrolysis data for low-rank coals, interpretation of mechanisms, and comparison between low-rank and bituminous coals;
2. heating tests of overburden cores from the field gasification site at Hoe Creek; and
3. determination of physical properties, particularly thermal diffusivity and thermal conductivity, of low-rank coals.

The overburden and physical property tests were initiated this year.

Coal block pyrolysis. Conventional pyrolysis tests on dry powders purposely minimize drying and side reactions so that thermal decomposition ("pure" pyrolysis) can be studied; block pyrolysis tests couple these effects with pyrolysis. By characterizing these couplings, models of UCG can be improved.

Correlations of block pyrolysis data for Wilcox (Texas) lignite[6] are consistent with previous findings for Wyodak subbituminous coal[7] and Pittsburgh bituminous coal.[8] As for Wyodak coal, drying of the lignite block forms a shrinking core of wet coal surrounded by a two-phase (steam-water) drying plateau. Steep temperature gradients then occur in the outer layer of dry coal when the block is heated at a rate of 3 K/min. Since steam gasification of char is thermodynamically favored above 950 K, H_2 and CO are produced in significant quantities if the internally generated steam is forced to escape through a char surface region $\geqslant$950 K (see Fig. 3.5)—a self-gasification mechanism. Similarly, pyrolysis tars formed at temperatures in the range of 625 to 825 K

6. P. R. Westmoreland and L. S. Dickerson, "Pyrolysis of Blocks of Texas Lignite," presented at the 86th National Meeting of American Institute of Chemical Engineers, Houston, Tex., Apr. 1–5, 1979.

7. P. R. Westmoreland and R. C. Forrester III, "Pyrolysis of Large Coal Blocks," *Am. Chem. Soc. Div. of Fuel Chem. Prepr.* 22(1), 173rd National Meeting of the American Chemical Society, New Orleans, La., Mar. 21–25, 1977.

8. P. R. Westmoreland, "Pyrolysis of Bituminous Coal Blocks," in *Proceedings of the 4th Underground Coal Conversion Symposium*, Steamboat Springs, Colo., July 17–20, 1978, Sandia Laboratories Report SAND 78-0941 (June 1978), pp. 423–33.

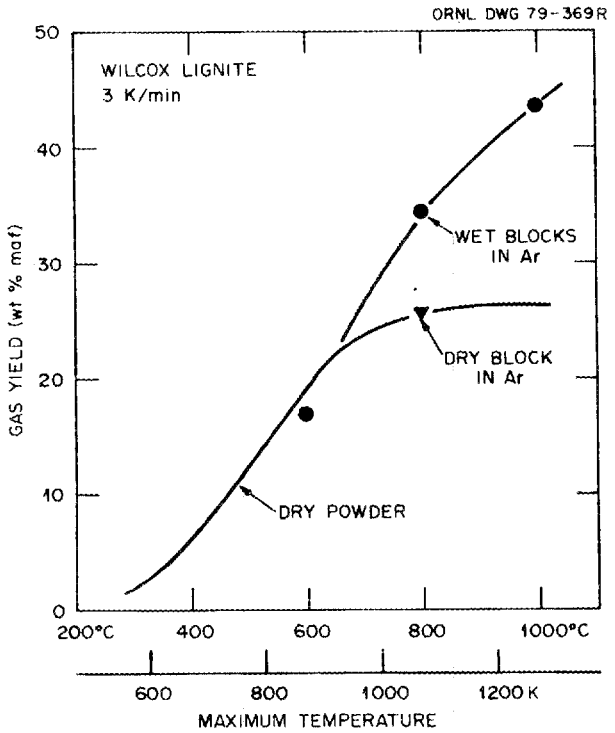

Fig. 3.5. Results from pyrolysis of Wilcox (Texas) lignite [gas yield (wt % moisutre- and ash-free coal) vs maximum temperature].

can be pyrolyzed to carbon and gas as they escape through hotter char regions.

Experiments conducted in a H_2 purge indicate that the outward flux of escaping steam inhibits the inward penetration of H_2. Hydrogasification occurred to a surprising extent in the range of 775 to 875 K when no steam flux was present, but little or no hydrogasification occurred at these same temperatures when the steam flux was present. However, the H_2 did have some effect, even on experiments producing a high steam flux, since oil yields and char pyrophoricity (spontaneous oxidation) data indicated that more secondary tar cracking took place in H_2 than in an inert purge gas.

Overburden tests. Characteristics of overburden (the strata overlying a coal seam) from the Hoe Creek UCG site have been measured. Six cored samples were tested for physical properties (density, shrinkage, thermal diffusivity), composition (moisture, carbon, hydrogen), friability when dried or heated, and thermal decomposition. Since the collapse of 15 m of overburden into a recent UCG experiment at Hoe Creek, such properties are clearly important for evaluation and control of the process.

Significant amounts of H_2, CO, and CO_2 were produced as the cores were heated to 1273 K, along with amounts of CH_4 and C_2- and C_3-alkanes. Overall gas yields (dry, wt % basis) as high as one-third of those from Wyodak coal were obtained. Inspection of the heat-treated cores indicated that two cores hardened into a solid brick-like material, two others had flaked apart at closely spaced bedding planes, and a few large cracks had opened up in another two cores.

Physical properties of coal and char. Accurate values of the physical properties are needed for models of UCG processes. New data or correlations have been obtained for thermal diffusivity, thermal conductivity, density, shrinkage upon drying, porosity, enthalpy, and specific heat.

Thermal diffusivity and conductivity measurements on lignite are significant because so few data exist for low-rank coals. Conduction models have been applied to determine thermal diffusivity by measuring temperature variations as wet or predried lignite is heated. Since good density and specific heat data are available, thermal conductivity can also be calculated. These measurements are in good agreement with the published data on low-rank coals, as shown in Table 3.1.

Table 3.1. Thermal diffusivity and thermal conductivity of lignite

Source of data	Thermal diffusivity, α (mm^2/sec)	Thermal conductivity, k (W/m-K)	Conditions
This study	0.09	0.14	Dry, 410–570 K, 30% porosity
Fritz[a]		0.151	Dry, 303 K, 32% porosity
This study	0.130	0.31	Wet (37% moisture)
Stanmore[b]	0.1315	0.32	Wet (41% moisture)

[a]W. Fritz, *Forschung auf dem Gebiete des Ingenieurwesens* 14(1), 1–10 (1943).

[b]B. R. Stanmore and A. R. Boyd, *The Second Conference on Heat and Mass Transfer*, pp. 195–20, University of Sydney, Sydney, Australia, 1977.

3.2 COAL CONVERSION ENGINEERING STUDIES AND PROGRAM ANALYSIS

Engineering studies related to coal conversion processes are being conducted for DOE's Office of Fossil Energy. These studies include technical and economic evaluations of commercial-scale conversion plants and processes, surveys of industrial equipment, and surveys of hot-gas cleanup and heat recovery processes. In addition, technical support is being provided in the development of process modeling techniques. Process and program analysis studies, which involve most of the coal conversion processes, are also being conducted to provide consistent technical and economic evaluations of competing processes and systems for coal conversion and utilization. The subprograms included in the studies are low-Btu gasification, high-Btu gasification, direct combustion, advanced power–combined cycle, liquefaction technology assessment, and in situ coal gasification.

The Chemical Technology Division coordinates these efforts and is responsible for the in situ gasification and the association subsystem studies. The direct combustion, advanced power, and low-Btu gas studies are being conducted by other divisions at ORNL. Certain portions of the high-Btu gas and liquefaction technology assessment studies are being performed under subcontract by industrial firms.

Process Modeling

Process modeling is a joing effort involving Purdue University, Lehigh University, and ORNL. The overall objective of the project is to develop computer programs for the design and cost estimation of coal conversion processes and facilities. Purdue is concentrating on the development of steady-state mass-balance and energy process design models; Lehigh is concentrating on unsteady-state models. ORNL will serve as the repository for the programs, and the ORNL computer facilities will be used for implementation. Additionally, ORNL will help to develop, augment, and update the programs, especially in the areas of equipment design and cost estimation. Some of the basic modeling programs are briefly discussed here.

Coordination with Purdue. Work continued on the implementation of the Purdue physical properties package (PPP) from Purdue's CDC system onto the ORNL IBM-360 system. The package has now been successfully executed on all seven test examples furnished by Purdue. Additional examples are being devised to ensure that all portions of the package are tested on the IBM-360 system. These examples are being run as part of a simulated process flowsheet so that testing conditions will be typical of those expected in actual practice. This has proved to be a valuable exercise in that several practical difficulties have been uncovered. Purdue is working with us on these difficulties and will soon supply new documentation and a new version of the PPP program to be used for future testing. To provide comparisons, examples will also be run using the Phillips Petroleum PDA program, which has a similar physical properties package.

Work continued on the development of routines for estimating capital costs for use in the Purdue program. Computational schemes using the Guthrie factored approach were written and transmitted to Purdue.

The Purdue mass-balance and energy programs have been successfully implemented in double precision on the IBM-360 system, and the results obtained on the example problems agree well with those obtained by Purdue.

Coordination with Lehigh. A software package, including the source decks and documentation for the Differential Systems Simulator, Version 2 (DSS/2), was received from Lehigh University. Modifications necessary for the installation of the programs on the IBM-360 computer at ORNL were completed, and test problems were successfully run. The numerical differentiation routines in the DSS/2 program were converted to double precision for use on the ORNL IBM-360; increased accuracy of results was thus obtained. A report describing the installation of DSS/2 on the ORNL computer system has been issued.[9]

The Lehigh subprogram INTEG, which is part of the DSS/2 program, was divided into 15 subroutines for the sake of convenience. These subroutines have all been compiled and tested successfully on the ORNL IBM-360 system and have been forwarded to Lehigh for use in the DSS/2 package. The ORNL-mounted DSS/2 program will soon be tested using the methanator example developed by Lehigh. The methanator example has been run successfully in single precision, and acceptable results have been obtained; conversion of the methanator to double precision is in progress. The DSS/2 has already been

9. D. M. Lister, *Installation of DSS-2 on the IBM 360-195 Computer at K-25*, K/CSD/TM-14 (June 1977).

converted to double precision and run successfully using the new INTEG routine.

We have developed a new program called "D.P. Converter-1" (DPC-1) to process a source code and convert all hard-coded floating-point constants to double precision. It has already been used to convert the real constants in the DSS/2 code. The new version of the DSS/2 is currently being tested, and documentation of the DPC-1 code has been started.

A new subroutine, COMPUR, was developed to compute UROUND (the round-off constant) so that the required value is generated regardless of which computer and level of precision are being used. In our tests, the subroutine gave the expected values on the IBM-360 in single, double, and extended precision.

ORNL programs. The discounted cash-flow program, PRP, developed at ORNL was modified to include several new options. The first of these permits the user to input escalation factors for capital investments, operating costs, feedsock prices, and product values. The second option permits debt capital to be repaid in constant annual amounts rather than in constant proportion to equity capital. The third option permits product values to be maintained in fixed ratios to each other in a multiproduct plant. A report on these changes is in preparation.

Survey of Industrial Coal Conversion Equipment Capabilities

The objective of this project is to survey the industrial capabilities for supplying critical equipment items for various coal conversion processes. The type, size, range of operating conditions, working fluids, and materials of construction have been tabulated for each equipment item; equipment manufacturers were surveyed to determine the current and future availability, costs, reliability, and potential problems that may be encountered. This project will also determine research and development needs (including lead-time requirements) for producing equipment of advanced design for the various unit operations of critical importance to the fossil energy programs.

Early stages of this survey included evaluation of rotating components, valves, hot-gas cleanup equipment, and heat recovery systems. Reports covering these four subject areas have been issued,[10–13] and results have been briefly described in the last annual report in this series.[14] During the past report period, the survey was expanded to include letdown valves, mechanical connectors, and expansion joints.

The survey indicated that industry has the capacity to supply letdown valves in the sizes required by the coal conversion industry; however, standard valves are not available for slurry letdown service. Valves currently require modifications and/or special trims, such as tungsten carbide, to extend valve life. Because of the complex nature of a slurry, however, the reliability of a letdown valve, even for commercial plants, may not be known until after the valve has been put into operation. Solutions to letdown valve problems depend not only on the development of better materials, but also on the design and configuration of letdown valves themselves.

Manufacturers of connectors and standard pipe fittings can supply equipment in sizes and for temperature and pressure conditions required by the coal conversion industry. The Gray Tool Company was the only one major manufacturer found capable of supplying proven higher-technology connectors, excluding flanged connections. Pilot-plant experience has demonstrated the availability of acceptable connectors.

Expansion-joint manufacturers currently have the technological expertise and the physical facilities needed to furnish expansion joints for coal conversion demonstration plants. Since most technological advances in the expansion-joint industry result from applied engineering to meet specific applications, any advances in coal conversion technology which result in more severe expansion-joint requirements must be acted on immediately in order to ensure equipment capability.

During FY 1977, information concerning rotating components, valves, hot-gas cleanup equipment, and heat recovery equipment was received from manufacturers, architect-engineers, and large industrial users of such equipment. In FY 1978, visits were made to several pilot plants to discuss equipment operating experience. This experience generally confirmed

10. W. R. Williams, J. R. Horton, W. F. Boudreau, and M. Siman-Tov, *Survey of Industrial Coal Conversion Equipment Capabilities: Rotating Components*, ORNL/TM-6074 (April 1978).

11. W. A. Bush and E. C. Slade, *Survey of Industrial Coal Equipment Capabilities: Valves*, ORNL/TM-6071 (June 1978).

12. J. P. Meyer and M. S. Edwards, *Survey of Industrial Coal Conversion Equipment Capabilities: High-Temperature, High-Pressure Gas Purification*, ORNL/TM-6072 (June 1978).

13. W. R. Gambill and W. R. Reed, *Survey of Industrial Coal Conversion Equipment Capabilities: Heat Recovery and Utilization*, ORNL/TM-6073 (July 1978).

14. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1978*, ORNL-5853 (August 1978).

results of the earlier survey work in which centrifugal slurry pumps were shown to be a major problem at all facilities visited; no successful application of multistage centrifugal pumps in slurry service was found. However, reciprocating slurry-charge pumps have been operated with some degree of success. Poor cyclone performance pointed out the need to anticipate solids at any point downstream from a solids-handling operation. Heat recovery, compressor, and oxygen-handling experience is not generally transferable to demonstration facilities. The chances of successful multistage centrifugal slurry-pump development are highly speculative. One manufacturer is now supplying single-stage centrifugal slurry pumps, which essentially meet API-610 standards and incorporate internal liners and low impeller tip speeds, to several pilot plants. They will also supply two-stage pumps of similar design, if ordered; therefore, any government-sponsored multistage pump development program should be deferred until the performance of these pumps is evaluated. Also, the economic justification for such a program should be reviewed.

Because of the recent decisions regarding various pilot-plant programs, there is now little incentive to pursue expander development. At the request of survey personnel, the MIT School of Chemical Engineering Practice at ORNL conducted a study of various expander options, which is summarized in Table 3.2.

Planned activities for the coming year include the publication of reports covering the surveys mentioned above and an executive summary report covering all the surveys conducted under this project. Price correlations are to be derived from data received on pumps, compressors, and heat exchangers; and a comparison of annual pumping costs for a slurry-charge system based on centrifugal, reciprocating, and pipe feeder technology is planned. Finally, a workshop to convey information gathered during this study to DOE project managers, coal conversion plant designers and operators, and equipment manufacturers and to provide a forum for discussions between these groups is also to be planned and held in Oak Ridge.

Technical and Economic Assessments of Processes

Technical and economic assessments are routinely performed for those systems or processes that appear to offer some unique potential but for which development has not progressed much beyond the conceptual stage. Data necessary for detailed engineering evaluations are generally lacking in these assessments, but experience coupled with a broad information base which generally defines coal conversion technology is usually sufficient for most timely decisions that must be made by the overall program management. Examples of current assessments within this category are summarized below.

Coal Liquefaction Advanced Research Digest. Reviews of current or potential processes relating to coal conversion technologies are provided by the *Coal Liquefaction Advanced Research Digest.* Format and procedures for issuing this periodical have been established, and the first two volumes were published during the last two reporting periods.[15,16]

15. F. M. O'Hara, Jr., *Synthetic Fuels Process Research Digest November 1977*, ORNL FE-1 (November 1977).

16. F. M. O'Hara, Jr., *Coal Liquefaction Advanced Research Digest*, ORNL FE-2 (February 1979).

Table 3.2. Expander options in substitute natural gas plants

Operating conditions		Export electricity (MW)	Installed cost of power recovery unit ($\$ \times 10^6$)	Substitute natural gas cost ($/GJ) [$/MM Btu]
Cleanup (K) [°F]	Expander inlet (K) [°F]			
1175 [1650]	1175 [1650]	306	300	4.55 [4.80]
865 [1100]	865 [1100]	276	293	4.57 [4.82]
425 [300]	1175 [1650]	300	361	4.68 [4.94]

Articles in the second issue included: (1) "Liquid Fuels from Coal by the SRC-II Process," (2) "Consol Synthetic Fuel Process," and (3) "Fischer-Tropsch Synthesis." Topics for the third issue have been selected, and literature searches and evaluation of information obtained from other sources are under way. The articles will address the following subjects: (1) the kinetics of coal hydrogenation, (2) the mechanism of coal liquefaction, and (3) characterization of coal-derived liquids.

Hot-gas purification processes. An investigation into the state of the art of hot-gas cleanup processes wa carried out, and the final report[17] for this project has been issued. The most interesting application was the removal of contaminants from coal-derived fuel gas prior to firing in combined-cycle turbines. The study concluded that reliable, commercially available, and economically competitive hot-gas cleanup systems for treating raw gasifier product gases to be used in turbines will not be available for some time.

State-of-the-art review of heat recovery processes. A review of industrial heat recovery processes and related equipment of potential use in coal conversion complexes was conducted, and a final report describing the results of this evaluation has been issued.[18] Major categories of heat exchange equipment and processes investigated included special shell-and-tube; periodic-flow and rotary regenerators; heat pipe arrays; direct phase contactors; heat and organic Rankine cycles for power generation from waste heat; and heat-pump applications to distillation. It was concluded that there is a clear need for more physical property data, improved heat transfer correlations for multiphase streams, and more information about rates of fouling, corrosion, and erosion.

Study of effluent control technology for hydrocarbon and carbon monoxide emissions from coal conversion plants. A technical and economic comparison of processes available for the control of gaseous hydrocarbons and CO emissions from coal conversion plants was carried out.[19] The evaluation did not consider control of sulfur emissions. The Lurgi gasification process was considered as the reference emission source, and comparisons of control technologies considered incineration as the reference control system. The most recently proposed EPA emission standards for CO and nonmethane hydrocarbons were used as upper limits for the residual contaminants in the treated effluent, and limited assessments of the technical and economic feasibility of ten processes were made. Of the processes studied, the two most promising were found to be incineration in a coal-fired boiler and catalytic incineration. Neither of these methods has been employed commercially under the projected operating conditions, although both are employed in other industries to carry out the basic reactions involved.

Process and Program Analysis

The objective of this activity is to provide, on a consistent basis, technical and economic evaluations of competing processes and systems for coal conversion and utilization. During this report period, process and program analysis studies included gas cleanup, coal benefication, liquefaction technology assessment, in situ coal gasification, low-Btu gasification, HYGAS modeling, and direct combustion processes. Some of the results in this area of activity are discussed below.

Low-Btu coal gasification. A survey of 102 reported low-Btu gasification processes was made. The most promising of these processes were further defined, and a few selected processes were described in greater detail. These results have been described in a two-volume final report,[20] the first of which lists the 102 gasification processes surveyed and summarizes 47 of these processes, including process characteristics. The second volume provides detailed descriptions of 21 selected processes of commercial or near-commercial interest.

Liquefaction technology assessment. A liquefaction technology assessment was performed to provide technical and economic evaluation of coal conversion liquefaction processes presently under development, with the selection of a limited number of high-potential process candidates for futher study. This project is being conducted under subcontract by the Ralph M. Parsons Company, and five high-potential candidate processes have been identified

17. J. P. Meyer and M. S. Edwards, *A Survey of Processes for High-Temperature, High-Pressure Gas Purification*, ORNL/TM-6178 (November 1978).

18. W. R. Gambill and W. R. Reed, *State-of-the Art Review of Heat-Recovery Processes*, ORNL/TM-6222 (August 1978).

19. J. F. Fisher and G. R. Peterson, *Control of Hydrocarbon and Carbon Monoxide Emissions in the Tail Gases from Coal Conversion Facilities*, ORNL/TM-6229 (August 1978).

20. H. F. Hartman et al., *Low-Btu Coal Gasification Processes Vol. 1. Summary, Screening, and Comparisons* and *Vol. 2. Selected Process Descriptions*, ORNL/ENG/TM-13/V1, V2 (November 1978).

which are capable of supplying synfuels by 1990. These processes have been evaluated in detail, and the results have been issued in a final draft report which is presently undergoing internal review and approval prior to publication. Processes included in the evaluation are an H-Coal–based catalytic hydroliquefaction process, an SRC-II based hydroliquefaction process, a CSF-based donor solvent process, a Fischer-Tropsch–based indirect process, and, by virtue of special interest, one configuration of the Mobil-M process for gasoline production.

High-Btu gas. An assessment of high-Btu gasification is being carried out under subcontract by the Scientific Design Company, Inc., and is divided into two areas of interest: (1) technical and economic evaluation of the Battelle Agglomerating Ash Burner Process for the production of high-Btu gas from coal and (2) monitoring and analysis of data from the HYGAS pilot plant.

The Battelle Agglomerating Ash Burner Process for the production of high-Btu gas was carried out in Phase I of this program, and the final report of this program has been issued.[21] As indicated in the last report of this series,[14] the capital cost of the Battelle process was found to be higher than costs of the other processes considered; thus the process appeared economically unattractive based on this comparative evaluation. Following release of the final report for this phase of the activity, it was decided that a second evaluation of the Battelle Agglomerating Ash Burner Process should be performed, this time studying the production of intermediate-Btu fuel gas. This second evaluation has been carried out, and a final draft report has been reviewed. Publication of this report is expected later this year.

Phase II work at the HYGAS pilot plant has been continuing with the monitoring and analysis of pilot-plant operations at the Institute of Gas Technology (IGT). Field reports from the Scientific Design engineering team at the IGT pilot plant suggest that the most critical problems to the further development of this process center on the development of accurate equipment for controlling and measuring the flows of solids to the preheater and to the gasifier. Furthermore, Scientific Design engineers have recommended that the operation of the pilot plant be demonstrated under conceptual design conditions. After these operations have been completed, the Scientific Design Company will issue a final report describing the tests in detail and noting conclusions which can be drawn with respect to the HYGAS process itself.

Solvent Refined Coal R&D Assessment

This project is an intensive, short-term assessment of current R&D activities of importance to the Solvent Refined Coal (SRC) demonstration program. The assessment includes acquisition and review of published information; discussions with R&D personnel involved in relevant activities; visits to sites of important R&D activities; monitoring of critical R&D operations; accessing, to the extent possible, the proprietary information of importance to the program; and cross matching R&D activities to the technical data needs of the industrial partners in the demonstration program. Based on the assessment of R&D activities as compared with the data needs of the SRC demonstration program, recommendations to be formulated will include priority of activities; adequacy of the R&D program; the need for possible acceleration, extension, or redirection of current activities; and possible new activities required beyond the scope of the current program.

A Phase I report has been submitted to the DOE–Oak Ridge Operations project manager which details the initial assessment of R&D needs in the SRC demonstration program. The report includes definitions of problems existing in each of the following areas (not listed in order of priority):

1. slurry mixing;
2. slurry metering;
3. heat exchangers;
4. fired heaters for slurries;
5. dissolver/reactor;
6. pressure vessels and piping;
7. block valves;
8. slurry letdown valves;
9. gas-liquid, liquid-liquid separations;
10. SRC-I solid-liquid separation;
11. SRC-II vacuum flash system;
12. centrifugal slurry pumps;
13. oxygen compressor;
14. gasification of SRC residues;
15. gasifier slag, solid-waste disposal;
16. acid-gas removal;
17. cryogenic separations;
18. physical properties;
19. materials erosion and corrosion (R&D);
20. process modeling;

21. M. Malow and A. S. West, *Evaluation of the Battelle Agglomerating Ash Burner High Btu Coal Gasification Process*, ORNL/Sub-7240/1 (June 1978).

21. wastewater control technology; and
22. plant area monitoring.

The relative importance or need for additional R&D in these areas was discussed, and preliminary recommendations resulting from this initial assessment were included. The qualitative criteria for ranking the areas include the importance assigned by SRC developers and others in coal liquefaction, potential operability and/or economic penalties associated with failure to obtain the missing information, and the extent of direct applicability to the demonstration plant project.

Additional documentation, further recommendations in less critical R&D areas, and estimates of staffing and funding necessary to adequately carry out the efforts identified will be provided in Interim and Phase II reports, which are scheduled to be delivered in draft form later in this calendar year. Team members are currently contacting institutions working in areas related to the problems identified in the Phase I report. The present and potential applicability of such work in support of the SRC demonstration program will be described in the Interim report where detailed recommendations will be offered for the more significant problem areas.

3.3 ENVIRONMENTAL CONTROL TECHNOLOGY FOR COAL CONVERSION PROCESSES

As an integral part of our continuing efforts in the development of a variety of coal conversion processes, we have several ongoing projects to investigate the nature and control of the various effluents from gasification and liquefaction processes. During this reporting period, our effort has been concentrated in the areas of environmental control technology for aqueous water treatment and the testing of catalytic incineration of CO and hydrocarbons from coal conversion tail gases. Another area of expanding involvement has been in the development of field monitoring and assessment programs for emerging coal conversion processes.

Aqueous Waste Treatment

Adsorption, ozonation, and wet oxidation processes have been studied as potential methods of tertiary water treatment, and investigations into the possibility of using wet oxidation as a treatment for sludge produced during secondary waste treatment have begun.

In the adsorption studies, three kinds of fly ash, three kinds of coal, and one char were contacted with either pure dilute solutions of organics or with biologically treated scrubber water from the ORNL bench-scale hydrocarbonization experiment. Typical results for equilibrium carbon loadings are shown in Table 3.3.

Table 3.3. Typical equilibrium loadings for sorbents

Sorbent	Sorbent loading (mg carbon/g sorbent)
Ashes[a]	0.6
John Sevier fly ash	0.6
Kingston fly ash	0.5
Wyodak hydrocarbonization ash	0.5
Coals[b]	
Colorado bituminous	0.2
Illinois bituminous	0.4
Texas lignite	<0.1
Texas lignite char	<0.1

[a]Solution composition – phenol; total organic carbon content – 150 ppm.
[b]Solution composition – scrubber water; total organic carbon content – 110 ppm. Scrubber water was obtained from the ORNL Bench-Scale Hydrocarbonization Experiment.

In the ozonation investigations, a 1-liter stirred vessel was charged with either a dilute synthetic solution or biologically treated waste from the ORNL bench-scale hydrocarbonization experiment, and ozone was bubbled through the waste. This semibatch system was used to study the influence of operating parameters on the effectiveness of ozone oxidation of the residual organics. Although reductions of >90% in phenol and in fluorescence (considered an indicator of gross polynuclear aromatics) were attained under a variety of operating conditions, the total organic carbon (TOC) content did not change appreciably, indicating the formation of new compounds and incomplete oxidation to CO_2.

Since neither ozonation nor carbon adsorption appeared to be adequate as a stand-alone polishing step, a tandem process was considered. As evidenced by chromatographic studies, considerably cleaner water was obtained by ozonation followed by carbon sorption than by carbon sorption followed by ozonation.

Wet oxidation was surveyed as an alternative to the water polishing and as a method of disposal for biological sludge. Results from the water runs are shown in Table 3.4, and those of the sludge in Fig. 3.6.

Table 3.4. Wet oxidation of hydrocarbonization wastewater

	Run number[a]							
	20	21	22A	22B	22C	23A	23B	23C
Pressure of O_2 at 300 K, MPa	1.01	1.03	1.02	1.02	1.02	0.99	0.99	0.99
Total pressure at 300 K, MPa	2.12	2.12	2.10	2.10	2.10	4.41	4.41	4.41
Maximum temperature, K	483	478	483	483	483	560	560	560
Maximum pressure, MPa	4.45	4.48				11.5	11.5	11.5
pH before run			7.9	9.3	11.3	8.0	9.5	11.4
pH after run			7.5	8.8	9.5	7.3	8.8	9.3
TOC before run, ppm	168	213	207	196	183			
TOC after run, ppm	135	135	114	131	144			
TOC reduction, %	19	36	45	33	21			
Fluorescence reduction, %								
Excitation, 254 nm Emission, 320 nm				72	50	94	93	88
Excitation, 360 nm Emission, 450 nm				40	71	92	96	96

[a]Runs 22 and 23 each contained three subsamples at three different pHs.

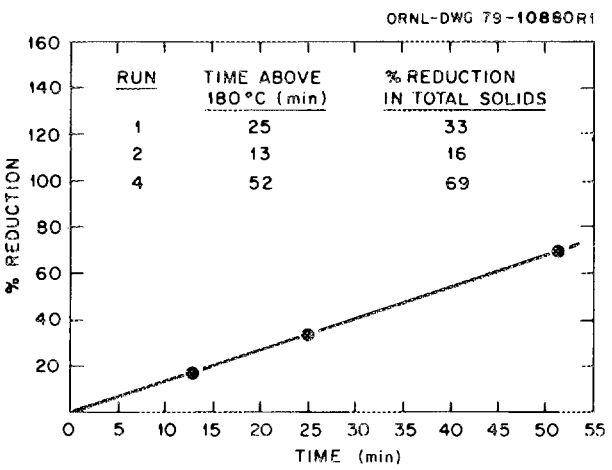

Fig. 3.6. Wet oxidation of sludge from denitrification biocolumn.

In both cases, total oxidation to CO_2 and H_2O was not achieved. However, there was a significant reduction in the fluorescence for the aqueous samples and considerable solids reduction for the sludge.

Effluent Hold Controls for Hydrocarbons and Carbon Monoxide

This project was initiated as a result of an economic review performed last year.[19] The objective is to assess the performance of commercially available catalysts for incineration of hydrocarbons and CO in tail-gas streams emanating from coal conversion plants.

During the past year, an existing experimental coal carbonizer was modified to include a catalytic incineration reactor in the vent stream from the carbonizer. The catalytic reactor was designed to utilize the diluted off-gas stream from the carbonizer as a simulated coal conversion tail-gas stream. The flowsheet for the apparatus is shown in Fig. 3.7. A detailed description of the flowsheet and equipment is given elsewhere.[2]

In summary, the unit consists of the coal carbonizer system (to the left of the sample bombs) and the catalytic incinerator system (to the right of the sample bombs). Gas can be fed to the incinerator from the carbonizer, or a simulated tail gas can be supplied from the gas bottles as shown. A process gas chromatograph provides on-line analysis of the incinerator feed and effluent streams for hydrocarbons, CO, and oxygen. Typical component concentrations in the tail gas are given in Table 3.5.

Samples of nine different incineration catalysts that are commercially available were obtained from vendors and will be tested for their performance with the tail-gas stream. All but one of the catalysts were formulated with precious metals impregnated on an alumina support.

Shakedown testing of the system has been performed using the bottled gas supply. Testing of catalysts using the carbonizer effluent as feed will commence in the near future.

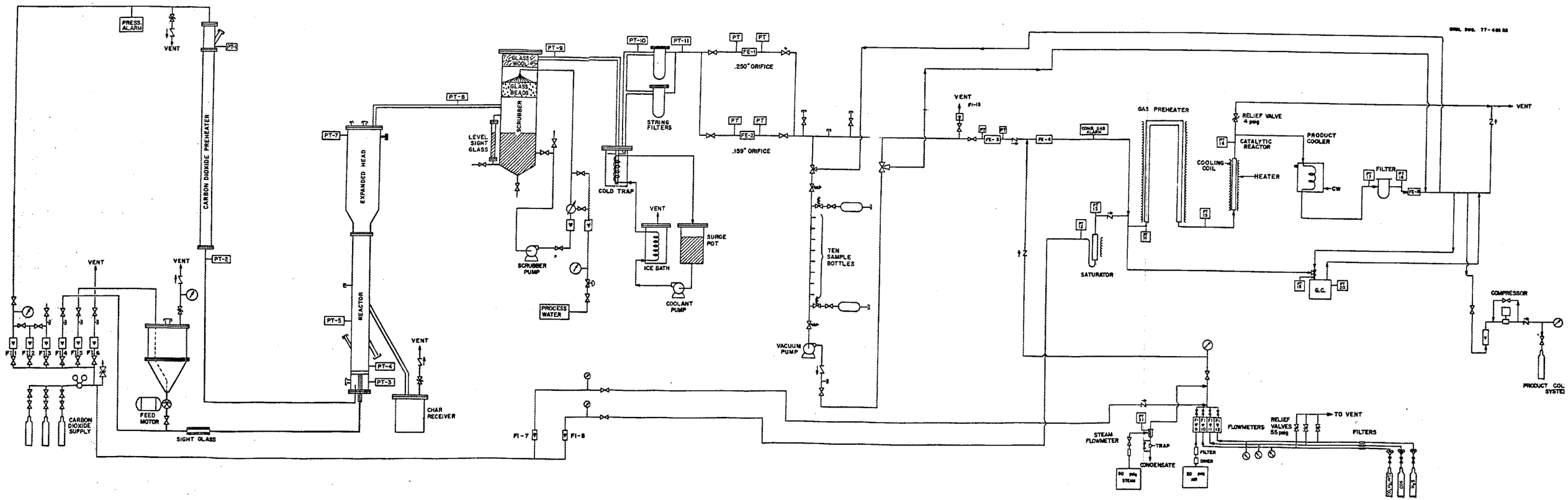
PRESS. ALARM
VENT
PT-6
CARBON DIOXIDE PREHEATER
PT-2
VENT
VENT
FI-1 FI-2 FI-3 FI-4 FI-5 FI-6
CARBON DIOXIDE SUPPLY
FEED MOTOR
SIGHT GLASS
PT-7
EXPANDED HEAD
PT-8
REACTOR
PT-5
PT-4
PT-3
VENT
CHAR RECEIVER
GLASS WOOL
GLASS BEADS
SCRUBBER
LEVEL SIGHT GLASS
PT-9
SCRUBBER PUMP
PROCESS WATER
PT-10
PT-11
STRING FILTERS
COLD TRAP
VENT
ICE BATH
SURGE POT
COOLANT PUMP
PT
FE-1
.250" ORIFICE
PT
FE-2
.159" ORIFICE
TEN SAMPLE BOTTLES
VACUUM PUMP
VENT
FI-13
FE-3
FE-4
COMB. GAS ALARM
GAS PREHEATER
SATURATOR
RELIEF VALVE 4 psig
CATALYTIC REACTOR
PRODUCT COOLER
COOLING COIL
HEATER
CW
FILTER
FE-5
G.C.
VENT
COMPRESSOR
PRODUCT COL SYSTEM
FI-7
FI-8
STEAM FLOWMETER
TRAP
CONDENSATE
50 psig STEAM
FILTER
DRYER
50 psig AIR
FLOWMETERS
RELIEF VALVES 55 psig
TO VENT
FILTERS
CO2 N2 H2

Table 3.5. Nominal tail-gas composition

Component	Concentration (m.f.)
CH_4	0.41
C_2H_4	0.32
C_2H_6	0.51
CO	0.14
H_2S	0.007
COS	0.007
H_2	0.16
O_2	5.9
N_2	22.0
H_2O	1.74
CO_2	Balance

Field Monitoring of Coal Conversion Facilities

Oak Ridge National Laboratory is carrying out a comprehensive, integrated assessment of the environmental suitability of small commercial gasifiers being installed in industry and local government applications as a part of DOE's Gasifiers in Industry Program. Initial emphasis has been placed on a gasifier that was installed in the heating plant at the Duluth campus of the University of Minnesota (UMD) and on a gasifier being installed for the county government at Pikeville, Kentucky. A similar program is also being initiated for the H-Coal coal liquefaction pilot plant at Catlettsburg, Kentucky.

Construction of the coal gasifier at UMD, the first project in the DOE Gasifiers in Industry Program, was completed during the past year. The gasifier was scheduled to start up October 1978; however, operation of the unit was limited to a 3-week period in October and November and another similar run in February 1979 because of operational difficulties and equipment modifications. Throughout the construction phase and the operation attempts, progress continued on the preparations for ORNL's environmental and health program at the UMD gasifier.

During construction, sample ports were installed at various locations for the ORNL program. Figure 3.8 is a flow schematic of the UMD gasifier, with the numbered circles indicating the sample port locations. Figure 3.9 is a photograph of an installed sample port (point 14), showing two 4-in. gate valves at right angles. In addition, a number of temperature, pressure, and flow signals from UMD instruments were made available for ORNL computer data logging.

A five-man onsite team was hired on a subcontract basis for the day-to-day running of the data and sample acquisition program. The members of this team have made extensive preparations for the

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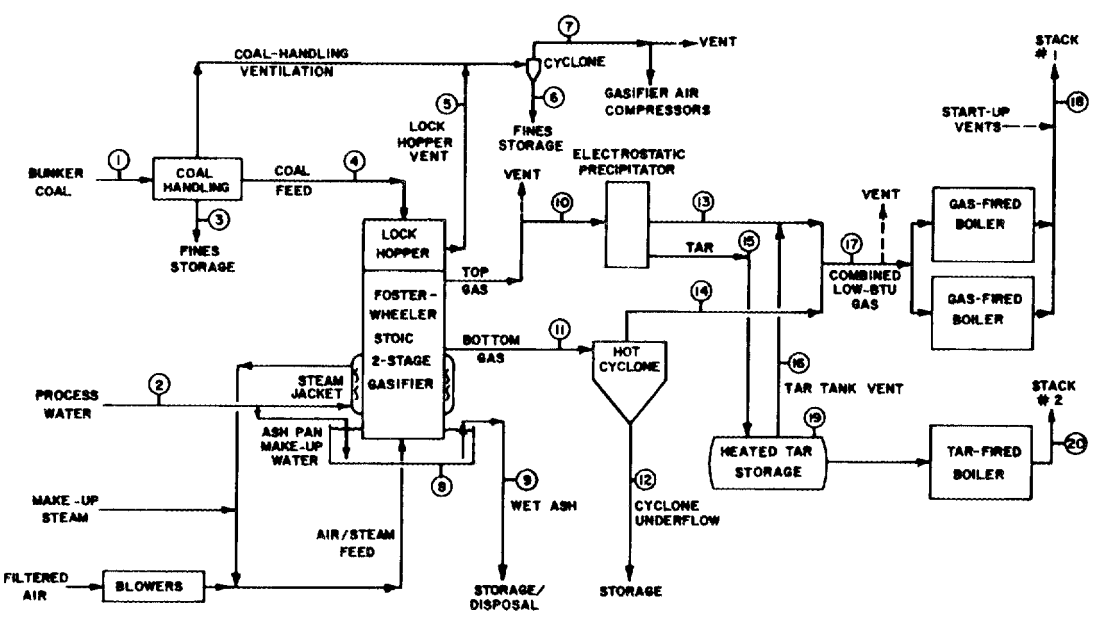

Fig. 3.8. Flow schematic and sampling points for University of Minnesota–Duluth heating plant.

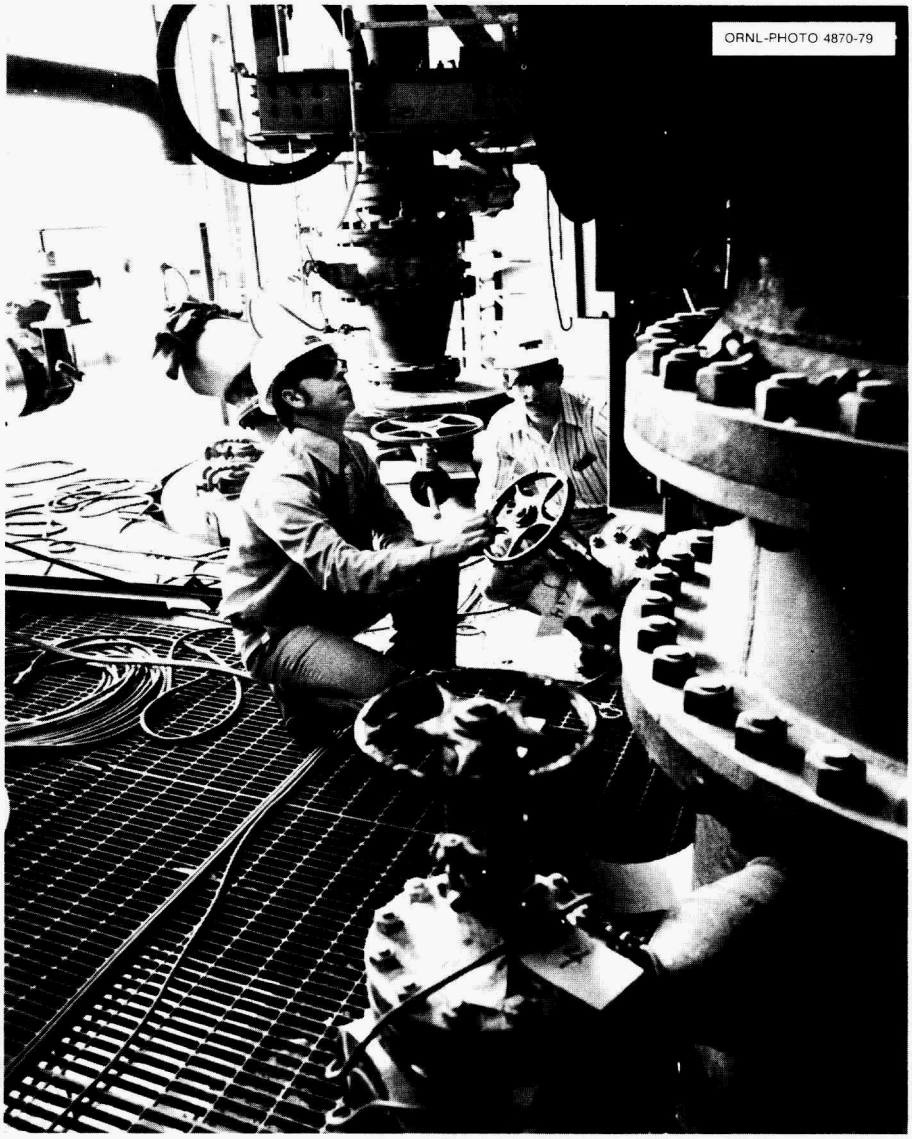

Fig. 3.9. Photograph of one sample location (joint 14) on the University of Minnesota–Duluth gasifier.

sampling program, and the industrial hygienist of the group has already been quite busy during the two brief runs.

The process gas chromatograph system, for continuous composition monitoring of points 13, 17, 18, and 20, was ordered, delivered, and completely installed. The SO_2/NO_x analyzer for the stack gas was also delivered and installed. Initial operation and testing of these instruments are awaiting the next gasifier startup. The data acquisition minicomputer was delivered, installed, and system-configured. The data-logging software to collect, store, plot, and otherwise manipulate the on-line date was installed, tested, and debugged. The data acquisition system was used during the February gasifier run to log and plot operating temperatures. The results were successfully transferred to ORNL on magnetic tape and stored in the overall project data base on the IBM-360.

The Radian Corporation of Austin, Texas, was awarded a subcontract to fabricate sampling trains and provide training in their use. Thus far, Radian has delivered one EPA Method 5 sampling train and a gas grab sampler and has provided tar removal

devices for ORNL's process gas chromatograph sample systems. A training session on EPA Method 5 sampling was held in Duluth. Delivery of the more sophisticated tar and particulate-sampling trains and the accompanying training session are awaiting the next gasifier operation.

The proposed environmental health program plan for the Pike County coal gasification facility has been completed, and the draft version has been reviewed by the advisory committee of the Gasifiers in Industry Program. The sample port locations for the gasifier are shown in Fig. 3.10. Startup is expected in early 1980, with our monitoring and sampling program to begin shortly thereafter.

The environmental and health program for the H-Coal liquefaction pilot facility is currently under development. Initial sample point locations are shown in Figs. 3.11 and 3.12. Since the plant is a pilot facility, sampling and monitoring will concentrate on the various inputs and effluents, with minimum emphasis on those units that may not be representative of a commercial-size plant.

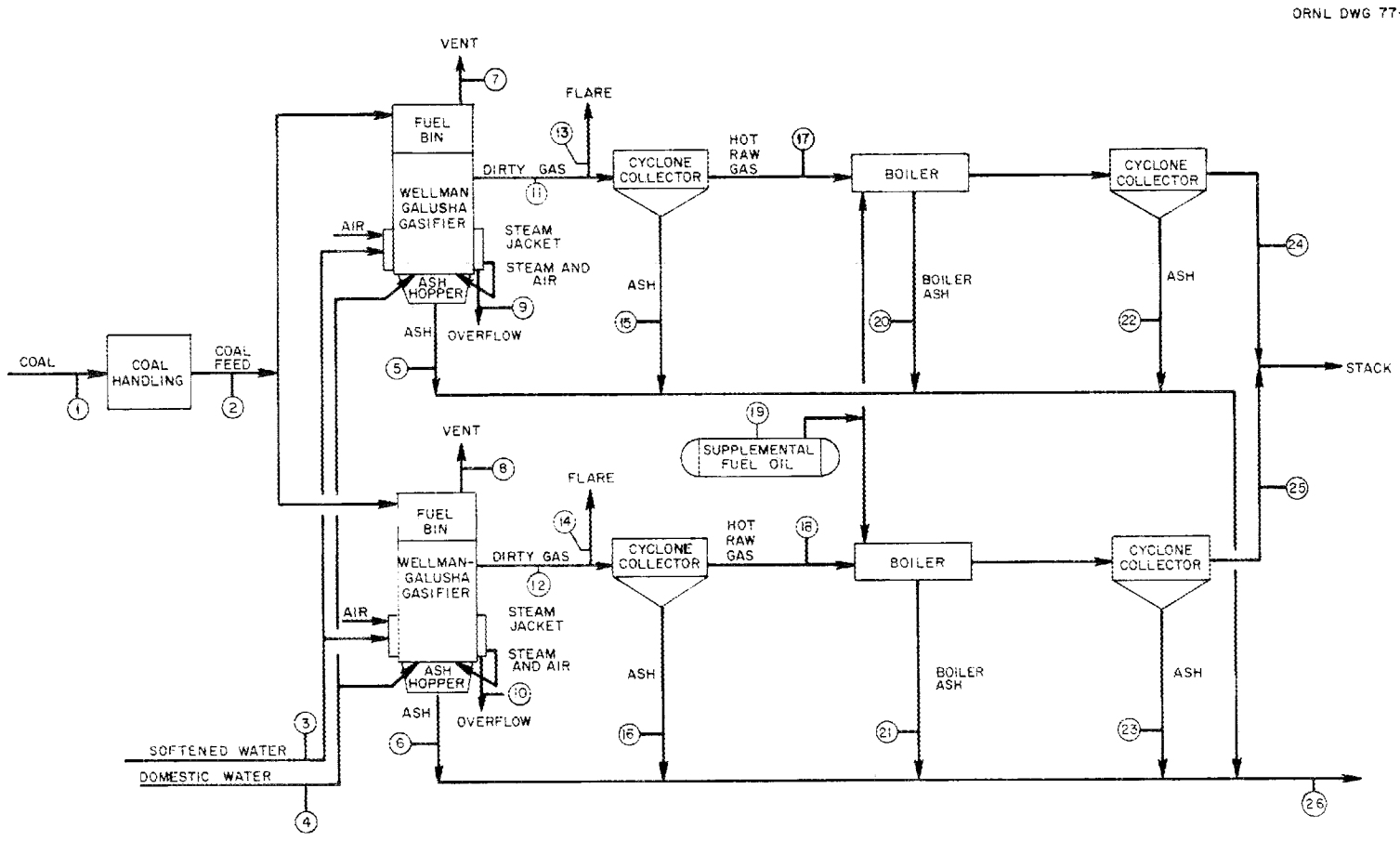

Fig. 3.10. Flow schematic and sampling points for Pike County gasifier (Pikeville, Kentucky).

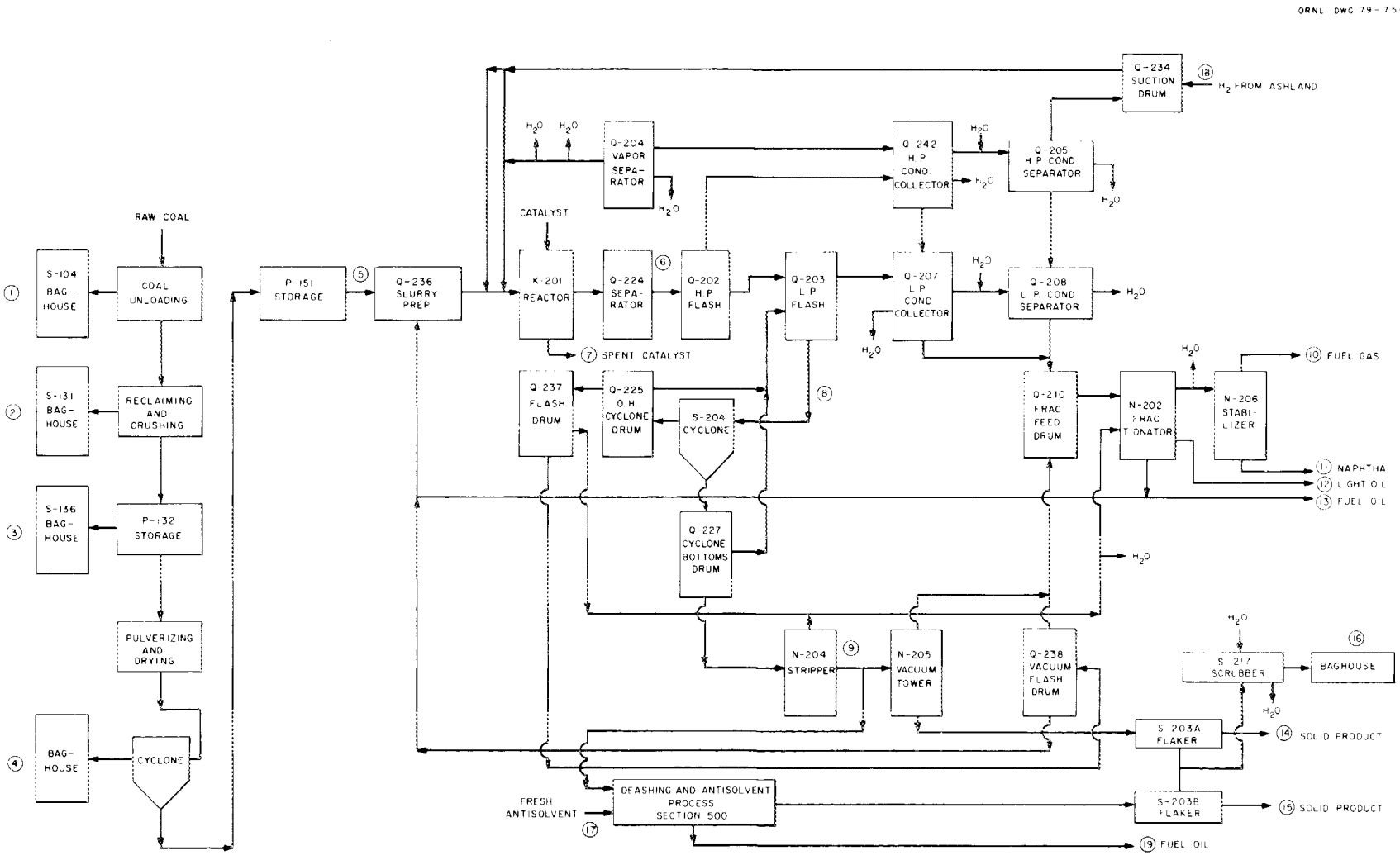

Fig. 3.11. Flow schematic and sampling points for H-Coal pilot plant (front end).

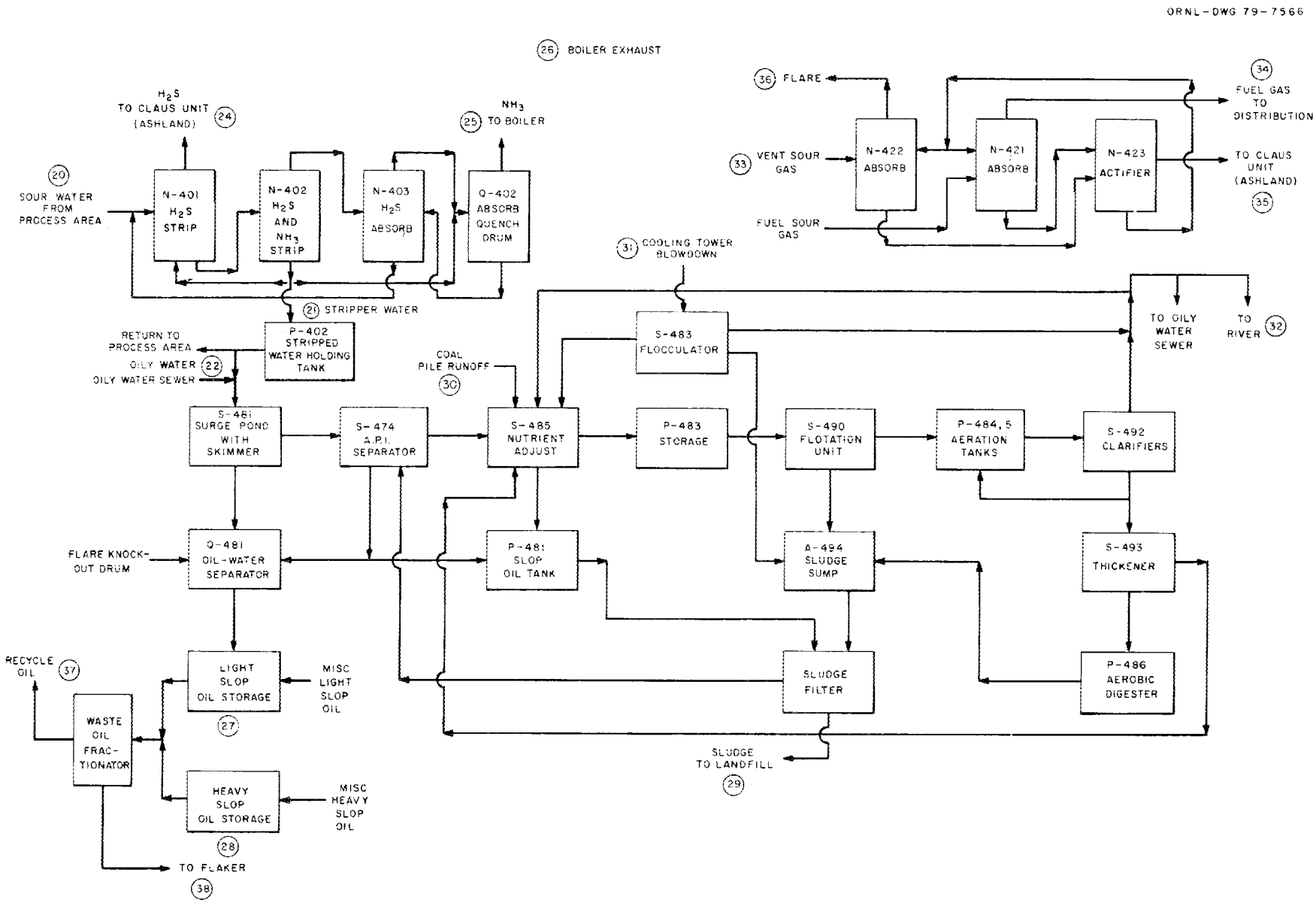

Fig. 3.12. Flow schematic and sampling points for H-Coal pilot plant (back end).

4. Waste Management

4.1 PARTITIONING AND TRANSMUTATION

This program was initiated at the beginning of FY 1977 to evaluate the technical feasibility and incentives for partitioning (i.e., recovering) long-lived nuclides from wastes and then transmuting them to shorter-lived nuclides in power reactors. Responsibility for the program was given to Oak Ridge National Laboratory (ORNL); however, many other organizations having special expertise have been involved. Experimental work ceased at the end of FY 1978, and the program is now in a final phase of cost-risk/benefit determination. During the present report period, the principal effort was devoted to (1) the documentation of previous experimental work; (2) the documentation of actinide transmutation calculations for pressurized water reactors (PWRs); (3) the conceptual design of a shipment cask for spent fuel containing recycled actinides; and (4) the direction and coordination of the conceptual design of fuel-cycle partitioning facilities and risk analyses of those facilities and a geologic waste repository.

Documentation of Experimental Programs

Documentation efforts have been under way at Argonne National Laboratory (ANL), the Rocky Flats Plant (RFP), and the Idaho Chemical Processing Plant (ICPP). The following reports are due to be completed in the near future:

D. W. Tedder, B. C. Finney, and J. O. Blomeke, ORNL, *Actinide Partitioning and Transmutation Final Report--II. Processes for Partitioning Actinides from LWR Reprocessing and Refabrication Plant Wastes*

C. W. Forsberg, ORNL, *Computer Simulation of Displacement Cation Exchange Chromatography: Separation of Trivalent Actinides and Lanthanides*

F. M. Scheitlin and W. D. Bond, ORNL, *Recovery of Plutonium from HEPA Filter Media by Continuous Leaching in a Packed Column with Electrolytically Produced Ce(IV) Nitrate and Nitric Acid*

C. W. Forsberg, ORNL, *Cation Exchange Chromatography Studies: Elution Sequence of Plutonium and Neptunium with Diethylenetriaminepentaacetic Acid (DTPA) and the Effects of Bidentate Impurities on Cation Loading*

E. P. Horwitz et al., ANL, *The Recovery of Actinides from TBP-Na_2CO_3 Scrub Waste Solutions: The ARALEX Process*

G. H. Thompson et al., RFP, *Final Report—Program for Waste Management Analysis of Nuclear Fuel Cycle—ORNL Actinide Recovery from Combustible Waste: The Ce(IV)-HNO_3 System*

L. D. McIsaac et al., ICPP, *Study of Bidentate Compounds for Separation of Actinides from Commercial LWR Reprocessing Wastes*

Transmutation Calculations

The program to evaluate the feasibility and incentives for partitioning-transmutation (P-T) as a waste management concept requires knowledge of the radionuclide characteristics of the P-T fuel cycle. Calculations were carried out at ORNL and at Savannah River Laboratory (SRL) to examine the nuclear characteristics of a reference light-water reactor (LWR) fuel cycle which does not recycle transuranium actinides and a fuel cycle which does use P-T. The radionuclide mass balances calculated from these model fuel cycles have been used to explore the technical and economic implications of a P-T fuel cycle with respect to the reprocessing, transportation, and fabrication components of the fuel cycle.

A technical report detailing the GLASS code calculations that were performed at SRL is in the

final stages of publication, and a summary report describing all transmutation calculations is in preparation at ORNL.

P-T Cask Design

A major fuel-cycle impact resulting from the introduction of P-T is the change in transportation requirements. Shipping casks must have substantial neutron shielding, in addition to extensive gamma shielding, due to the enhanced recovery and recycle of the waste actinides after several irradiations. The neutron shielding problem exists for both fresh and spent fuel, and the heat load of a spent P-T assembly is very large due to the quantity of curium isotopes. Few shipping cask designs exist that even approach the requirements for shielding P-T fuel, and these designs are primarily for breeder fuel, which is both shorter in length than the PWR assemblies considered in this study and less neutron active. However, these designs for fast breeder reactor (FBR) fuels provide an excellent basis for the conceptual design of a P-T shipping cask.

The shield design developed for this program is a multilayer configuration which generally helps to reduce the weight and alleviate spectral hardening (Fig. 4.1). The cask is capable of holding six 1.5-year-old P-T fuel assemblies with a dose rate of ~1.5 mrem/hr at a distance of 6 ft from the surface. Calculations were made using the computer code ANISN[1] assuming the absence of the lithium hydride zone, which was considered to possibly be the worst type of accident. Accident-condition dose rates were on the order of ~100 mrem/hr. The weight of the shield over the actual assembly length (405.9 cm) is ~84 metric tons, fully loaded, but this does not include the weight of the end pieces.

Recent calculations indicate that fifth-recycle spent P-T fuel (25 years into a P-T nuclear strategy) has a neutron emission rate of $\sim 5 \times 10^{10}$ neutrons per

1. W. E. Engle, Jr., *ANISN, A One-Dimensional Discrete Ordinates Transport Code with Anisotropic Scattering*, K-1693, RSIC Report CCC-82 (March 1967).

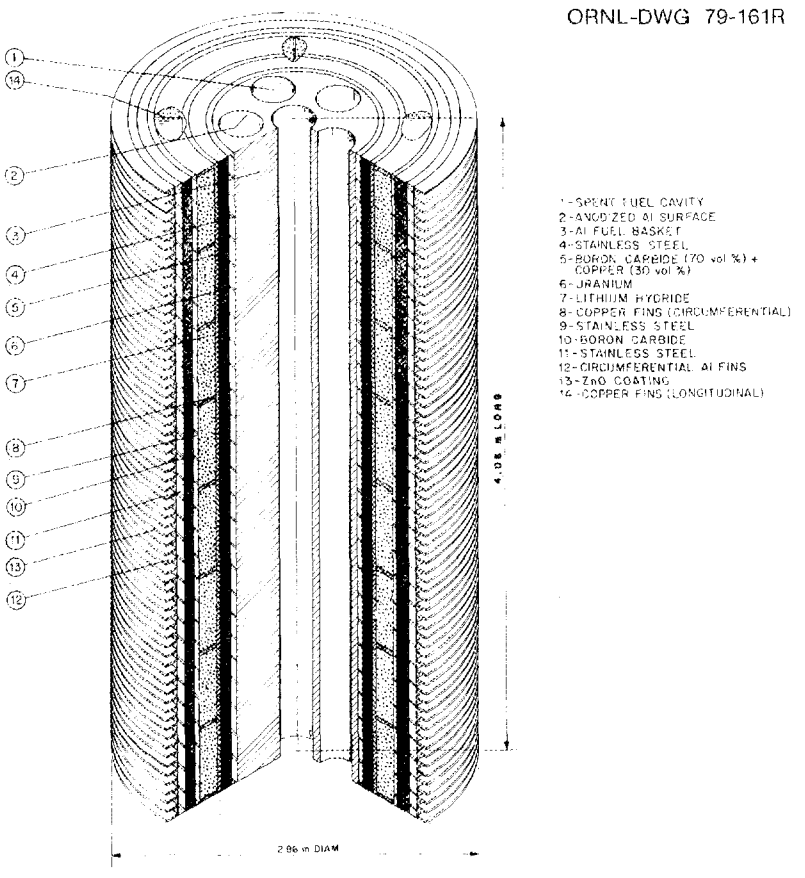

Fig. 4.1. Conceptual shielding design for spent P-T fuel.

second per assembly. Calculations beyond the fifth recycle have not been made, but the shield has been sufficiently over-designed to compensate for the anticipated growth in the neutron emission rate in fuels that exceed the fifth recycle.

Economic Analysis

An economic analysis is being carried out by The Ralph M. Parsons Company (Pasadena, Calif.). This study includes an analysis of waste-treatment facilities (WTF) for both the fuel reprocessing plant and the fuel fabrication plant. These facilities treat all actinide wastes that are produced during the fuel recycle, recover the actinides, and recycle them to the main reprocessing and fabrication facilities.

A conceptual study will be completed on both the WTFs and the shipping cask. The WTF study includes the following: completion of project and instrumentation drawings, equipment sizing and inventory calculations, shielding requirement calculations, building and process layouts, ventilation analysis, site services and location, construction material estimates, and cost estimates. This information will be presented as a final report at the end of FY 1979.

Fuel Cycle Facility Risk Analysis

Greater risk is expected to result from increased processing of the actinide-bearing wastes and the increased amounts of shorter-lived actinides in the nuclear fuel cycle. ORNL has contracted with Science Applications, Inc., Palo Alto, Calif., to perform a preliminary risk analysis of fuel cycle facilities and operations that would be significantly affected if P-T were implemented. This work was initiated during the summer of 1978 and will be completed by October 1979.

Routine doses will be calculated using source terms supplied by ORNL coupled with standard dispersion and dose models. In the case of transportation, the routine dose will be calculated based on the number of shipments, assuming a fixed dose per shipment. Occupational dose will be calculated by assuming a constant average exposure per employee and basing the facility staffing estimates on the conceptual design study by The R. M. Parsons Company.

The net result of this work will be an estimate of the extra short-term risk that would be expected if P-T were implemented. These results will be available on both an absolute and a differential basis and will be compared to the costs and benefits of P-T in the final overall analysis.

Repository Risk Analysis

One of the principal beneficial effects of P-T would be to reduce the long-lived nuclide content of the radioactive wastes isolated in a repository. Los Alamos Technical Associates, under a subcontract with ORNL, is currently performing a repository risk analysis which quantitatively assesses the magnitude of this benefit. The work being conducted is a straightforward application of a computer code for a waste repository risk analysis that was previously developed by S. E. Logan et al.[2] This code, called AMRAW, performs a probabilistic risk analysis of a radioactive waste repository using fault-tree analysis.

The general approach taken in the repository risk analysis is to perform two parallel analyses, one on a repository containing partitioned (actinide-depleted) wastes and the other on a repository containing normal wastes. The repository site considered in this analysis is the Los Medaños area in southeastern New Mexico, which is under study as the location of the Waste Isolation Pilot Plant (WIPP). The AMRAW computer code will calculate the probabilistic risk from the two waste repositories (with and without P-T) over 1 million years.

The results of the repository risk analysis will be a calculation of the expected long-term dose from the repository. The results of this calculation can be expressed in radioactivity release (curies), dose rate and dose (rem/year and man-rem), health effects, and monetary units. These results will be used to compare the performance of the two repositories with each other, with natural background radiation, and with the short-term risks and costs of P-T. The risk analysis will indicate which nuclides in the waste predominate the repository impacts in both cases. AMRAW will also be used in its "consequence analysis" mode to calculate the effects of a specific type of repository accident assumed to occur at a specific time. This type of analysis is required to determine the maximum dose rates that result from a particular accident.

This study, which was started during the summer of 1978, is expected to be completed by October 1979. At the present time, changes in AMRAW to accommodate the heavier actinides and new output tables have been completed and verified. The risk analysis of the base case is currently under way.

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2. S. E. Logan and M. C. Berbano, *Development and Application of a Risk Assessment Method for Radioactive Waste Management*, EPA 520/6-78-005, vols. I–IV (July 1978).

4.2 CEMENT AND CONCRETE TECHNOLOGY

Programs that involve the use of cementitious materials in nuclear waste management are: (1) the development of grouts suitable for the disposal of the waste sludges generated at ORNL by hydraulic fracturing, (2) an investigation of the potential of incorporating high-specific-activity waste in concrete, and (3) the development and testing of cementitious mixtures suitable for plugging holes in the vicinity of a repository which otherwise may represent a hazard in the isolation of radioactive waste.

Hydrofracture Mix Development Studies

In connection with the new hydrofracture facility to be built at ORNL, work continues on the development of grout mixes that are suitable for locally generated radioactive waste sludge and on the evaluation of various admixtures for use in the sludge-slurry transfer to the new site. Studies on the bulk-flow properties of the dry solids that will be used at the new facility were completed and have been reported elsewhere.[3] The results showed that a hopper opening measuring 122 cm (48 in.) in diameter would be required for the mass flow of nonaerated solids. The solids will be aerated when stored at the hydrofracture facility; thus, these results plus past experience indicate that a hopper opening of >20 cm (8 in.) but <122 cm (48 in.) is required at the new facility. Other flow measurements demonstrated that the type of coating used on the hopper walls would not affect the flowability of the stored solids.

Results from laboratory studies suggested that the viscosity, pumpability, and phase separation of hydrofracture grouts that contain slurries would be affected primarily by the viscosity of the initial slurry but would be essentially independent of the composition of the sludge in the slurry. In these tests, the radioactive sludge was simulated by the use of powdered iron, Fe_2O_3, and Al_2O_3, either separately or as mixtures. Slurries of 5 to 15 wt % of these ingredients were prepared in a solution of 0.1 *N* $NaNO_3$ raised to a pH of 10. The slurries were added to a dry mix consisting of 46 wt % Type I Portland cement, 46 wt % fly ash, and 8 wt % Indian red clay, and the properties of the resulting grouts were measured.

Evaluation tests demonstrated that slurries containing up to 15 wt % simulated sludge could be maintained in a pumpable suspension by the addition of bentonite clay. If necessary, the viscosity of the suspension could be decreased by adding small amounts of FX-32c, a proprietary thinning agent. Since the accumulated sludge currently stored in Gunite tanks at ORNL must be slurried with water and pumped a distance of 1980 m (6500 ft) through a 4.45-cm (1.75-in.)-ID pipe to the new hydrofracture facility for disposal, suspending agents and possibly thinning agents will be required to maintain pumpable suspensions. A pressure drop of 2.1 MPa (300 psi) is considered to be about the upper limit of the pressure range that could be used to maintain laminar flow in this transfer line. Calculations using laboratory flow data showed, for example, that a slurry containing 13 wt % Fe_2O_3 and 3 wt % bentonite clay would require a pressure drop of 1.7 MPa (241 psi) across the 1980-m (6500-ft) pipe. The pressure drop could be decreased to 0.53 MPa (77 psi) by the addition of 0.2 wt % FX-32c to this sludge-clay suspension.

Preliminary data were obtained on the leachability of cesium and strontium from grouts containing simulated sludge. Assuming that diffusion is the controlling leach mechanism, as was found in previous grout leach studies,[4,5] the average effective diffusivity for either cesium or strontium is on the order of 10^{-14} cm^2/sec into water from a local spring and 10^{-12} cm^2/sec into distilled water. Long-term studies are in progress to verify the leach mechanisms and calculate exact leach rates.

Studies continue on the feasibility of the disposal of shredded solid waste by hydraulic fracturing. To obtain waste solids concentrations of ≥10 wt % in a grout that is suitable for hydrofracture, laboratory tests demonstrated that the shredded waste must be pelletized and added directly to the dry-mix ingredients. A pumpable grout containing 13.6 wt % waste was prepared using a mix-to-water ratio of 0.8 kg/liter (7 lb/gal) and a dry mix consisting of 30 wt % pelletized waste, 45 wt % cement, 15 wt % fly ash, 8 wt % pottery clay, and 2 wt % bentonite clay.

3. E. W. McDaniel and H. O. Weeren, *The Flowability of Bulk Solids Used in Shale Fracturing Grouts Determined by the Jenike and Johanson Method*, ORNL/TM-6882 (in press).

4. J. G. Moore, H. W. Godbee, A. H. Kibbey, and D. S. Joy, *Development of Cementitious Grouts for the Incorporation of Radioactive Wastes. Part 1: Leach Studies*, ORNL-4962 (April 1975).

5. J. G. Moore, *Development of Cementitious Grouts for the Incorporation of Radioactive Wastes. Part 2: Continuation of Cesium and Strontium Leach Studies*, ORNL-5142 (September 1976).

Although the 2-hr phase separation was 7%, either this water could be recycled or the dry-mix composition could be adjusted to reduce the phase separation. Slurries of the shredded or pelletized waste are not as satisfactory for grout preparations. The waste content is severely limited since some of the waste ingredients (paper, cloth, etc.) sorb water, thus increasing the viscosity and reducing the pumpability of the slurries and the grouts.

Fixation of Wastes in Concrete

Concretes *f*ormed *u*nder *e*levated *t*emperatures *a*nd *p*ressures (FUETAP concretes) are being evaluated as potential hosts for radioactive wastes. In this concept, the waste (including high-specific-activity material) will be mixed with cementitious materials that contain suitable admixtures to fix the radionuclides and then allowed to solidify and cure at temperatures and pressures of up to 300°C and 6.9 MPa (1000 psi), respectively. During the past year, an experimental plan was developed and studies were initiated using simulated radioactive waste.[6,7] The data showed that these ceramic solids hold much promise as radioactive waste hosts. Strong, retentive solids containing up to 15 wt % simulated radioactive sludge could be made by curing cementitious mixtures for 24 hr at temperatures ranging from 100 to 250°C and a pressure of 4.1 MPa (600 psi).

An example of the mix used in the preparation of FUETAP concretes is shown in Table 4.1. Type I cement was chosen as the cement base for current tests since preliminary data showed that Type I and Type III cement produced quite similar solids. High-alumina cement was found to be unsuitable for preparing these solids. The density, compressive strength, thermal conductivity, and permeability values for the resulting solids were inferior to concretes prepared with Type I cement. Fly ash was added to the mix to react with the lime released during the hydration of the cement and possibly reduce the strontium leachability. An illitic clay was present to fix any cesium in the waste. The simulated nonradioactive waste used in these preparations was based on the analysis of radioactive waste stored at the Nuclear Fuel Services Plant[8] which typified existing high-level radioactive waste (Table 4.2).

Table 4.1. Example of FUETAP concrete mix

Component	wt %
Cement	27.55
Fly ash	22.50
Illitic clay	8.95
Simulated waste[a]	10.00
Suspending agent	0.40
$NaNO_3$	2.60
Water	28.00

[a]Composition listed in Table 4.2.

Table 4.2. Composition of simulated waste sludge

Component	wt %
Fe_2O_3	75.18
Al_2O_3	14.89
Cr_2O_3	4.94
NiO	4.78
SrO	0.14
$Ru(OH)_3$	0.03
CeO_2	0.04

Except for an increase in porosity with temperature, there were no marked correlations between temperature and the physical properties of specimens cured at temperatures ranging from 100 to 250°C and a pressure of 4.1 MPa (600 psi), as shown in Table 4.3. The resulting solids had an average compressive strength of ~30 MPa, a thermal conductivity of 0.50 W/m.K, and a permeability on the order of 10^{-5} darcy. Curing at a higher pressure, 6.9 MPa (1000 psi), caused no significant change in the physical properties. Longer curing periods of 48 or 72 hr produced solids with 20 to 30% less compressive strength. To obtain an indication of the durability of the solids, a portion of the specimen prepared at 250°C was contacted with ten volumes of either simulated Sandia Type B brine or groundwater for 96 hr at 250°C and 17.2 MPa (2500 psi). Analysis of the resulting liquids indicated calcium losses of ≤2.4 and ≤0.58% into the brine and groundwater,

6. J. G. Moore, E. Newman, and G. C. Rogers, *Radioactive Waste Fixation in FUETAP (Formed Under Elevated Temperature and Pressure) Concretes—Experimental Program and Initial Results*, ORNL-TM-6573 (March 1979).

7. R. E. Blanco and A. L. Lotts (compilers), *High-Level Waste Program Progress Report for October 1, 1978 through March 31, 1979*, ORNL-TM-6866 (in press).

8. Nuclear Regulatory Commission, *Alternative Process for Managing Existing Commercial High-Level Radioactive Wastes*, NUREG-0043 (1976).

Table 4.3. Effect of curing temperature on the physical properties of FUETAP concrete[a]

Curing temperature[b] (°C)	Compressive strength (MPa)	Thermal conductivity (W/m·K)	Porosity (%)	Permeability (darcy)
c	19.8	0.59	36	9×10^{-5}
100	29.0	0.43	38	3×10^{-6}
160	30.8	0.55	41	1×10^{-5}
180	28.3	0.50	40	1×10^{-5}
250	27.3	0.51	43	2×10^{-5}

[a]Prepared with Type I Portland cement and the mix shown in Table 4.1.

[b]Except for the control, specimens were cured at 4.1 MPa (600 psi) for 22.5 hr after an initial 1.5-hr period that was required to heat the specimen to the desired temperature.

[c]Control sample. This specimen was cured at ambient temperature and pressure for 28 days.

respectively. Additional studies will have to be made to determine the significance of the loss and the limiting parameters.

Sufficient data have not been collected to determine the mechanism(s) controlling the leachability of various radionuclides from FUETAP concretes. If it is assumed that diffusion is the controlling mechanism, then current data indicate effective diffusivities on the order of $\leqslant 10^{-17}$, $\leqslant 10^{-13}$, and $\leqslant 10^{-10}$ cm^2/sec for plutonium, cesium, and strontium, respectively, into either distilled water, spring water, or Sandia Type B brine. Initial results show that the strontium leachability may be decreased by the addition of BaO, Na_2SiO_3, and MnO_2 to the dry mix used to prepare the concretes.

A major concern in the evaluation of solids that contain radionuclides is the prospect of canister pressurization resulting from the radiolytic decomposition of water in the solid. Results from laboratory reaction-rate studies demonstrated that if the hydrogen and oxygen produced by radiolysis remain in close proximity to the FUETAP concrete, then the recombination rate would exceed the production for even very high concentrations of alpha waste in the product. For example, on passing nitrogen containing 4.1% hydrogen and 1.7% oxygen at a rate of 1800 ml/hr over 300 g of FUETAP concrete fragments that range in size from 1 to 10 mm, the recombination rate exceeded the production rate that would be obtained with a solid having a ^{244}Cm concentration of 2.85 mg/g. To verify these results, glove-box tests involving FUETAP concretes that contain alpha material are planned.

Borehole Plugging

This is an ongoing program supported by the Office of Nuclear Waste Isolation (ONWI) to assist them in devising, developing, and testing cementitious mixtures suitable for plugging holes that may represent a hazard to a waste isolation repository. A thermal-property measurements program is also in progress to aid the ONWI in making thermal analyses of possible repository sites by obtaining data on selected specimens of appropriate geologic media.

Methods and procedures for accurately measuring the physical properties of plug-solid candidate formulations were emphasized in the Borehole Plugging Program over the past year, and systematic studies were started using pozzolanic (fly ash)-cement and salt-cement mixtures. In addition, plans were developed and experiments were initiated (1) to examine the properties of plug solids made from recipes proposed for use in the initial field tests to be made at the WIPP site and (2) to devise cementitious mixes that would eventually form thermodynamically stable solids and improve the probability of long-term plug durability in various geologic media. Details of these studies have been reported elsewhere;[9] however, some of the more significant results are summarized below.

In parametric studies, 10 to 60 wt % of the sand in standard mortar mixes (23 wt % cement, 63.2 wt %

9. J. G. Moore, M. T. Morgan, E. W. McDaniel, H. B. Greene, and G. A. West, *Cement Technology for Borehole Plugging: Progress Report for the Period October 1, 1977 to September 30, 1978*, ORNL-5524 (August 1979).

sand, and 13.8 wt % water) was replaced with salt and/or fly ash. The inclusion of 10 wt % salt in a standard mortar doubled the initial and final set times. The slump and bleed capacities of the wet mix increased, but the bleeding rate decreased. The inclusion of fly ash in these saltcretes decreased both the bleeding capacity and the rate, depending on the amount and kind of fly ash. The set time of the saltcrete was decreased by the addition of a bituminous fly ash but was increased by a lignite fly ash.

Procedures for measuring the compressive strength of solids that gave precisions ranging from ±2% to ±8% were developed. Mathematical expressions that showed the compressive strength as a function of the sand concentration were obtained by using results from measurements on mortars. For example, after 91 days of curing,

$$y = 45.3 - 0.47x ,$$

where y is the compressive strength (MPa), and x is the wt % sand in the mortar.

The compressive strengths of cement–fly ash concretes varied with curing time and were found to be dependent on the composition of the fly ash. The strengths of saltcretes decreased with increasing salt concentration. The addition of fly ash to the saltcretes produced solids that were stronger than the standard mortars and independent of the fly-ash composition. For example, a saltcrete containing 23.0 wt % Type I Portland cement, 30 wt % NaCl, 20 wt % fly ash, 13.2 wt % sand, and 13.8 wt % water had a compressive strength of 58.3 MPa (8500 psi), which is 28% higher than that of the standard mortar control.

Gas and liquid permeability measurements were made using a Hassler cell[10] procedure. The gas permeability measurements were dependent on the degree of drying experienced by the specimen. Procedures were developed for vacuum drying to remove unbound water without damaging the specimens. Any microcracking that occurred was easily detected by anomalous behavior observed during the gas flow measurements.

The apparent liquid permeability of saltcretes, as calculated from gas flow measurements, decreased with increasing salt content. The permeability varied from 6×10^{-7} darcy for 0 wt % salt to 1.25×10^{-8} darcy for a saltcrete containing 63.2 wt % salt. Preliminary experiments using water as the permeating fluid indicated that liquid permeability values were about two orders of magnitude less than those calculated from gas measurements.

The thermal conductivities of cementitious solids increased with density and with increased concentration of sand and/or salt. Measurements made at temperatures ranging from 30 to 300°C revealed that the thermal conductivities of saltcretes decreased with increasing temperature but remained almost constant in neat cement pastes. The conductivity ranged from 0.5 W/m·K for a neat cement paste to 1.8 W/m·K for a saltcrete.

Thermal conductivity measurements are in progress on a suite of eight standard rocks supplied by the U.S. Bureau of Mines. The measurements are made on specimens cored along the x, y, and z coordinates and dried under vacuum to a constant weight. Values at 100°C have been determined for three of the rocks and range from 2.26 to 5.74 W/m·K (Table 4.4).

Table 4.4. Thermal conductivities of selected standard rocks at 100°C

Specimen	Thermal conductivity (W/m·K)		
	x core	y core	z core
Westerly granite	2.26	2.32	2.40
Dresser basalt	3.16	3.20	3.01
Sioux quartzite	5.74	5.63	5.31

The thermal conductivities of dome-salt samples from the Avery Island and Jefferson Island mines in southern Louisiana were measured and have been reported.[11] These values, which were related to the density and fragility of the salt, ranged from 4 W/m·K at 70°C to 2 W/m·K at 300°C. The average conductivity at 100°C was ~25% less than that of single-crystal salt at the same temperature.

4.3 REMOVAL AND SEGREGATION OF RADIOACTIVE NUCLIDES AND NITRATE FROM LIQUID WASTE STREAMS

A three-task study, which began in FY 1977, is concerned with the removal of certain radionuclides

10. R. E. Wyckoff, H. G. Botset, and M. W. Reed, *Rev. Sci. Instrum.* 4, 394 (1933).

11. M. T. Morgan, *The Thermal Conductivity of Rock Salt from Louisiana Salt Domes*, ORNL/TM-6802 (June 1979).

and other chemicals (e.g., NH_4^+, NO_3^-) from aqueous process and effluent streams that are associated with the nuclear fuel cycle and with special situations in DOE facilities.

Many of the processing steps in the nuclear fuel cycle generate aqueous effluent streams bearing contaminants that can, because of their chemical or radiological properties, pose an environmental hazard. Concentrations of such contaminants must be reduced to acceptable levels before the streams can be discharged to the environment. Two classes of these contaminants are nitrates and heavy metals. Specific techniques aimed at the removal of nitrates and radioactive heavy metals by biological processes are being developed, tested, and demonstrated. High-rate denitrification processes that utilize denitrifying bacteria which adhere to particles of anthracite coal or sand are also being developed. The particles, with adhering bacteria, are fluidized by the flow of the aqueous stream being treated as it passes upward through a columnar bioreactor.

Task I: Iodine Removal from Waste Vapor or Condensate Streams

Task I has been completed, and the terminal report is in preparation.

Task II: Biological Denitrification

The stricter enforcement of nitrate disposal limits [20 to 40 g N $(NO_3^-)m^3$] has forced uranium-metal fabrication and gaseous diffusion plants and other nuclear fuel cycle processors to seriously consider biological denitrification as the best available technology for acceptable nitrate disposal.

Studies of the fluidized-bed denitrification bioreactor have continued, with emphasis on the effects of metal inhibitors, excess biomass, and calcium ion interference. It was found that aluminum and nickel (expected major contaminants) do not increase denitrification if sufficient phosphate is available for biological growth. The use of a vibrating screen has been shown to be an effective procedure for removing excess bacteria from the −30/60 mesh coal fluidization particles (Fig. 4.2).

Acid-waste effluent must be neutralized with NaOH, NH_4OH, or CaOH to a pH of 7.0 for biological denitrification. Sodium and ammonium ions form soluble compounds within the bioreactor; however, $CaCO_3$ is insoluble and forms a solid precipitate which may coat the top of the bacteria in the bioreactor. The vibrating screen is capable of removing the $CaCO_3$ as well as the biomass, and a 16-week test has demonstrated that no adverse operational problems exist.

ORNL is helping the Goodyear Atomic Gaseous Diffusion Plant (GAGDP) and the Fernald-Feed Material Preparation Center solve their nitrate waste problems through the Denitrification Assistance Program. This assistance will continue via laboratory testing and pilot-plant tests at ORNL and design consultation funded by the individual sites.

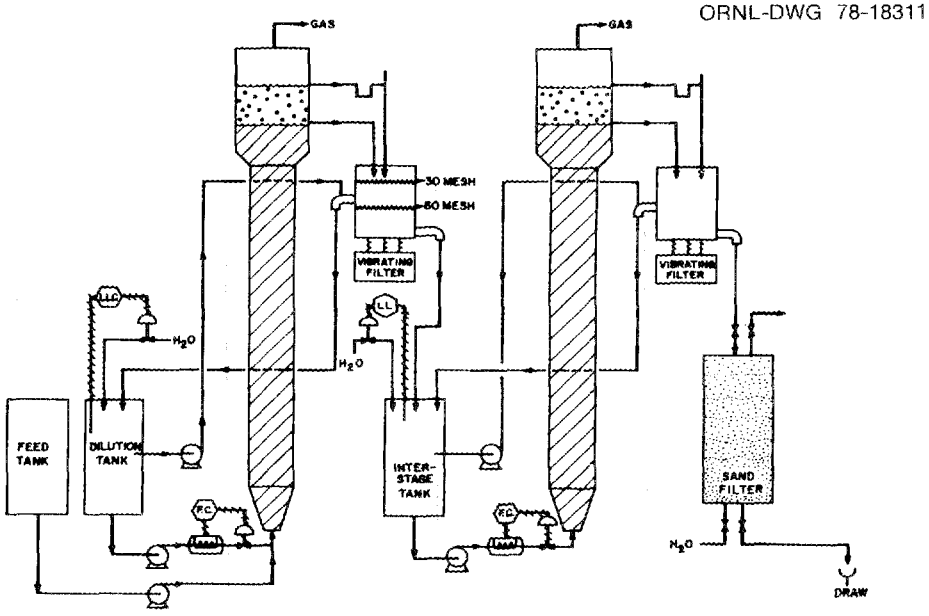

Fig. 4.2. A dual bioreactor system with mechanical coal cleaning and controlled flow.

The design of a denitrification pilot plant with two 10-cm-ID by 8-m-tall fluidized-bed bioreactors connected in a series (Fig. 4.3) has been completed. This facility is proposed for the GAGDP site. A projected nitrate feed concentration of 4000 g/m^3, an effluent concentration of 20 to 40 g/m^3, and a flow rate of 18 liters/min, resulting in a denitrification rate of 80 to 90 kg N (NO_3^-)/day-m^3, form the basis for the design.

Task III: Isolation of Uranium Using Microbial Cells

The process principle being explored consists of using microbial cells as "biosorbents" to adsorb or complex dissolved metal species (e.g., uranium) from aqueous solutions. Thus, the stream is decontaminated by removing the insoluble cell-metal complex from a treated stream.

Applied microbiological research was focused on characterizing two cultures for use in uranium isolation processes. These were a yeast, *Saccharomyces cerevisiae,* and the mixed culture of denitrifying bacteria described in Task I. Through the use of transmission electron microscopy and energy-dispersive x-ray (EDX) analysis, it was determined that uranium is accumulated extracellularly (at the cell surface) by *S. cerevisiae* (Fig. 4.4). The mixed culture of denitrifying bacteria was tested for effectiveness in removing uranium from a solvent-extraction raffinate waste solution obtained from the GAGDP, Portsmouth, Ohio. The waste solution was tested both as received (4 g uranium/m^3) and supplemented with additional uranyl nitrate (100 g uranium/m^3). Through the combined effects of pH adjustment and contact with the microbial cells, the soluble uranium concentration was reduced by >99.5% in each case. This degree of decontamination was achieved with additional dissolved metal species (Al, Fe, Cu, Cr) that were present in concentrations considerably greater than that of uranium.

Testing of contactor designs for continuous heavy-metal removal has indicated that a countercurrent contacting column (Fig. 4.5) may be quite effective. Denitrifying bacteria grown on coal particles in the fluidized-bed denitrification bioreactor (Task II) were metered into the top of a 5-cm-ID contacting column. As the coal particulates with attached bacterial film settled to the bottom of the contacting column, a solution containing uranium at an inlet concentration of 25 g/m^3 was pumped up through the column. The effluent uranium concentration at steady state was ~0.5 g/m^3, even though the mean

ORNL-DWG 79-363

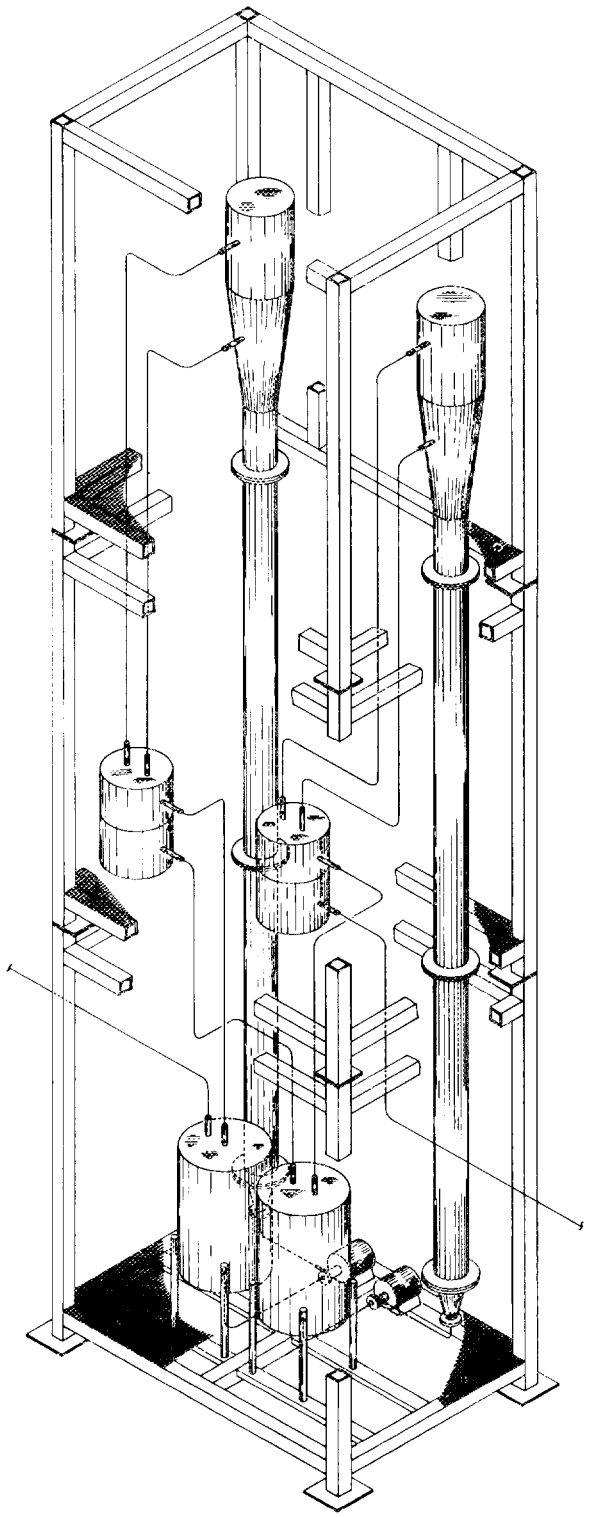

Fig. 4.3. Pilot-plant design of the Goodyear Atomic Gaseous Diffusion Plant.

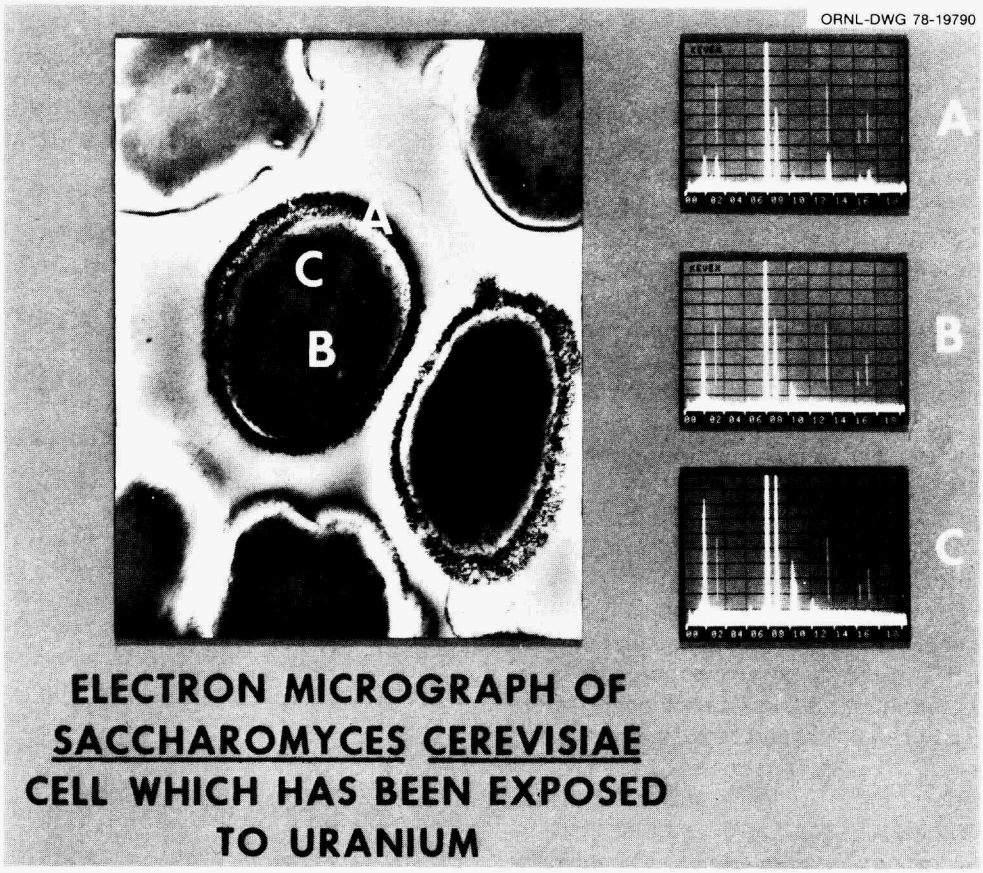

Fig. 4.4. Transmission electron micrograph (35,000X) and energy-dispersive x-ray spectra of sectioned yeast cell indicate that uranium is accumulated at the cell surface (point A). The bound uranium appears as fibrils covering the cell surface.

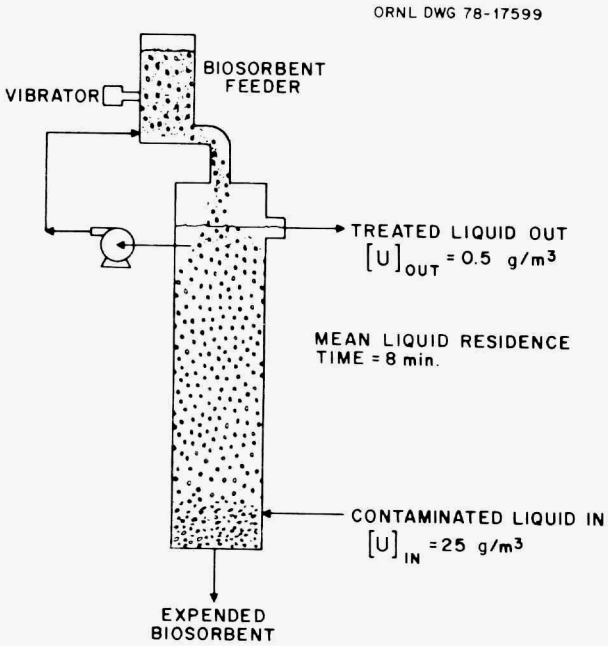

Fig. 4.5. Contactor for the continuous removal of uranium from aqueous streams.

liquid residence time was only ~8 min (80-cm-long contacting zone).

Portions of this work have been reported in the journal *Biotechnology and Bioengineering.*[12]

4.4 UPDATING OF THE ORIGEN COMPUTER CODE

The effort to update the ORIGEN computer code and its associated data bases, which began during FY 1976, continued during this report period. The principal goal is to place the ORIGEN code and data bases on as firm a theoretical basis as possible. This involves modification of the original ORIGEN code to more accurately reflect the neutronic behavior of the actinides during irradiation, calculation of effective cross sections using more sophisticated

12. S. E. Shumate II, G. W. Strandberg, and J. R. Parrott, Jr., "Biological Removal of Metal Ions from Aqueous Process Streams," *Biotechnol. Bioeng. Symp.* 8, 13–20 (1978).

reactor physics codes,[13,14] and updating the other data libraries.

During this report period, a report documenting the updated uranium-plutonium cycle pressurized water reactor (PWR) and boiling-water reactor (BWR) models was published.[15] This report summarized the cross sections, material compositions, and overall characteristics of the models as well as the calculations methodology used in developing the cross-section data. A report documenting the updated ORIGEN decay and photon libraries was also published.[16] The decay library includes information about the half-lives decay-branching ratios, recoverable heat per decay, and Radionuclide Concentration Guide values for the 1299 nuclides considered by ORIGEN. The photon library gives the photons per decay for ~450 of the most important nuclides considered by ORIGEN.

At the present time, reactor physics calculations have been completed, and ORIGEN calculations are available for PWRs fueled with denatured $^{233}UO_2$ in ThO_2, PuO_2 in ThO_2, and low-enrichment $^{235}UO_2$ irradiated to a burnup of 50,000 MWd per metric ton of heavy metal. Reactor physics calculations are presently under way for a PWR fueled with self-generated, denatured $^{233}UO_2$ and denatured $^{235}UO_2$ in ThO_2. These reactor models will be documented during the next report period.

Updating the LMFBR models in ORIGEN was recently initiated by beginning reactor physics calculations on an advanced oxide $(Pu,U)O_2$ core fuel with UO_2 blankets. The type of information developed here will be similar to that for the light-water reactors (LWRs). Three to five alternative fuel-cycle LMFBR models will also be developed along with an early oxide model.

Upon completion of the alternative fuel-cycle PWR models, reactor physics calculations will be initiated for D_2O-moderated reactors of the CANDU type. Other ORIGEN-related activities planned for the future will include issuing a users' manual for the latest version of ORIGEN and documenting the computer code and all of the updated information in a summary report.

4.5 ASSISTANCE TO OFFICE OF NUCLEAR WASTE ISOLATION

The Geologic Disposal Technology (GDT) Program was established in the Chemical Technology Division of ORNL on July 1, 1978, when the management responsibility for the overall National Waste Terminal Storage Program passed from the Office of Waste Isolation (OWI), Union Carbide Corporation–Nuclear Division, Oak Ridge, to the Office of Nuclear Waste Isolation (ONWI), Battelle Memorial Institute, Columbus, Ohio. The GDT Program serves as a liaison between ONWI and several programmatic efforts at ORNL in their area of responsibility. These efforts, which were initiated under the auspices of OWI, are reported elsewhere since they are separate studies and involve several divisions. In addition, significant attention is being given to specific requests for information, reviews of program documentation, and technical advice in general.

The principal portion of the effort on the GDT Program is devoted to a series of review and analytical studies that are outlined below.

Reviews of Waste-Rock Interactions

Brine migration in salt. Available theoretical and experimental information on the migration of small inclusions in salt deposits was reviewed and evaluated, and the results were published as ORNL-5526.

Volatiles in spent fuel. A comprehensive review of the chemical characteristics of spent fuel was also completed. The emphasis in this review was focused on the potential problems posed by gaseous and volatile constituents in spent fuel stored retrievably in a salt repository.

Radiolysis of brines. This review was undertaken solely to evaluate the potential of radiolysis in brine solutions in order to determine whether additional experimental work would be necessary to adequately handle the phenomena in repository safety analyses.

Thermal Analysis

Comparison of heat transfer codes. A large number of different heat transfer codes are currently

13. N. M. Greene, J. L. Lucius, L. M. Petrie, W. E. Ford III, J. E. White, and R. Q. Wright, *AMPX: A Modular Code System for Generating Coupled Multigroup Neutron-Gamma Libraries from ENDF/B*, ORNL/TM-3706 (March 1976).

14. T. B. Fowler, D. R. Vondy, and G. W. Cunningham, *Nuclear Reactor Core Analysis Code: CITATION*, ORNL/TM-2496, Rev. 2 (July 1971).

15. A. G. Croff, M. A. Bjerke, G. W. Morrison, and L. M. Petrie, *Revised Uranium-Plutonium Cycle PWR and BWR Models for the ORIGEN Computer Code*, ORNL/TM-6051 (September 1978).

16. A. G. Croff, R. L. Haese, and N. B. Gove, *Updated Decay and Photon Libraries for the ORIGEN Code*, ORNL/TM-6055 (February 1979).

in use throughout the waste disposal program. This study consisted of a direct comparison between them in order to accomplish a collective verification and, at the same time, to identify any significant discrepancies.

Limits of applicability. This study, which is an extension of the above comparison of heat transfer codes, will serve to define the particular strengths and weaknesses of the various codes, the types of waste disposal problems they were well suited to handle, and the ranges in which each was inappropriate.

Special Assignments

Reference repository conditions. At the request of ONWI, a special study was initiated to define the expected ranges of temperature, pressure, chemical and radiation conditions at various locations throughout a repository in salt, all as a function of time. The resulting document will serve to establish and limit the range of experimental conditions for which consequences must be evaluated.

International Atomic Energy Agency Document. In response to a specific request, a document entitled *Site Investigations for Repositories for Solid Radioactive Waste in Deep Continental Rocks* was prepared for publication by the International Atomic Energy Agency.

Assignment to the Federal Republic of Germany. As a part of the United States–Federal Republic of Germany bilateral agreement, an ORNL staff member has been sent on a 2-year assignment to the Institute für Tieflagerung, Glausthal-Zellerfeld. His mission is to represent the entire U.S. waste disposal program in Germany and throughout Europe and, in particular, to seek out opportunities for implementing joint or cooperative technical programs.

4.6 TRANSPORTATION TECHNOLOGY PROGRAM

The Transportation Technology Program has undergone substantial changes over the past year. Guidance for the program has been shifted from the OWI, which was disbanded, to the ONWI, operated by Battelle Memorial Institute, Columbus, Ohio. On October 1, 1978, all responsibilities for the transport of commercial and defense waste were transferred to the Transportation Technology Center (TTC), operated by Sandia Laboratories in Albuquerque, New Mexico. The ORNL effort was and, for the most part, continues to be aimed at the movement of commercial waste in support of ONWI's needs, although ~10% of our work is presently aimed at defense-waste transportation. All funding for the ORNL work now passes through TTC for coordination purposes and, as a result, programmatic details are worked out between TTC, ONWI, and ORNL.

Current efforts at ORNL are focused in a number of areas, including logistics assessments, the development of a legislative data base, the development of package system–facility interface criteria, a comparison of transportation-fleet-servicing facility concepts, criticality studies, and fission product release studies.

The spent fuel logistics model is designed to evaluate the optimal transportation routes for a wide range of shipping scenarios. The model can predict the manner in which spent fuel shipments will be made between reactors and away-from-reactor storage facilities (AFRs), between AFRs and repositories, and directly from reactors to repositories. The model also estimates the radiation exposure to the public resulting from those shipments. A number of constraints have been incorporated into the model in order to reflect the operational limitations of the receiving facilities and transportation systems, including fuel handling rates, storage capacities, and the number of truck and rail casks built per year.

The following information is generated for each shipping scenario:

1. total transportation costs;
2. destination of all fuel shipments;
3. inventories of stored fuel at the reactors, AFRs, and repositories;
4. cask fleet requirements for each type of shipping cask considered;
5. the optimal modal split for the transportation systems, when options are available;
6. the radiation exposure to the public;
7. total transportation distance (cask-kilometers) for each of the general transportation links;
8. the age distribution of fuel being stored at the AFRs and repository;
9. the number of shipments received at each receiving facility.

The nuclear data base associated with the model contains detailed information describing the spent fuel discharges and pool capacity for all reactors that are expected to be in commercial operation by 1990

(updated as of September 1978).[17] The data base also projects the installation of additional units between the years 1990 and 2010. The capacity of these units matches the 1978 DOE midrange capacity projection (325 GW in the year 2000).

A computer program to codify federal, state, and local regulations has been developed at ORNL. Most of the developmental work was done by the Ecological Science Information Center and was aimed at the retrieval, from the data base, of all current legislation that could affect the movement of radioactive materials through the states and local communities. The program will be utilized in conjunction with the spent fuel logistics model to determine viable shipping routes for radioactive materials.

A report[18] on spent fuel cask-facility interface criteria has been completed. This information is part of a larger study to develop interface criteria for all types of waste.

A fleet-servicing facility has been studied by Allied-General Nuclear Services (AGNS)[19] to evaluate the construction cost. The purpose of such a facility would be to service the fleet of spent fuel casks and vehicles that transport packages to and from a receiving site and to ensure that the transport systems are safe and operational when moving through the public domain. A substantial savings could probably be realized by colocating or integrating the fleet servicing facility and the receiving facility; current efforts at ORNL and AGNS are being directed toward quantifying the savings that might be accrued from such actions.

Criticality work is aimed at determining practical limits on the number of spent fuel assemblies that can be transported in one cask. NRC licensing procedures normally require that fresh fuel (in its most reactive condition) be carried in the cask for calculational purposes. This effort is intended to determine how restrictive that requirement is.

All available information on radioactive material releases resulting from transportation accidents is being collected.

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17. J. H. Allen, *U.S. LWR Spent Fuel Inventories*, ORNL Sub-78 4258 1, Nuclear Assurance Corporation (September 1978).

18. P. N. McCreery et al., *Interface Criteria for Shipping Casks and Fuel Handling Facilities*, Y OWI Sub-78 1, Allied-General Nuclear Services (January 1979).

19. P. N. McCreery et al., *The Conceptual Design of a Spent Fuel Cask Fleet Servicing Facility*, AGNS-1040-1.5-48, Allied-General Nuclear Services (September 1978).

5. Basic Science and Technology

5.1 SEPARATION SCIENCE

New Separations Agents

Continued interest exists in new separations agents with improved selectivity, stability, and physical properties for applications such as fuel reprocessing, waste-stream treatment, and resource recovery. Performance requirements are becoming more demanding in all these areas because of new hydrometallurgical problems and increased environmental concerns.

The following compounds were obtained during this reporting period for testing: one carbamoylmethylphosphonate, dihexyl(piperidinocarbonylmethyl)phosphonate, one diphosphine dioxide, two perfluorocarboxylic acids, and one crown ether. A standardized program for the evaluation of extractants is being established, and the results of this screening, along with information regarding the source and availability of the reagents, are being recorded in a catalog of reagents.

Distribution Equilibria

Extraction of iron from sulfate solutions by a primary amine. A detailed investigation of the extraction of Fe(III) from $(NH_4)_2SO_4$ and Na_2SO_4 solutions into solutions of a branched primary amine sulfate (Primene JM-T[1]) was prompted by a need for definitive information about a system for the separation of iron and aluminum. Recovery of a pure Al_2O_3 product from a sulfate solution such as a Calsinter leach solution (see p. 45) requires that several metals such as iron and titanium be effectively separated from the aluminum-bearing solution; solvent extraction is one very efficient method of accomplishing this separation. Since the distribution of aluminum from the aqueous phase to the organic phase in this type of system is negligible, only the iron distribution was considered here.

Extraction kinetics studies indicate that complete system equilibrium is not achieved until after ~20 hr of contact, although the variation between 1 hr and 20 hr is small and would have little, if any, effect on a process. Loading isotherms (Fig. 5.1) for 0.05, 0.125, 0.25, and 0.445 *M* Primene JM-T sulfate in toluene in equilibrium with 2.0 *M* $(NH_4)_2SO_4$ solutions of $Fe_2(SO_4)_3$, traced with ^{59}Fe, at pH 1.5 all show a slope of 1 at low loading (i.e., low organic-phase iron concentration), indicating that the iron exists in the same degree of self-association in both organic and aqueous phases. At the saturation-loading plateau, the ratio of amine sulfate to iron appears to approach 3. The upward swing of the curves above this loading level suggests a species change at high aqueous iron concentrations. A study of the dependence of the iron distribution coefficient, D_{Fe}, on amine concentration (Fig. 5.2) suggests a complex system in which the amine sulfate displays

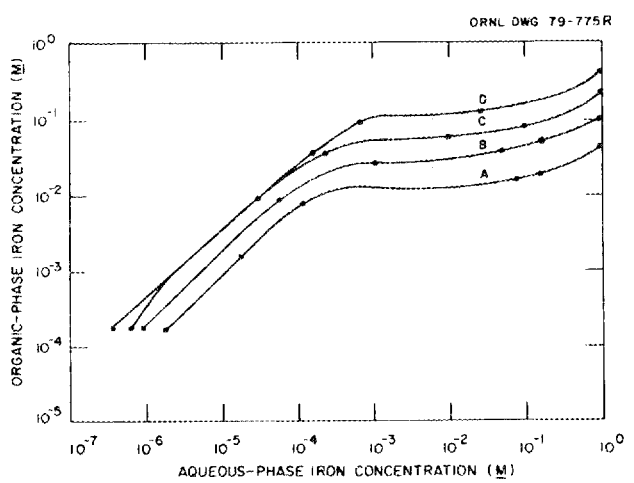

Fig. 5.1. Equilibrium loading curves for iron extraction by Primene JM-T sulfate in toluene. Organic phase: A, 0.05 *M*; B, 0.125 *M*; C, 0.25 *M*; and D, 0.445 *M* amine sulfate. Aqueous phase: 2.0 *M* $(NH_4)_2SO_4$ solutions containing varying concentrations of $Fe_2(SO_4)_3$, pH 1.5, traced with ^{59}Fe. Equal-volume-phase equilibration for 20 hr.

1. Manufactured by Rohm and Haas Company, Philadelphia. Purified by sequential dilute-acid and caustic scrubs.

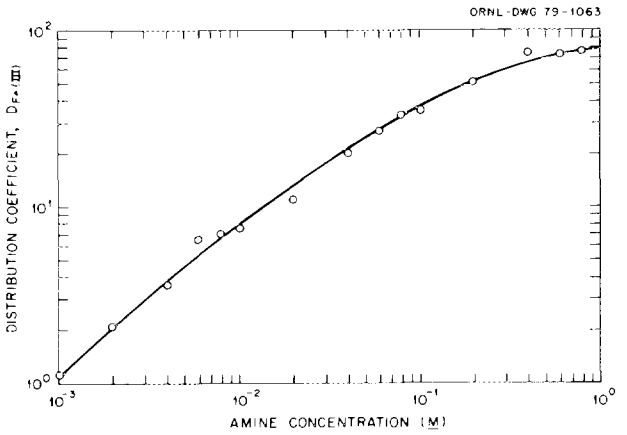

Fig. 5.2. Dependence of the iron extraction coefficient, D_{Fe}, on the organic-phase concentration of Primene JM-T sulfate. Aqueous phase: 2.0 *M* $(NH_4)_2SO_4$ solutions of 0.0001 *M* Fe(III) traced with ^{59}Fe.

trimeric behavior at low concentrations. As the amine concentration increases, the slope of the curve (defined by log D_{Fe} vs amine concentration) decreases, thus indicating further aggregation of the amine sulfate. It has previously[2] been shown that the reagent dependence is related to the degree of aggregation of the amine salt and the stoichiometry of the extracted species by the linear equation,

$$\log D_{Fe} = \frac{n}{j} \log [((RNH_3)_2SO_4)_j] + \log Q \ ,$$

where n is the number of amine sulfate molecules associated with each iron molecule in the organic-phase complex, j is the number of amine sulfate molecules per amine sulfate aggregate (not associated with iron), and Q is the equilibrium quotient. In a plot of log D_{Fe} vs log $[((RNH_3)_2SO_4)_j]$, the slope n/j is thus dependent on both the complex stoichiometry and the extractant aggregation. With the value of n equal to 3, as derived from Fig. 5.1 (six molecules of amine, or three of amine sulfate), the slope at low amine concentrations (n/j = 1) suggests amine sulfate trimers, and the slope at high amine concentrations (0.25) suggests an aggregation number of 12. This is consistent with earlier measurements of amine sulfate aggregation by light-scattering methods.[3]

2. K. A. Allen and W. J. McDowell, *J. Phys. Chem.* 64, 877 (1958).

3. K. A. Allen, *J. Phys. Chem.* 62, 1119 (1958).

Crown ethers as size-selective extraction synergists. Studies on the use of macrocyclic polyether molecules as solvent extraction reagents have been continued. The strength of the interaction with an alkali-metal ion of a given radius can be correlated with the size of the polyether ring, thus giving rise to a size-selective behavior. Crown ethers are poor extractants per se; however, when used in conjunction with a liquid cation exchanger such as di(2-ethylhexyl)phosphoric acid (HDEHP), the strong extraction characteristics of the ion exchanger are modified by a synergistic enhancement that is size selective. Figure 5.3 illustrates the size-dependent increase in the extraction of the alkali metals when a 0.125 *M* solution of HDEHP in benzene contains 0.250 *M* dicyclohexyl-18-crown-6. The extractability of the alkali metal depends on the size correspondence between the alkali-metal ion diameter and

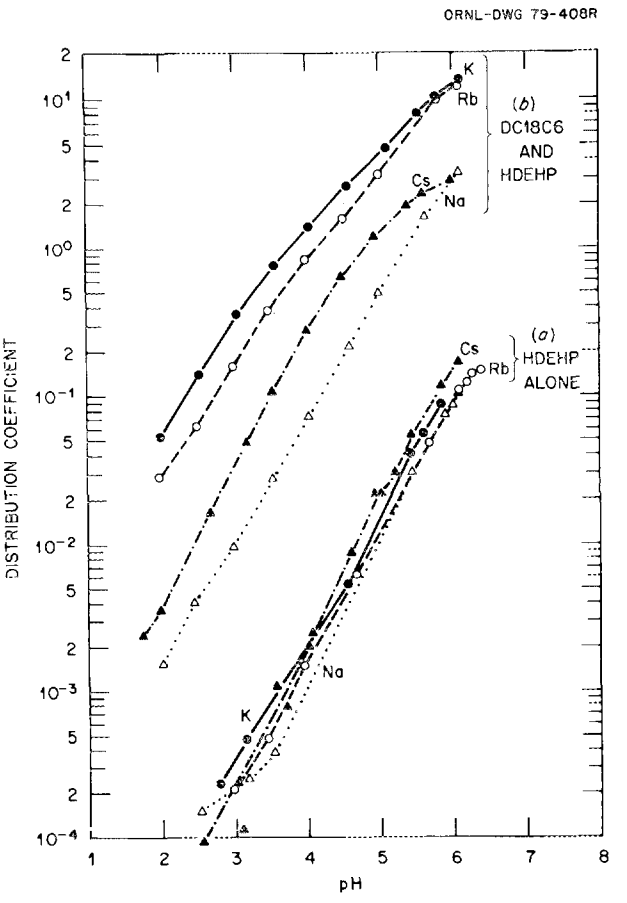

Fig. 5.3. Extraction of tracer-level alkali metals by HDEHP in benzene, (*a*) 0.125 *M* HDEHP alone and (*b*) HDEHP mixed with 0.25 *M* dicyclohexyl-18-crown-6, as a function of pH.

the crown ether cavity and on the pH of the aqueous phase. Figure 5.4 illustrates the synergistic factor (ratio of the distribution coefficient of the mixture to the sum of the distribution coefficients of the two components when used separately) for the following crown ethers: 12-crown-4 (12C4), cyclohexyl-15-crown-5 (C15C5), dicyclohexyl-18-crown-6 (DC18C6), and dicyclohexyl-24-crown-8 (DC24C8). The DC18C6 shows the largest synergistic effects in this solvent extraction system, presumably at least in part because of the best size fit between the potassium ion and the crown ether cavity. Part of the observed effect may also be due to the organic-phase solubility and aqueous-phase distribution characteristics of the compounds. The maximum synergistic factor for potassium, which in this case is ~400, is at pH 4, where the distribution coefficient for the mixture (from low-ionic-strength solutions)

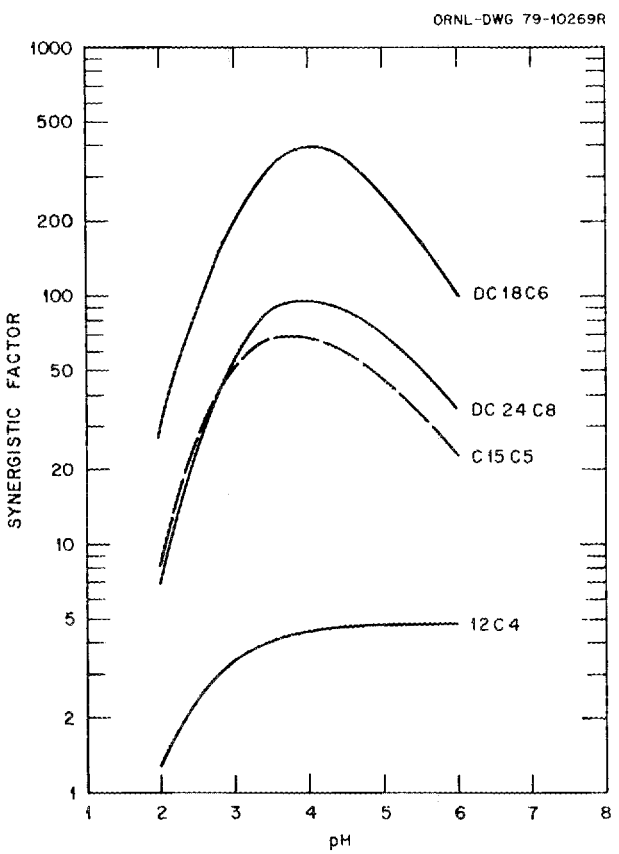

Fig. 5.4. The synergistic factor (ratio of the distribution coefficient of the mixture to the sum of the distribution coefficients of the individual components) of potassium extraction by HDEHP and four crown ethers: DC18C6, C15C5, 12C4, and DC24C8. Conditions are identical to those in Fig. 5.3.

is ~1.4 and the separation factor from sodium is in the range of 18 to 20.

Studies are under way on the interactions of crown ethers with the alkaline-earth metals. Preliminary results indicate that relatively little interaction occurs between crown ethers and highly hydrated metal ions, and that this behavior may be a strong function of ionic strength.

In addition to HDEHP, two other organic-soluble cation exchangers—didodecylnaphthalenesulfonic acid and a long-chain, branched carboxylic acid, Versatic 1519—have been tested in synergistic combination with DC18C6. A mixture consisting of 0.1 *M* sulfonic acid and 0.2 *M* DC18C6 in benzene was used to extract potassium from 0.1 *M* HNO_3 with a coefficient of 20. The synergistic factor compared to the sulfonic acid alone was 50. Similar tests with the carboxylic acid in benzene gave a coefficient of 0.02 and a synergistic factor of 10. However, these values were not necessarily obtained under conditions designed for maximum effect.

Extraction of weak and unusual acids. In this work, we have completed studies of acetic acid and thiocyanic-acid using the following five basic extractants: 1-nonyldecylamine (1NDA), didecylamine (DDA), the tertiary amine Adogen-364, trioctylphosphine oxide (TOPO), and tributyl phosphate (TBP). These and similar data to be obtained on other acids will provide a common basis for comparing the extraction of different acids. The data will also provide information that can be used directly in the cleanup of water from coal and petroleum processing. Figure 5.5 shows the neutralization of these bases, in 0.10 *M* toluene, by equilibration with aqueous acetic acid in sodium acetate at a total ionic strength of 1.0 *M*. Figure 5.6 shows the same bases neutralized by thiocyanic acid in potassium thiocyanate at a total ionic strength of 1 *M*. Differences in the extraction of thiocyanic acid by the various bases at a given pH are much greater than those for acetic acid. These data already suggest possible separations, as well as providing fundamental data about these systems.

Alcohol extraction. The systematic and fundamental investigation of the extraction of weakly acidic compounds by basic and neutral extractants has been extended to the study of ethanol separation from aqueous solutions. This type of information may be of use in the design of a process that would eliminate the distillation step in the dehydration of ethanol. Initial experiments have concentrated on the determination of distribution coefficients from

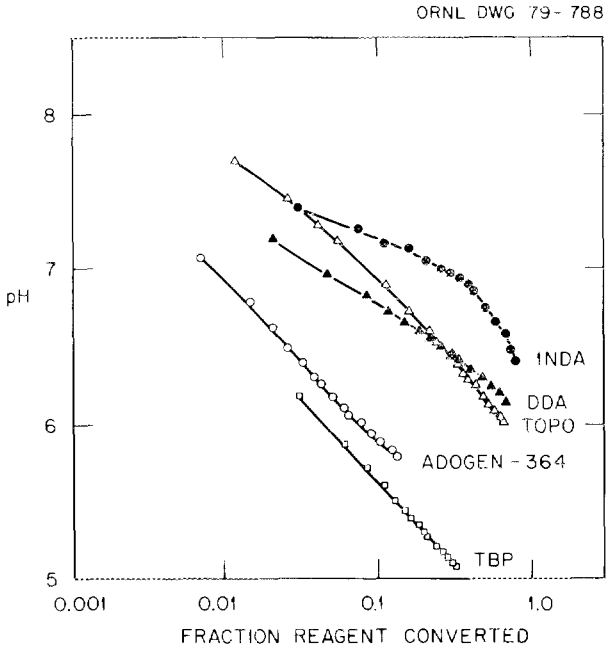

Fig. 5.5. Neutralization of the bases INDA, DDA, Adogen-364, TOPO, and TBP with acetic acid at 1.0 *M* total equilibrium anion concentration.

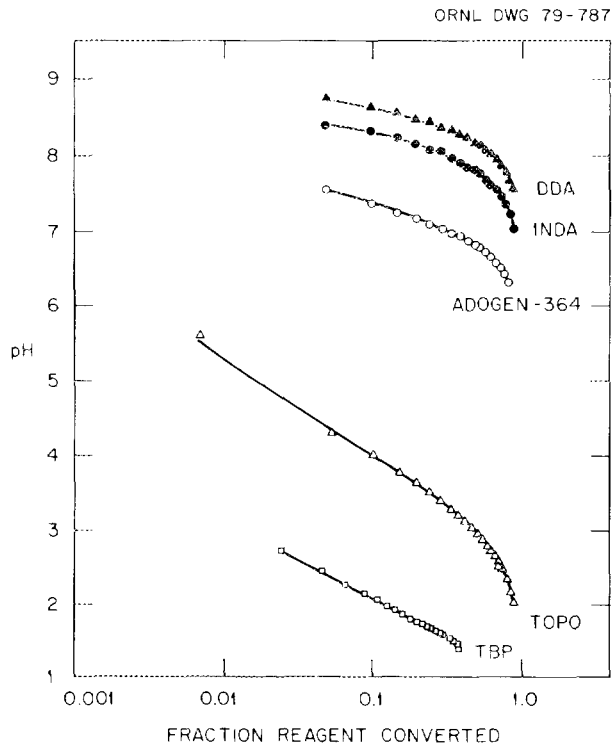

Fig. 5.6. Neutralization of the bases INDA, DDA, Adogen-364, TOPO, and TBP with thiocyanic acid in 1.0 *M* total equilibrium anion concentration.

simulated fermentation liquors (~9 vol % ethanol) using several classes of undiluted organic liquids as the extractants. The order of extractability was as follows: aliphatic hydrocarbons < saturated ring structures < unsaturated ring structures < ethers < ketones < oximes = alcohols < organic phosphates = phosphonates. A range of approximately two orders of magnitude was obtained for the coefficients (0.006 to 0.4). Separation factors from water were equal to ~10 at the higher extraction coefficients and generally increased as the alcohol extraction coefficient decreased.

Uranium extraction with sulfoxide. A fundamental study of the extraction of metal ions by organic sulfoxides has been initiated by a renewed investigation of the extraction of uranium with di(2-ethylhexyl) sulfoxide. The measured extraction coefficients at various HNO_3 concentrations (0.05 to 10 *M*) were ~50% lower than the values obtained earlier,[4] with about the same acid dependence over the entire range of acid concentrations. Vacuum distillation of the reagent produced a material whose extraction coefficients were still lower by ~7%, indicating that further investigation of the reagent purity is required.

Applications-Oriented Research

Ash removal from Solvent Refined Coal. Four salt melts have been examined to determine their effectiveness in removing mineral matter from the unfiltered oil of the Solvent Refined Coal-I (SRC-I) process. The most promising results have been obtained with a potassium-lithium-sodium chloride eutectic and a sodium-potassium hydroxide eutectic. The hydroxide eutectic was more effective than the chloride eutectic in reducing both the ash level and the sulfur content of the unfiltered oil. Contact of the molten hydroxide eutectic with the unfiltered oil for 30 min yielded product oils that contained <0.1% ash (after a water wash) and <0.1% sulfur.

Operating conditions for the molten-salt de-ashing process will be further refined in the next phase of the investigation.

Chemistry for resource recovery from fly ash. Until recently, a major portion of our applications-oriented research had been directed toward developing chemistry for the recovery of aluminum from fly ash. The developmental part of this work is now supported separately and will be described elsewhere

4. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977*, ORNL-5295, p. 35.

in this report. Two new methods of solubilizing the fused, refractory fly ash have been established in this program: a salt–sodium carbonate sinter/water–dilute acid leach method and a calcium sulfate–calcium carbonate sinter/dilute acid leach method. The latter, which is called the Calsinter process, is particularly attractive since it can use flue-gas scrubber sludge, a waste material, as one of the reagents.[5]

Uranium milling problems. Considerable attention is now being given to chemical problems associated with uranium milling. The present use of lower-grade ores and ores containing a wider variety of elements than those used previously is generating new problems for the mill operators. Currently, we have two projects under way that are related to uranium milling. The problem of separating uranium from vanadium in carbonate leach solutions is being considered in the first project. Extraction by a mixture of HDEHP and TOPO appears to be a rather promising solution. In the second project, we are involved in a cooperative effort with Arizona State University to investigate the fate of some of the less-studied uranium daughters in uranium milling. Alpha liquid-scintillation spectrometry methods developed at ORNL are being relied on heavily for uranium daughter assay. This solvent extraction–liquid scintillation method has recently been applied to uranium and ^{230}Th assays in phosphatic materials.[6]

Computer-Searchable Separations Systems Data Base

A user's manual for the separations systems data base was published as ORNL/TM-6593. The abstract is as follows:

Separations Systems Data Base: A User's Manual, by J. W. Roddy and W. J. McDowell. *Abstract:* A data base called "Separations Systems Data Base," designed specifically for the retrieval of information needed in chemical separations problems (i.e., how to perform a given separation under given conditions), is described. Included are descriptions of the basic methods of searching and retrieving information from the data base, the procedure for entering records into the data base, a listing of additional references concerning the computer information process, and an example of a typical record.

The initial entries are concerned primarily with liquid-liquid extraction methods for metal ions and salts. However, the data base is constructed so that almost any separation process can be accommodated.

Each record is indexed with information provided under the following fields: author, title, place of publication, date of publication, organization sponsoring work, brief abstract of work, abstract number if the work has been so referenced, type of separation system used (e.g., flotation), specific or generic name of the separation agent used (e.g., gold, copper), qualitative description of the supporting medium or matrix containing the substances before separation (e.g., nitrate), type of literature where the record was printed (e.g., book), and type of information that the article contains. Each of these fields may be searched independently of the others, and the last six fields contain specific key words which are listed in the report. Definitions are provided for the 33 information terms.

At present, the data base contains ~1500 items; this represents only a fraction of the total body of reference material available (considering only solvent extraction and ion exchange separations). However, considerable interest in this special-purpose data base has already been indicated.

Waste-Stream Processing Studies

Studies were continued to evaluate plutonium-loss mechanisms during fuel reprocessing that can contribute to undesirably high plutonium concentrations in process waste streams. These mechanisms include plutonium complexation with solvent-degradation products and the formation of insoluble molybdates that carry significant concentrations of plutonium.

During this report period, studies involving the spectrophotometric analysis of plutonium complexes in 30% TBP–*n*-dodecane (NDD) and the relative complex strengths of plutonium, uranium, zirconium, and thorium with hydrogen dibutylphosphate (HDBP) and dihydrogen monobutylphosphate (H_2MBP) were completed. The effects of radiolysis and chemical hydrolysis on the TBP degradation rate are presently being studied. Initial studies indicate that the formation rates of both HDBP and H_2MBP can be determined by spectrophotometric analysis of the plutonium-complexed species.

Work to date has shown that both HDBP and H_2MBP formation rates due to alpha radiolysis and HNO_3 hydrolysis of TBP are a strong function of temperature. For example, when 30% TBP–NDD that contains 0.6 *M* HNO_3 is exposed to an alpha dose of 5 Whr/liter, sufficient amounts of HDBP and H_2MBP are formed to complex 0.2, 1.0, and 8.5 g

5. F. G. Seeley, W. J. McDowell, and V. A. DeCarlo, "New Processes for the Recovery of Resource Materials from Coal Combustion Wastes," presented at 13th Intersociety Energy Conversion Engineering Conference, San Diego, Calif., Aug. 20–25, 1978 (to be published in the *Proceedings*).

6. E. J. Bouwer, J. W. McKlveen, and W. J. McDowell, "A Solvent Extraction–Liquid Scintillation Method for Assay of Uranium and Thorium in Phosphate Containing Material," *Nucl. Technol.* **42**, 102–111 (1979).

of plutonium per liter at 298, 323, and 353 K, respectively. Similarly, the $H_2MBP/HDBP + H_2MBP$ ratio increases with increasing temperature; at 298, 323, and 353 K, the percentages of plutonium complexed by H_2MBP were 5, 10, and 40, respectively.

Continued studies of insoluble molybdate formation have involved the identification and characterization of various species by x-ray diffraction, plutonium-carrying behavior, and formation-rate studies in HNO_3 as a function of acid concentration, metal concentration, and solution temperature.

X-ray powder patterns have now been obtained for 11 molybdate and tellurate compounds that can precipitate from a HNO_3 solution. Nine of these compounds have not been previously reported in the literature. Crystallographic indexing of these compounds is presently in progress.

Studies involving plutonium-carrying behavior by zirconium molybdate were summarized in a recently published paper.[7] This paper also reported the first published crystallographic data for plutonium molybdate and identified the zirconium species as $ZrMo_2O_7(OH)_2 \cdot 2H_2O$.

Continued studies on the precipitation rates of insoluble molybdates as a function of system variable were primarily concerned with thorium molybdate behavior. At temperatures of 363 K or higher, precipitation can occur at HNO_3 concentrations ranging from 1 to 12 *M*; precipitates start to form after ~3 hr in 3 *M* HNO_3.

Molybdate precipitation reactions are characterized by two kinetically distinguishable regions. Following solution makeup, an induction period occurs during which no precipitate formation is observed. This period is then followed by rapid precipitate formation. The induction period is a function of the degree of supersaturation of the solution; higher supersaturation leads to shorter induction periods. The rate of precipitation has a similar relationship to the degree of supersaturation. Both the induction period and the precipitation half-time, which is a measure of the precipitation rate, have been treated by classical and nonclassical precipitation theories, and areas of applicability for each of these theories have been found. These measurements therefore provide a basis for predicting the stability of fuel reprocessing solutions.

7. R. A. Penneman, R. G. Haire, and M. H. Lloyd, "Polymolybdates as Pu(IV) Hosts," submitted for publication to the *American Chemical Society Actinide Symposium Series.*

5.2 CHEMICAL ENGINEERING RESEARCH

Agglomeration Studies

The stability of coal-derived particles in benzene and cyclohexane was determined spectrophotometrically, and the results were compared to standard mixtures of carbon black in these solvents. Coal-derived solids settled more slowly than carbon black particles in the absence of an organic electrolyte, but the carbon black particles were rendered more stable in the presence of Aerosol OT (AOT).[8] The light transmittance of the coal-derived particle mixtures increased from 20% initially to 35% after 1 hr and 75% after 4 days. The transmittance of asphaltene mixtures increased to only 24% after 4 days, and the transmittance of carbon black mixtures did not increase at all during this period.

A 1-mm-deep square cell was constructed to quantify zeta potential (ζ) values. Results from the apparatus compared well with those obtained from a commercial zeta-meter device[9] and with literature values of A. Kitahara[10] for mixtures of carbon black benzene and carbon black cyclohexane. The ζ values of coal-derived solids were measured in cyclohexane, and the results are compared to carbon black in Fig. 5.7. Values determined for coal-derived particles in coal-derived oils are given in Table 5.1.

Derjaguin[11] lists the following stability criterion for an energy barrier of 7 kT:

$$\zeta = \frac{20\ kT}{Da},$$

where

k = Boltzmann's constant;

T = absolute temperature, K;

D = dielectric constant;

a = particle diameter.

Under the conditions of these experiments, this formula indicates the stability of particles with ζ values $\geqslant$13.6 mV. Davies and Rideal[12] favor a more stringent requirement,

8. Marketed by American Cyanamid Co.

9. Zeta-Meter, Inc., New York.

10. A. Kitahara, A. Karasowa, and H. Yamada, *J. Colloid Interface Sci.* **25**, 490–95 (1967).

11. B. V. Derjaguin, *Trans. Faraday Soc.* **36**, 203, 730 (1940); *Trans. Faraday Soc.* **18**, 85 (1954).

12. J. T. Davies and E. K. Rideal, *Interfacial Phenomena*, 2nd ed., Academic Press, New York, 1963.

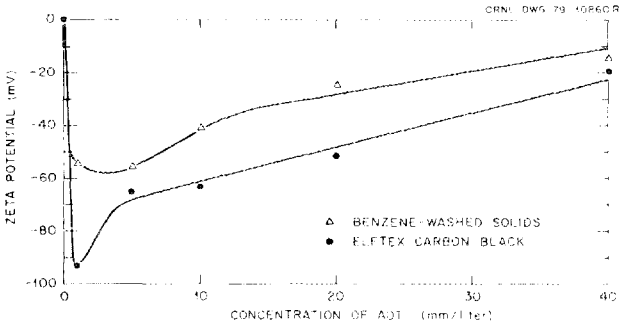

Fig. 5.7. Solvent refined coal solids compared to carbon black in cyclohexane mixtures.

$$\zeta^2 = \frac{45\ kT}{Da},$$

corresponding to an energy barrier of 15 kT. This formula indicates the stability of particles with ζ values $\geqslant$20.5 mV. Both criteria, along with the ζ values in Table 5.1, show that a significant portion of the stability of coal-derived particles in coal-derived liquids is due to surface charge.

Future experiments will correlate ζ and stability and will attempt to determine the charge-stabilizing species. Possible methods of charge destabilization to effect agglomeration will also be explored.

Continuous Chromatography

Studies on the separation of various metals in a sulfate solution have resulted in significant improvements over results reported previously.[13] The sulfate system is contained in two of the proposed flowsheets for the recovery of resource materials from coal residues, the most promising being the Calsinter process (Sect. 5.3). This process consists of sintering with limestone and flue-gas desulfurization sludge followed by leaching with H_2SO_4 to extract the metal values. The major metals involved are aluminum and iron. The separation of these metals by continuous chromatography is shown in Fig. 5.8. The feed material was a simulated leach liquor containing 4.0 g of iron and 7.0 g of aluminum per liter. This material was continuously fed to the column at the rate of 4 ml/min. Separation was performed using gradient-elution techniques with two eluents. A 1.0 M $(NH_4)SO_4$–0.025 M H_2SO_4 solution was used as the eluting agent in quadrants 1 and 2, while a solution of 0.5 M $(NH_4)_2SO_4$ and 0.025 M H_2SO_4 was used in quadrants 3 and 4. The feed point was located in quadrant 4 approximately 33° from the boundary of quadrant 1, and the rotation rate was 210°/hr. These conditions were chosen so that iron could be eluted by the lower-concentration material and aluminum by the more-concentrated reagent. This scheme was necessary in order to avoid the high dilution of metals during the separation.

The column effluent was monitored with a spectrophotometer to determine the iron at 401 nm; aluminum, however, cannot be detected by this method. Samples taken at 4.5° intervals were analyzed by atomic absorption for both iron and aluminum to determine the concentration profiles.

13. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1978*, ORNL-5383, p. 41.

Table 5.1. Solids in coal-derived oils

Coal-derived liquid	Solids	Additive	Zeta potential (mV)	
			Pyridine-washed solids	Benzene-washed solids
Oils	0.05 wt % SRC solids		+17.7 ± 0.7	+23.7 ± 0.4
Oils	0.001 wt % SRC solids	20% decane		+12.7 ± 0.2
Oils	0.001 wt % SRC solids + 1.0 wt % asphaltenes		+24.4	+23.4 ± 0.8
Oils	0.001 wt % SRC solids + 1.0 wt % asphaltenes	20% decane		+24.3 ± 2.8
Oils + resins	0.05 wt % SRC solids			+24.1 ± 0.5

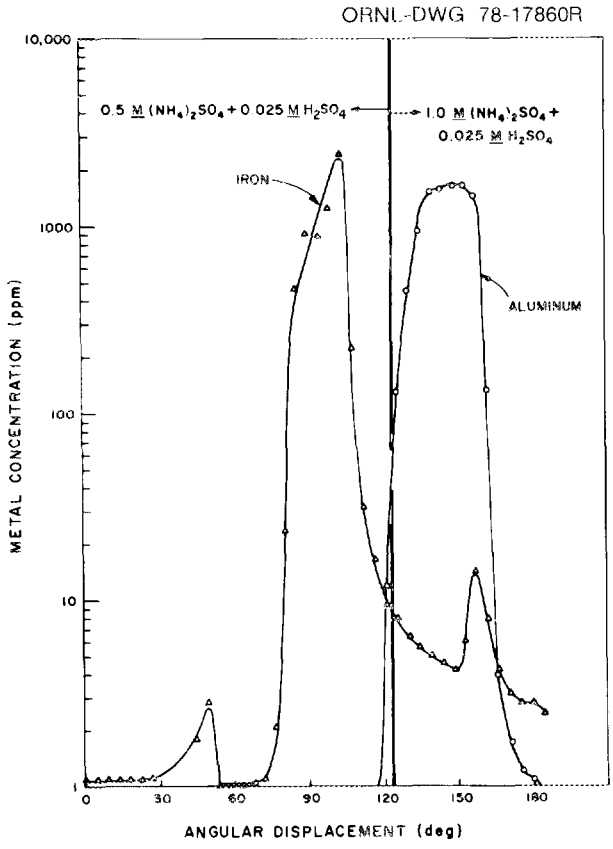

Fig. 5.8. Separation of iron and aluminum sulfates using gradient-elution techniques on the continuous annular chromatograph.

Peak concentrations of 2.34 and 1.65 g/liter were measured for iron and aluminum respectively. The dilution factors for collected fractions containing the two metals were reduced from 19 for iron and 50 for aluminum (achieved in earlier experiments with a single eluent) to ~8 for each metal (Table 5.2), while still maintaining reasonable recoveries. Cross-contamination refers to the concentration of the opposite component that would be present if the collected fraction were reduced to the metal. The higher contamination of iron in the aluminum is a result of a minor iron peak occurring near the aluminum peak.

Further studies of this system are planned in which other metals will be added to the system. These metals may include titanium and chromium. The possibility of separating trace metals such as chromium, strontium, copper, and others will also be examined. This type of separation might be performed after the major components have been removed.

Experimental work on the cobalt-nickel system has allowed the height equivalent of a theoretical plate (HETP) to be determined as a function of the superficial eluent velocity in the column. This relationship for cobalt-1 is shown in Fig. 5.9. Studies have also characterized the effect of feed concentration on the resolution for the Cu-Ni-Co system. Resolution is defined as

$$R = \frac{2(\theta_2 - \theta_1)}{W_1^c + W_2^c} ,$$

where θ_i is the elution position of the peak concentration of species i, and W_i^c is the exit bandwidth of species i in angular units. Figure 5.10 shows the decrease in resolution that is experienced with this system as the concentration increases. Data from this system have also been utilized in the development of a model for multicomponent separations on the continuous annular chromatograph. This differential model accurately predicts solute peak positions in the column effluent and qualitatively predicts trends in solute resolution as a function of the increasing bandwidth of the solute feed pulse. The primary advantages of the model are its simplicity, in terms of the calculations involved, and the fact that it

Table 5.2. Continuous ion exchange separation of iron and aluminum[a]

Element	Effective K value	Dilution[b]	Recovery (%)	Cross-contamination (%)
Fe	1.31	7.4	92	0.029
Al	2.36	8.5	98	0.66

[a]Conditions: feed – simulated H_2SO_4 leach liquor adjusted to pH 2.0; eluent – gradient elution with 0.5 *M* $(NH_4)_2SO_4$ and 1.0 *M* $(NH_4)_2SO_4$, both containing 0.025 *M* H_2SO_4.

[b]Ratio of metal concentration in the feed to the metal concentration in the separated fraction.

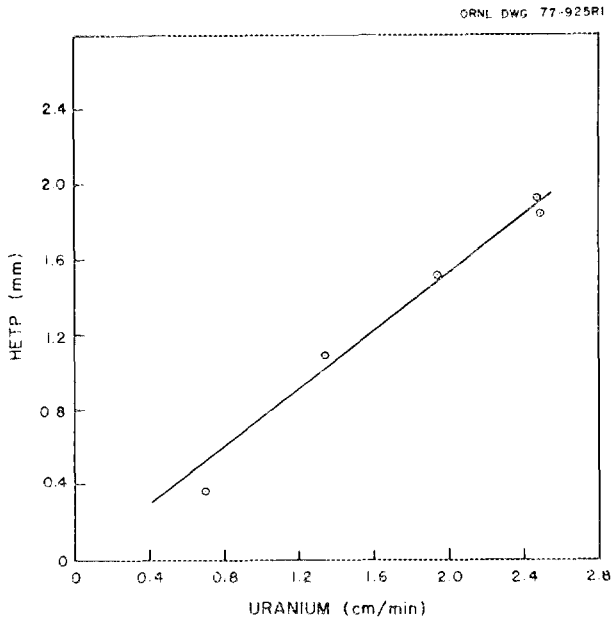

Fig. 5.9. Effect of superficial eluent velocity on the HETP for cobalt-1 with 1 M $(NH_4)_2CO_3$.

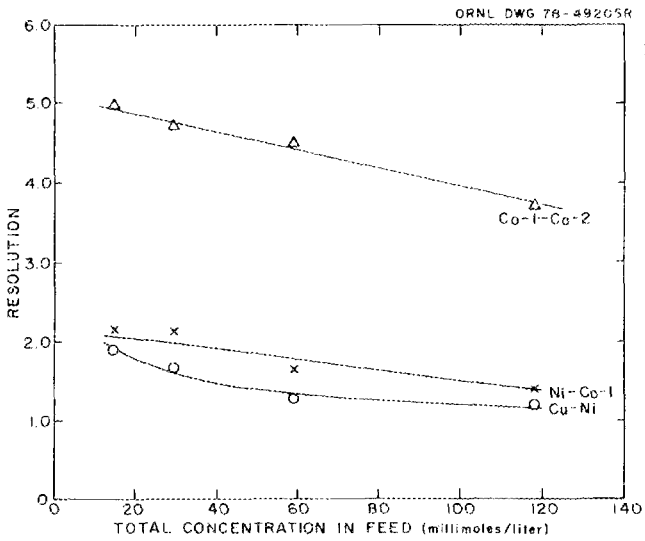

Fig. 5.10. Effect of total feed concentration on column resolution for the Cu-Ni-Co system with 1 M $(NH_4)_2CO_3$.

incorporates the nonlinear solute-resin binding isotherms common in many ion exchange separations. Dispersion effects are not considered in the present model, but work is under way to include them in an improved version.

Preliminary work has been performed on the separation of zirconium and hafnium sulfates with H_2SO_4. This system is important primarily because of the demand for hafnium-free zirconium in nuclear reactors. Work thus far has been done on a new, smaller chromatograph (10 cm in diameter), which is useful for scouting studies.

Other work has included planning for the construction of a larger chromatograph to test scale-up relationships and to better demonstrate the device. Much of the design work on this machine and its associated systems has been completed.

Deep-Bed Filtration

The removal of very small particles from process and waste streams is both expensive and difficult, but the need for such separations arises frequently in energy-related processes such as nuclear fuel reprocessing and particularly coal conversion. Deep-bed filtration is a solid-fluid separation process that shows considerable promise. One novel deep-bed filtration process is currently being studied that uses a packed bed of solids (diameters of ~0.5 to 1.0 mm) in an electric field as a filter. The electric field polarizes the solids in the bed so that charged, colloidal particles are attracted to the solids. The liquid-solid suspension is passed through the bed, and the solids are retained on the packing by the electrical attraction mechanism.

An experimental system has been assembled to study this type of filtration, as shown in Fig. 5.11. The system consists of (1) a feed tank, (2) a pump for circulating the feed, (3) rotameters and valves for metering the flow rate, (4) a filter column with provision for application to an electric field, (5) a manometer for measuring bed pressure drop, and (6) an effluent receiver on an electronic balance used for continuous monitoring and recording of the effluent flow rate. In addition, the solids concentration of the effluent is continuously monitored with a spectrophotometer. Data from the electronic balance and spectrophotometer are monitored and recorded with an on-line minicomputer.

Some shallow, "differential" beds have been tested in this system and have yielded some interesting results. The data in Fig. 5.12 were obtained using a 2.5-cm-deep bed of 1-mm-diam glass spheres. The suspension was 0.05 wt% TiO_2 (~1.0 μm in diameter) in cyclohexane. Removal efficiency (η) is expressed as a function of liquid velocity and field strength in Fig. 5.12. As might be expected, high removal efficiency is attained at high field strengths and low suspension flow rates. Runs made with no applied

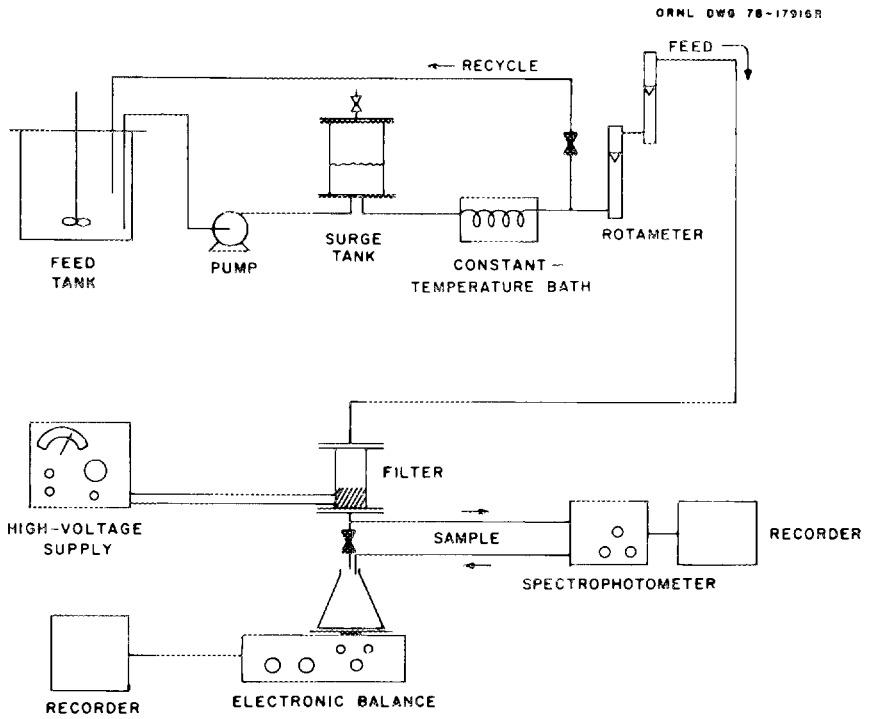

Fig. 5.11. Schematic of deep-bed filtration system.

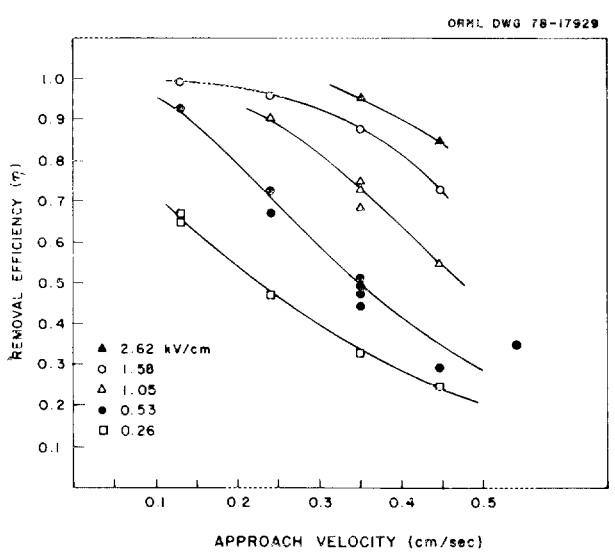

Fig. 5.12. Raw data obtained from shallow-bed experiments.

field (not shown in Fig. 5.12) showed no removal of solids ($\eta = 0.0$).

In addition to the experimental program, an effort has been made to understand the fundamental mechanisms of the removal process. The forces on a suspended particle in a flowing stream near a sphere in an electric field have been analyzed. The pertinent equations have been written and cast in dimensionless form, yielding dimensionless parameters that characterize the system. These parameters correspond to inertial, gravitational, electrical, and other forces; only the electrical parameter, however, is necessary to characterize the system. The data presented in Fig. 5.12 are plotted as removal efficiency vs the electrical parameter in Fig. 5.13, where

e = electrophoretic mobility of the particles, $cm^2/V\text{-}sec$;

E_0 = applied field strength, V/cm;

U_0 = characteristic liquid velocity, cm/sec.

As shown in Fig. 5.13, the shallow-bed filtration data are adequately correlated to the single electrical parameter.

Further work on this concept is progressing. Runs using much deeper beds have produced very high removal efficiencies ($\eta \rightarrow 1.0$) for long run times. The modeling effort has focused on the mechanics of deeper beds and transient breakthrough phenomena.

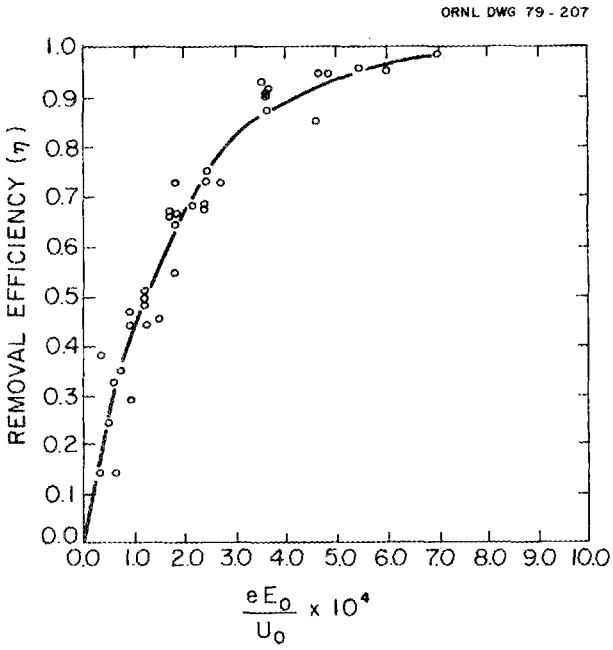

Fig. 5.13. Correlation of data obtained from shallow-bed experiments.

Because of the promising results that have been obtained with this filtration process, a system for the filtration of coal liquids has been assembled and is currently being installed. Results from this unit are expected soon.

High-Temperature Slagging

The most important metallurgical extraction processes depend on reactions involving slag-gas-metal systems. The thermodynamics of these reactions are often well established, but the kinetics of the systems have received less attention. The objective of this study is to develop improved contacting equipment for a specific slag-metal application. The removal of copper from scrap metal is a major problem in the recycle of many iron-base metals and is currently of primary interest.

The experimental investigation can be divided into three distinct areas of research: (1) contactor performance with the mass transfer rate limited by the extracting slag phase, (2) contactor performance with the mass transfer rate limited by the base-metal phase, and (3) evaluation of slagging media for the extraction of copper from molten iron. In the first area of research, a potential high-temperature slagging process has been simulated using a gas-sparged, mercury-water contactor. An electrochemical technique[14] was used to measure aqueous-film mass transfer coefficients enhanced by gas sparging through interface. The film coefficient measurements were determined from the diffusion-limited, electrically driven reduction of quinone to hydroquinone at the mercury surface. The variables of interest included gas flow rate, viscosity of the aqueous phase, and contactor size.

Several experiments were performed to determine the effects of aqueous-phase physical properties on mass transfer rates in gas-sparged, mercury-water contactors with square cross sections. Typical mass-transfer-coefficient data as a function of gas (nitrogen) sparge rate with a 10.2- by 10.2-cm contactor are shown in Fig. 5.14. The data were obtained

14. C. H. Brown, Jr., *Mass Transfer in Two-Phase Nondispersing Liquid-Liquid Contactors with a High-Density-Difference System*, ORNL/TM-6670 (1979).

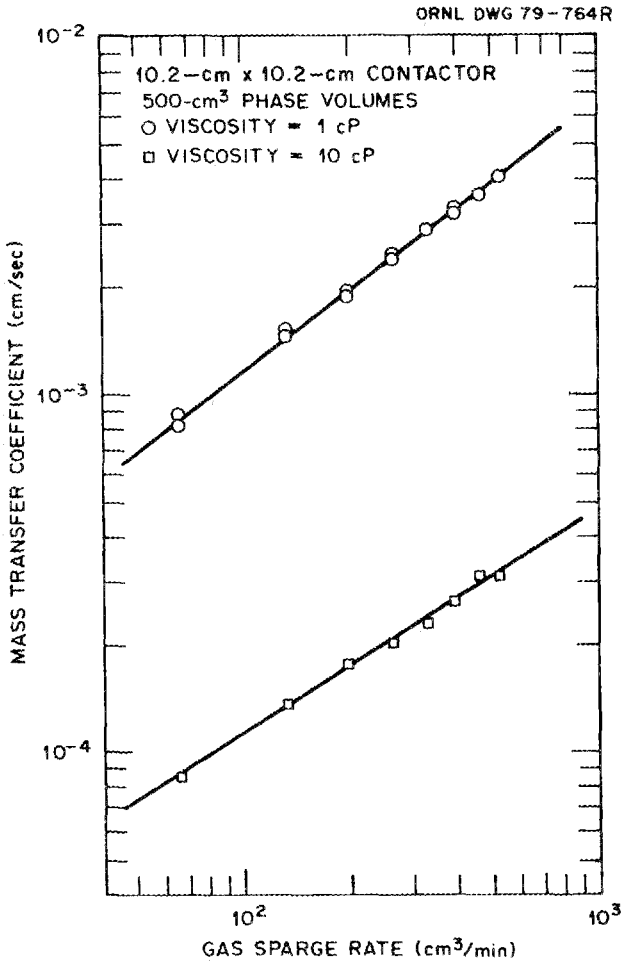

Fig. 5.14. Effect of gas sparge rate and aqueous-phase viscosity on the mass transfer coefficient in a mercury-water contactor.

at two aqueous-phase viscosities, 1 and 10 cP (45 wt % sucrose solution). Increasing the gas sparge rate induced greater motion at the mercury-water interface; however, the sparge rate was limited to values that did not permit the formation of dispersed droplets in either phase. The aqueous-film mass transfer coefficient is proportional to the gas sparge rate raised to a power between 0.6 and 0.8 and is inversely proportional to the aqueous-phase viscosity. The mass transfer data compare favorably with data obtained in a mechanically agitated, nondispersing contactor.[15]

No experimental work has been done in the second area of research; the third area is presently focusing on the selection of suitable slagging media for the extraction of copper from molten iron. The initial scouting experiments used small, unagitated crucibles; however, in subsequent studies the proposed slagging materials will be tested in gas-sparged contactors at a high temperature (1800 K). The extraction of copper from iron-base scrap metals using sodium sulfide as the light phase appears to be a potentially attractive high-temperature slagging application,[16] and we hope to test efficient metal-slag contactors with this system.

5.3 RESOURCE RECOVERY

The increased use of coal as a source of energy will lead to additional problems in the disposal of large quantities of ash, particularly if the ash is declared a hazardous waste. The total amount of ash produced each year currently exceeds 60 million tonnes.[17] This ash is a finely divided material that contains some metals of potential value (principally aluminum). Consideration is being given to the possibility of recovering those metal values having economic utility and/or presenting environmental hazards.

Process Chemical Development

We have reported preliminary laboratory-scale investigations of several methods for the recovery of aluminum and other metal values from the fly ash of an eastern Tennessee coal that had been fired at ~2023 K (1750°C). These investigations include processes such as lime-sinter and lime-soda-sinter that were initially developed for the recovery of aluminum from clays. In our tests, these processes proved capable of recovering only 50 to 60% of the aluminum from fly ash. A maximum of ~65% of the aluminum was recovered by direct-acid leach methods.[18-23]

Two new methods of recovering aluminum from fly ash that were developed at ORNL[18-23] are presently being evaluated for chemical optimization and economic feasibility. Both methods are capable of recovering >95% of the aluminum that was originally present in the fly ash by using a combination of sintering and dilute-acid leach techniques. The recoveries of Fe, Ti, Mn, U, and Th are also high. In the first of these two new methods, salt-soda sinter, fly ash is sintered with a $NaCl$-Na_2CO_3 mixture at a temperature of 800°C and subsequently leached, first with water and then with 1 *N* HNO_3 or H_2SO_4. In the second method, Calsinter, fly ash is sintered with a mixture of $CaCO_3$ and $CaSO_4$ (or SO_2 scrubber sludge solids) at temperatures ranging from 1273 to 1473 K (1000 to 1200°C). The resulting sinter cake is then leached with 2 to 4 *N* H_2SO_4. This latter method offers

15. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977,* ORNL-5295, pp. 55–56.

16. Y. A. Topkaya and W-K. Lu, "The Nature of Reactions Between Sodium Sulphide Slag and Carbon-Saturated-Iron and -Copper Alloys," *Metal-Slag-Gas Reactions and Processes,* ed. by Z. Foroulis and W. W. Smeltzer, pp. 11–139, Electrochemical Society, May 1975.

17. J. H. Faber, *Ash at Work,* National Ash Association, vol. X, No. 4 (1978).

18. V. A. DeCarlo, F. G. Seeley, R. M. Canon, W. J. McDowell, and K. B. Brown, *Evaluation of Potential Processes for the Recovery of Resource Materials from Coal Residues: Fly Ash,* ORNL/TM-6126 (March 1978).

19. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1978,* ORNL-5383, pp. 45–46.

20. F. G. Seeley, W. J. McDowell, and V. A. DeCarlo, "New Processes for the Recovery of Resource Materials from Coal Combustion Wastes," in the *Proceedings of the 13th Intersociety Energy Conversion Engineering Conference,* San Diego, Calif., Aug. 20–25, 1978, pp. 487–93.

21. R. M. Canon, F. G. Seeley, V. A. DeCarlo, W. J. McDowell, J. S. Watson, and K. B. Brown, "Removal and Recovery of Metals from Fly Ash," in the *Proceedings of Conference on Ash Technology and Marketing,* London, England, Oct. 22–27, 1978.

22. F. G. Seeley, R. M. Canon, and W. J. McDowell, "Chemical Development of New Processes for the Recovery of Resource Materials from Coal Ash," in the *Proceedings of the 5th International Ash Utilization Symposium,* Atlanta, Ga., Feb. 25–27, 1979.

23. R. M. Canon, F. G. Seeley, and J. S. Watson, "Engineering Analysis and Comparison of New Processes for the Recovery of Resource Materials from Coal Ash," in the *Proceedings of the 5th International Ash Utilization Symposium,* Atlanta, Ga., Feb. 25–27, 1979.

considerable product-option flexibility. Aluminum recovery can be accomplished after an extraction step (which recovers Fe, Ti, U, and Th) or after an iron-aluminum separation that is effected by an ion exchange adsorption–gradient elution procedure.

An analysis of all the Calsinter process data for aluminum solubilization from fly ash at sinter temperatures of 1073 to 1473 K (800 to 1200°C) for mixtures of fly ash with flue-gas desulfurization (FGD) scrubber sludge and limestone-sintering reagents, followed by H_2SO_4 leaching, showed:

1. Aluminum solubilization was independent of the sinter composition, provided the fly ash content was less than ~60%. The addition of limestone to scrubber sludge and fly ash did not increase aluminum solubilization.
2. Aluminum solubilization was directly dependent on the sinter temperature (Fig. 5.15). Temperatures of 1473 K (1200°C) or higher were required in order to attain >90% solubilization.
3. Aluminum solubilization was independent of the H_2SO_4 concentration used in the batch-leach step, provided the acid concentration was 4 *N* or higher.
4. Individual tests displayed considerable scatter due to cumulative experimental and analytical uncertainties; replicate tests were required to establish solubilization trends.

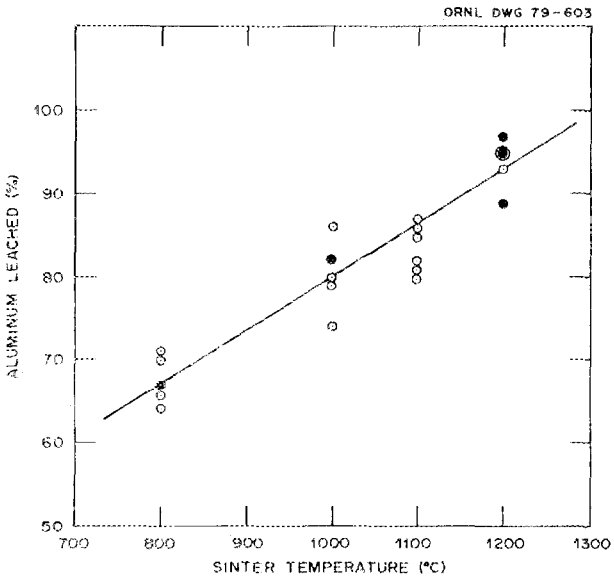

Fig. 5.15. Least-squares plot of aluminum leached vs Calsinter sinter temperature for one programmed temperature sequence.

This analysis was based on results obtained with only one TVA fly ash and one TVA scrubber sludge. Work is now under way on fly ashes obtained from nine power plants that burn coal from both eastern and western coal supply regions.

Current investigations show that recoveries of other metals such as Fe, Ti, Mn, and U all improve with increasing sintering temperature in the Calsinter process (Fig. 5.16). The fractions of eight metals (Ba, As, Cr, Pb, Se, Cd, Hg, and Ag), designated as being hazardous by the U.S. Environmental Protection Agency, that were leached by the H_2SO_4 solution were determined under Calsinter process conditions. As shown in Table 5.3, As, Cr, Cd, and Ag were completely solubilized, whereas Ba, Pb, Se, and Hg were essentially retained in the solids.

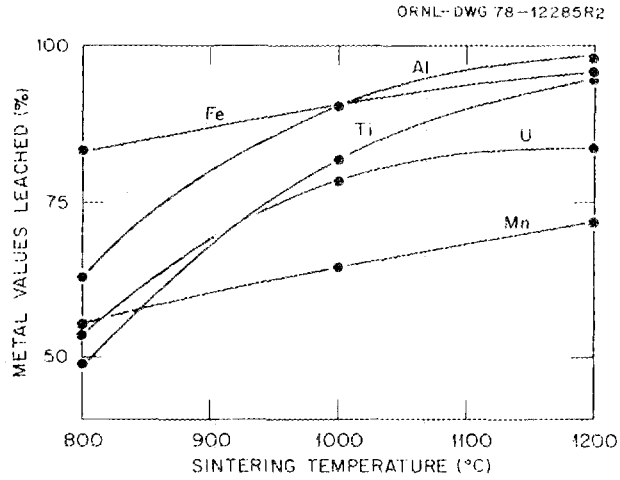

Fig. 5.16. Effect of sintering temperature on the recoveries of Al, Fe, Ti, Mn, and U by the Calsinter process.

Table 5.3. Distribution of hazardous metals to a H_2SO_4 leach solution

Metal	Concentration in fly ash (μg/g)	Percent solubilized
Ba	800	<3.5
As	340	100
Cr	132	100
Pb	121	5
Se	13	10
Cd	1.5	100
Hg	0.20	5
Ag	4.5×10^{-4}	100

Engineering Development

Engineering studies have included evaluations of overall process flowsheets for the treatment of fly ash and initial studies of processes for resource recovery from coal conversion (gasification and liquefaction) wastes. Preliminary economic evaluations and energy balance calculations for four proposed fly ash processes were completed. Although the results must be viewed with caution because so few data are available at this time, they clearly show that the recovery of metals can be attractive, even when reductions in ash disposal costs are not taken into consideration. The study also revealed the importance of calcium sulfate costs to the Calsinter process and the importance of the market price of cement to the lime-soda (or lime-sinter) process. Calsinter requires low-cost (preferably free or negative value) flue-gas desulfurization sludge.

Clear choices between the proposed processes cannot be made due to uncertainties in the economic analyses. Further studies on any or all of the reviewed processes appear to be justified. Experimental efforts included the construction of a bench-scale unit for studying subsequent separation steps, as well as sintering and leaching operations. One study demonstrated the use of a continuous chromatograph[24] to separate aluminum and iron from sulfate leach (Calsinter) liquor (see Sect. 5.2); further studies are planned to examine the feasibility of separating or isolating the hazardous (trace) metals from Calsinter liquors via continuous ion exchange.

Experimental studies of resource recovery from other coal wastes have also been initiated. Three materials have been studied thus far (Table 5.4). Char from a hydropyrolysis[25] unit at ORNL was burned in air at a temperature of 1173 K (900°C) to produce ash. This ash was extremely susceptible to direct-acid leach, and 90% of the aluminum was recovered by H_2SO_4 leaching. Ash from another gasifier, however, was essentially inert to any reasonable acid leaching, showing neither weight loss nor aluminum dissolution. After this ash had been sintered in the Calsinter process, over 90% of the aluminum was finally removed by an 8 N H_2SO_4 leach. The third waste, ash from a third gasifier, was also readily attacked by acids; gas evolution suggested the presence of excess carbonate. Chemical analyses have not been completed at this time, but aluminum recovery is expected to be high. These results indicate significant differences between the wastes of the proposed coal conversion processes. These differences will be important in assessing both the difficulties encountered in recovering the resources and the cost of the processes. In addition, the differences may affect disposal costs, even if resource recovery is not attempted.

Table 5.4. Aluminum recovery from gasifier ashes by direct-acid leach

Gasifier No.	Leach reagent	Aluminum recovery (%)
1	4 N H_2SO_4	86.9
2	4 N H_2SO_4	2.1
1	8 N H_2SO_4	94.5
2	8 N H_2SO_4	2.5
3	8 N H_2SO_4	95.5

5.4 INTERPHASE TRANSFER KINETICS

Zirconium Equilibrium and Kinetics

The solvent extraction chemistry of zirconium has been studied by numerous investigators[26–33] using

24. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979*, ORNL-5542, Sect. 5.2.

25. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979*, ORNL-5542, Sect. 3.

26. N. M. Adamskii, S. M. Karpacheva, I. N. Mel'nikov, and A. M. Rozen, "The Distribution of Zirconium on Extraction with *n*-Tributyl Phosphate," *Radiokhimiya* 2, 400 (1960).

27. K. Alcock, F. C. Bedford, W. H. Hardwick, and H. A. C. McKay, "Tri-*n*-butyl Phosphate as an Extracting Solvent for Inorganic Nitrates—I. Zirconium Nitrate," *J. Inorg. Nucl. Chem.* **4**, 100 (1957).

28. V. V. Fomin and S. A. Potapova, "Reproducibility of the Results in the Extraction of Microquantities of Zirconium from Nitric Acid Solutions of Di-*p*-Cresylphosphoric Acid," *Radiokhimiya* **10**, 162 (1968).

29. A. Sarsenov, Din Tkhi Lien, O. A. Sinegribova, and G. A. Yagodin, "The Extractability of Zirconium Nitrate as a Function of the Initial Compound Used to Prepare the Solutions," *Z. Neorg. Khim.* **19**, 2519 (1974).

30. V. B. Shevchenko, A. S. Solovkin, I. V. Shilin, L. M. Kirilov, A. S. Rodionov, and V. V. Balandina, "The Influence of Hydrocarbons of the Fatty and the Aromatic Series on the Extraction of U(VI), Pu(IV), Zr(IV), and Ce(III) with Tri-*n*-butyl Phosphate from Nitric Acid Solutions," *Radiokhimiya* 2, 281 (1960).

31. T. H. Siddall III, "Trialkyl Phosphates and Dialkyl Alkylphosphonates in Uranium and Thorium Extraction," *Ind. Eng. Chem.* **51**, 41 (1959).

32. A. A. Vashman, I. S. Pronin, L. V. Ilozheva, and A. L. Solovkin, "NMR Study of Tributyl Phosphate and Aqueous Nitric Acid Solutions of Zirconium Nitrate," *Z. Neorg. Khim.* 22, 2374 (1977).

33. G. A. Yagodin, O. A. Sinefribova, and A. M. Chekmarev, "The Effect of the Polymerization of Zirconium and Hafnium on Their Extraction by Different Classes of Organic Compounds," p. 2209 in the *Proceedings of the International Solvent Extraction Conference* (1974).

both tracer and macro zirconium concentrations. The tracer work showed that zirconium distribution depends on the TBP concentration to the second power[26,27] and the HNO_3 concentration to about the third power.[26,27,31] Studies that used macro zirconium concentrations demonstrated that certain nonequilibrating species could be separated by extracting the zirconium with TBP solutions and then back-scrubbing with HNO_3.[29] The aqueous species remaining after this treatment behaved as an equilibrium mixture.

The aqueous hydrolytic behavior of zirconium has been summarized,[34] and hydrolysis and polymerization constants for zirconium are known. Based on these data and the expected distribution behavior of zirconium, the reactions of zirconium are as follows:

$$Zr^{4+} + H_2O \overset{K_1}{\rightleftharpoons} Zr_3OH^{3+} + H^+ , \quad (1)$$

$$3Zr^{4+} + 4H_2O \overset{K_2}{\rightleftharpoons} Zr_3(OH)_4^{8+} + 4H^+ , \quad (2)$$

$$Zr_3(OH)_4^{8+} \xrightarrow{\text{heat}} \text{oxo-polymers} , \quad (3)$$

$$Zr^{4+} + 4NO_3^- + 2TBP \overset{K_3}{\rightleftharpoons} Zr(NO_3)_4 \cdot 2TBP , \quad (4)$$

$$ZrOH^{3+} + 3NO_3^- + 2TBP \overset{K_4}{\rightleftharpoons} Zr(OH)(NO_3)_3 \cdot 2TBP . \quad (5)$$

The equilibrium quotients for Eqs. (1), (2), (4), and (5) are, respectively,

$$K_1 = \frac{[ZrOH^{3+}][H^+]}{[Zr^{4+}]} = 0.28 , \quad (6)$$

$$K_2 = \frac{[Zr_3(OH)_4^{8+}][H^+]^4}{[Zr^{4+}]^3} 2.5 \times 10^5 , \quad (7)$$

$$K_3 = \frac{[Zr(NO_3)_4 \cdot 2TBP]}{[Zr^{4+}][NO_3^-]^4[TBP]^2} = 0.004 , \text{ and} \quad (8)$$

$$K_4 = \frac{[Zr(OH)(NO_3)_3 \cdot 2TBP]}{[ZrOH^{3+}][NO_3^-]^3[TBP]^2} = 1.0 , \quad (9)$$

where the terms in brackets are molar concentrations. It is recognized that if the activities are known, they should be used in the quotients. In the studies with HNO_3 solutions, the hydrogen and nitrate ion activities of Davis[35] were in better agreement with experimental results and were used; molar concentrations were used in all other cases. The TBP concentrations were taken as the initial TBP concentration minus the HNO_3 extracted (assumed to be the 1:1 TBP-HNO_3 complex). The values of the equilibrium quotients K_1 and K_2 were obtained from ref. 34; the values of K_3 and K_4 were obtained by trial-and-error fitting of distribution data—both tracer-level data[27] and data obtained using macro concentrations of zirconium. Some of the low-concentration data, corrected to a hypothetical 30% total TBP solution, are shown in Fig. 5.17. The line

34. C. F. Baes, Jr., and R. E. Mesmer, *The Hydrolysis of Cations*, pp. 152–58, Wiley, New York, 1976.

35. W. Davis, Jr., and J. J. de Bruin, "New Activity Coefficients of 0–100 Percent Aqueous Nitric Acid," *J. Inorg. Nucl. Chem.* 26, 1069 (1964).

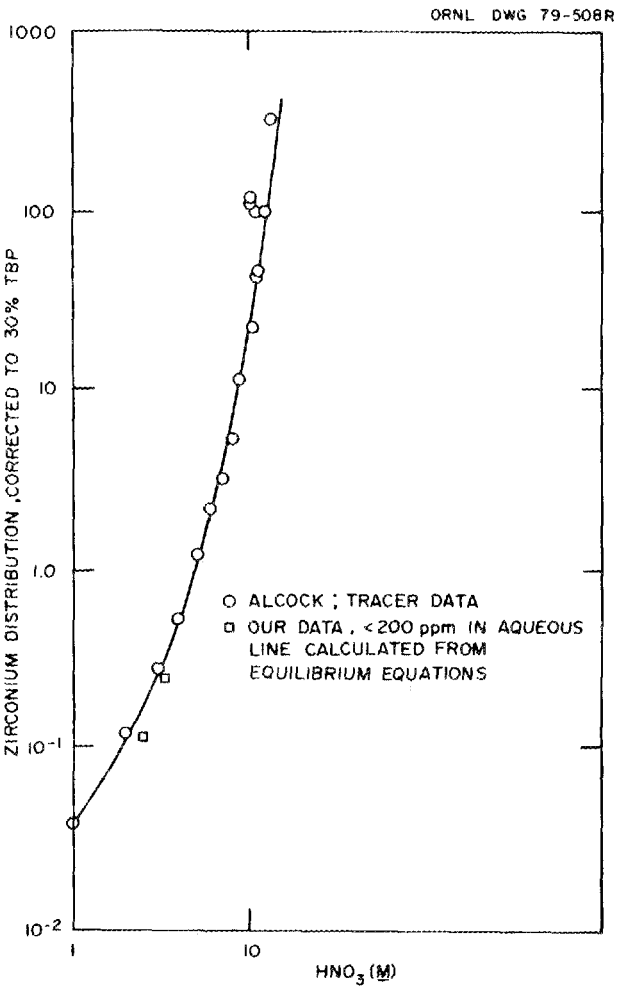

Fig. 5.17. Zirconium distribution vs HNO_3 concentration for low zirconium concentration. Data obtained from K. Alcock et al., "Tri-n-butyl Phosphate as an Extracting Solvent for Inorganic Nitrates—I. Zirconium Nitrate," *J. Inorg. Nucl. Chem.* 4, 100 (1957).

was calculated from the equilibria of Eqs. (6), (8), and (9). No polymeric species are possible at these low zirconium concentrations, and the agreement is excellent.

In our studies of the behavior of macro concentrations of zirconium, the zirconium solutions were prepared by first extracting zirconium from HNO_3 by TBP solutions and then back-scrubbing with 2 to 3 *M* HNO_3. Analyses were performed by x-ray fluorescence. Tests showed that the solvent extraction behavior of these solutions was different from that of the initial aqueous solutions, presumably because the nonequilibrating and nonextracting oxo-polymers had been removed. Subsequent to this treatment, the extraction behavior of the back-scrubbed zirconium solutions did not change over a period of 30 days at room temperature. The extraction behavior of zirconium in 2.5 *M* HNO_3 as a function of aqueous concentrations is shown in Fig. 5.18. The line was calculated by Eqs. (6)–(9). The agreement is excellent, leading to the conclusion that these equilibria do indeed represent the behavior of zirconium in HNO_3.

Since the concentration of the extractable Zr^{4+} and $ZrOH^{3+}$ ions can be calculated for solutions that are free of oxo-polymers, it is possible to study the extraction kinetics of these ions. All kinetic studies used a simple two-phase apparatus (Lewis cell) in which each phase is mixed by a paddle, with minimal disturbance to the interface. The equations used for the kinetic analyses are given below:

$$\frac{dC'}{dt} = -\frac{k'C'A}{V'} + \frac{kCA}{V}$$

(change in aqueous concentration), (10)

$$\frac{dC}{dt} = -\frac{kCA}{V} + \frac{k'C'A}{V}$$

(change in organic concentration), (11)

where C is the molar concentration of Zr^{4+} or $ZrOH^{3+}$ in the aqueous phase, or the zirconium complex in the organic phase, A is the interfacial area, V is the phase volume, and k is a rate constant. The primed symbols refer to the aqueous phase, and the symbols without primes refer to the organic phase. Since two extractable species, Zr^{4+} and $ZrOH^{3+}$, exist in the aqueous phase, interpretation of the kinetic results can be difficult. In the two cases to be presented, the experimental conditions are such that a single species dominates the extraction of zirconium. Figure 5.19 shows the effect of TBP concentration on the forward rate constant for Zr^{4+} at 3.5 *M* HNO_3 (Zr^{4+} predominates over $ZrOH^{3+}$ under these conditions). The power effect is ~2. Figure 5.20 shows the effect of neutral nitrate on the forward rate constant for $ZrOH^{3+}$ from mixtures containing 0.5 *M* HNO_3 and added $NaNO_3$ ($ZrOH^{3+}$ predominates over Zr^{4+} under these conditions).

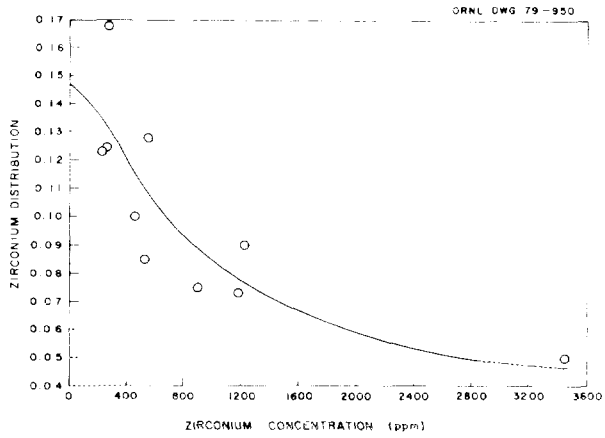

Fig. 5.18. Effect of aqueous zirconium concentration on zirconium distribution; 2.5 *M* HNO_3–30% TBP in normal paraffin diluent. Line is calculated from Eqs. (6) to (9).

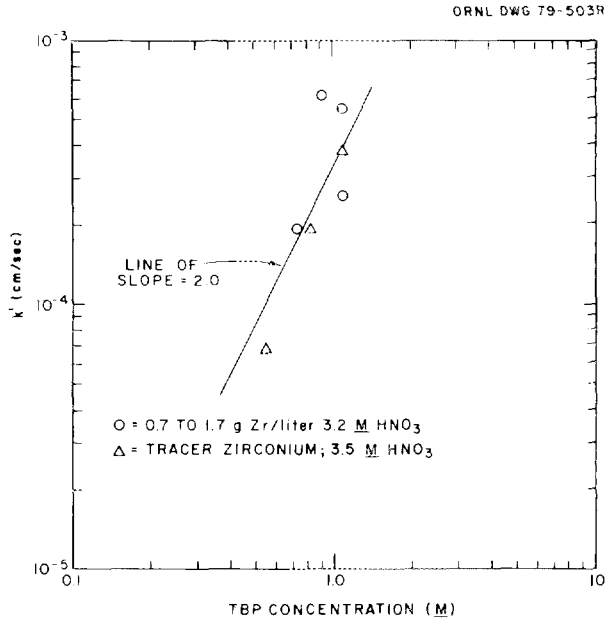

Fig. 5.19. Aqueous-to-organic rate constant of Zr^{4+} vs TBP concentration at 3.5 *M* HNO_3.

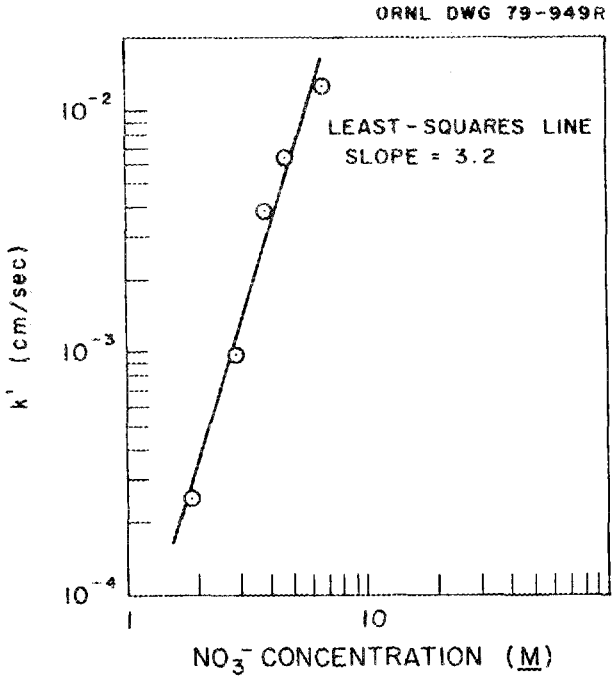

Fig. 5.20. Aqueous-to-organic rate constant of $ZrOH^{3+}$ vs nitrate concentration at 1 *M* free TBP (corrected for HNO_3 complexing of TBP).

5.5 ACTINIDE OXIDES, CARBIDES, AND NITRATES

Thermodynamics of the Actinide-C-O Systems

The carbothermic reduction of thorium and uranium-thorium dioxide to monocarbide has been assessed. Equilibrium calculations have yielded Th-C-O and U-Th-C-O phase equilibria and CO pressures generated during reduction. The CO pressures were found to be at least five orders of magnitude greater than the pressures for any of the other 15 gaseous species considered. This confirms that the monocarbide can be successfully prepared by carbothermic reductions.

Measurements of CO pressures as a function of temperature in the $ThO_2 + ThC_2 + C$ system are being made and are confirming the results of the calculated assessments. They will also be used to derive thermodynamic values for the dicarbides.

Thermodynamics of LWR Fuel Systems

Equilibrium thermodynamic calculations were performed on the Cs-U-Zr-H-I-O system that is assumed to exist in the fuel-cladding gap of light-water reactor fuel under in-reactor, steam, and 50% air conditions. The in-reactor oxygen potential is assumed to be controlled by either $UO_{2+x} + Cs_2UO_4$ or $Zr + ZrO_2$. The important in-reactor condensed phases are UO_{2+x}, Cs_2UO_4, and CsI, and the major gaseous species are Cs, Cs_2, CsI, and Cs_2I_2. The presence of steam does not alter these species, although CsOH gas also becomes a major gaseous species. In a 50% steam–50% air mixture, an equilibrium situation exists in which zirconium metal can react with iodine, ZrI_3, or liquid ZrI_2. In addition, the gaseous species ZrI_3 and ZrI_4 have large partial pressures under these conditions.

Transition Metal–Actinide-C Phase Equilibria

The chemical compatibility of uranium carbides and potential cladding alloys has been evaluated by thermodynamic modeling. In the thermodynamic modeling, it is assumed that the uranium carbide and the clad are in contact. The interface is then determined as the reaction area between bulk fuel (uranium carbide) and bulk clad alloy. Equilibrium thermodynamic calculations and experimental phase studies were used to determine the phases present in the interface.

We have made thermodynamic calculations at temperatures of 973 K and 1273 K for the fuel-clad interface of uranium carbides with Cr-Fe-Ni compositions of seven alloys: type 316 stainless steel, type 330 stainless steel, A286, M813, PE-16, Inconel 706, and Inconel 718. The following species were considered to be possible reaction products: [Cr, Fe, Ni]; [$UNiC_2$, $UFeC_2$]; [UFe_2, UNi_2, UCr_2]; [$Cr_{23}C_6$, $Fe_{23}C_6$]; [Cr_7C_3, Fe_7C_3]; UNi_5; UC; $UCrC_2$; Cr_3C_2; $UNi_{3.67}$; $UNi_{3.33}$; U_2C_3; U_2NiC_3; U; and C. Note that the bracketed species denote solid solution. This list includes all known binary and ternary compounds in the U-C-Cr-Fe-Ni system.

No thermodynamic data were available for the $UNiC_2$ compound; hence, it was necessary to evaluate its standard free energy of formation, ΔG_f°, from phase studies. A specimen having the elemental composition 2U:2C:3Cr:6Ni was arc melted and annealed for 1.2×10^6 sec (2 weeks) at 1273 K. The phases in this specimen were determined by x-ray diffraction and x-ray electron spectroscopy as UNi_5, UC, $UNiC_2$, and a chromium carbide. From the known thermodynamic values of other compounds in the UN–(Cr, Ni) system, the ΔG_f° of $UNiC_2$ at 1273 K is calculated to be in the range of −189 to −198 kJ/mole.

At 1273 K, the solid solutions [$UNiC_2$, $UFeC_2$] and [UFe_2, UNi_2, UCr_2] are the principal reaction

products in all of the calculated interfaces. The compounds UNi_5 and Cr_7C_3 are also calculated to be present in interfaces involving alloys that contain large amounts of nickel such as Inconel 718 and PE-16. At temperatures of <1173 K, the complex carbides [$UNiC_2$, $UFeC_2$] reportedly[36] are not formed because of kinetic reasons. Thus, the principal reaction products at 973 K are UNi_5 and Cr_7C_3 for all of the calculated interfaces.

Type 316 stainless steel was significantly less reactive than any of the other alloys we considered. At temperatures where the complex carbides do not form, there is very little reaction between uranium monocarbide and the Cr-Fe-Ni content of type 316 stainless steel. This is due to its relatively higher iron content when compared to the other alloys. Nickel forms complex carbides and intermetallic compounds with large negative free energies of formation, and chromium forms carbides with large negative free energies of formation. Iron can take part in the formation of these compounds, but the contribution to the free energy of formation by nickel and by chromium is much more significant. Inconel 718, which contains the largest proportion of nickel of any of these potential clad alloys, also produced the greatest amount of reaction product in the interface.

5.6 FUSION ENERGY STUDIES

Cryosorption Vacuum Pumping

Cryosorption vacuum pumps continue to be the principal type of pump considered for power-producing fusion reactors.[37] In these reactors, the use of liquid helium-cooled (4.2 K) cryocondensation pumps for hydrogen in neutral-beam injector systems may be precluded because of the high level of neutron heating. Cryosorption pumps operating at higher temperatures (10 to 20 K) can withstand higher heat fluxes and continue to operate effectively at these conditions. The liquid helium-cooled cryosorption pump is still the only identifiable pump for recovering helium from the plasma or divertor chambers which meets all fusion reactor constraints on speed, tritium containment, and quality of vacuum.

In a continuing effort to determine the best adsorbent and operating temperature for cryosorption pumps designed to collect only hydrogen, additional data have been collected for a panel coated with molecular sieve type Na-Y (MS-Na-Y). Pumping speeds were measured at various temperatures ranging from 12 to 26 K, at six feed rates. Results confirm that MS-Na-Y shows some promise for pumping at speeds that are an order of magnitude higher than those for MS-5A at temperatures near 15 K. The speeds also appear to be unaffected by any variation of the chevron temperature in the range of 79 to 200 K. Panel temperature has been found to be nonuniform at temperatures <30 K; a variation of as much as 5 K appears to exist near 15 K. Efforts to eliminate these differences by changing the helium coolant flow rate and direction were unsuccessful. Temperature differences appear to be a function of the panel design rather than the cooling configuration.

Pumps designed to accommodate mixtures of hydrogen and helium generally employ the compound pump concept in which the helium pump is placed behind the hydrogen pump so that hydrogen will not condense on and hence block the 4.2 K helium cryosorption surface. To obtain an optimal design for such a pump, the amount of hydrogen which can reach the helium panel must be determined. Figure 5.21 shows the results of several tests in which helium-hydrogen mixtures were fed to the 4.2 K MS-5A cryosorption pump. In this pump, cyclic variations in pumping speed[38] occur for helium

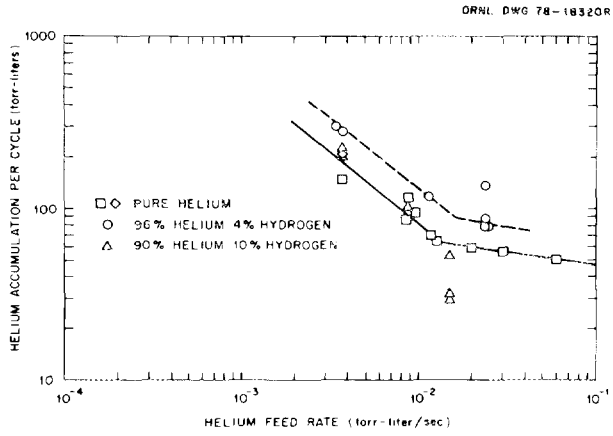

Fig. 5.21. Helium accumulation between instabilities as a function of helium feed rate for a 320-cm^2 MS-5A panel at 4.2 K.

36. J. C. Passefort, F. Anselin, and D. Calais, "Reactions between Nickel and the Carbides and Nitrides of Uranium and Their Solid Solutions," *Sci. Ceram.* 4, 421 (1967).

37. J. S. Watson and P. W. Fisher, "Vacuum Aspects of Tritium Recovery and Processing," pp. 690–96 in the *Proceedings of the Third Topical Meeting on the Technology of Nuclear Fusion*, vol. 2, American Nuclear Society, Santa Fe, N.M., May 9–11, 1978, CONF-780508.

38. P. W. Fisher and J. S. Watson, "Helium Pumping at 4.2 K by Molecular Sieve 5A," *J. Vac. Sci. Technol.* 16, 75 (1979).

at feed rates which exceed 2×10^{-3} torr-liter/sec. These data indicate that up to 10% hydrogen can be tolerated in the helium without adversely affecting the performance of the helium pump.

Fusion Reactor Blanket Processing Studies

A molten-lithium blanket has many advantages for breeding tritium in fusion reactors. One of the techniques being considered for the recovery of tritium from liquid lithium involves sorption on a hydrogen-gettering metal. Tritium sorption from molten lithium has been studied in a batch contactor at temperatures of 520 to 670 K using samples of yttrium metal.[39] With the static system, yttrium has shown significant removal rates from molten lithium, and the controlling mass transfer resistance appears to be in the liquid-lithium phase. Consequently, the mass transfer rate should be increased significantly with forced convection.

The results of tritium sorption from molten lithium in a static system enhance the feasibility of sorption as the first step in a blanket tritium-recovery process. A possible method for recovering tritium from yttrium getters involves heating the yttrium to temperatures well above the sorption temperature in the presence of an inert sweep gas.

To determine the sorption rate increase in a practical system, a flowing tritiated-lithium loop has been designed and assembled (see Fig. 5.22). Tritiated lithium is drawn from a liquid-metal reservoir into a transfer tank at temperatures between 470 and 670 K. The liquid lithium is then recirculated electromagnetically through a flowmeter and a sample chamber holding the yttrium sample. The liquid lithium is sampled by placing a tube attached to capillary tubing, the end of which leads to a manifold supplying both argon and vacuum, into the transfer lock formed by an O-ring seal and ball valve. The lithium samples are dissolved in water, the evolved tritium is oxidized, and the resulting solutions are analyzed for tritium by scintillation counting. The entire lithium loop is enclosed in an inert-atmosphere glove box to reduce oxygen and nitrogen contamination and to provide secondary tritium containment.

In one of the initial runs with this system, two metal samples (total weight, 8.31 g; total surface area, 28.95 cm^2) were contacted with flowing lithium (320 cm^3/min) at 570 K. The concentration of tritium in lithium decreased from 734 ppb to 7.0 ppb in 314 hr. The results of this run are shown in Fig. 5.23, where the tritium concentration, C, divided by the initial tritium concentration, C_0, is plotted as a

39. S. D. Clinton and J. S. Watson, "Tritium Removal from Liquid Metals by Sorption on Yttrium," pp. 1647–49 in the *Proceedings of the Seventh Symposium on Engineering Problems of Fusion Research*, vol. II (October 1977).

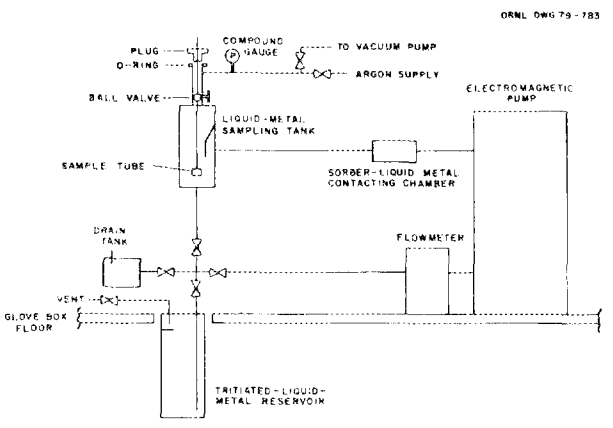

Fig. 5.22. Contacting apparatus for tritium sorption studies using forced convection of lithium.

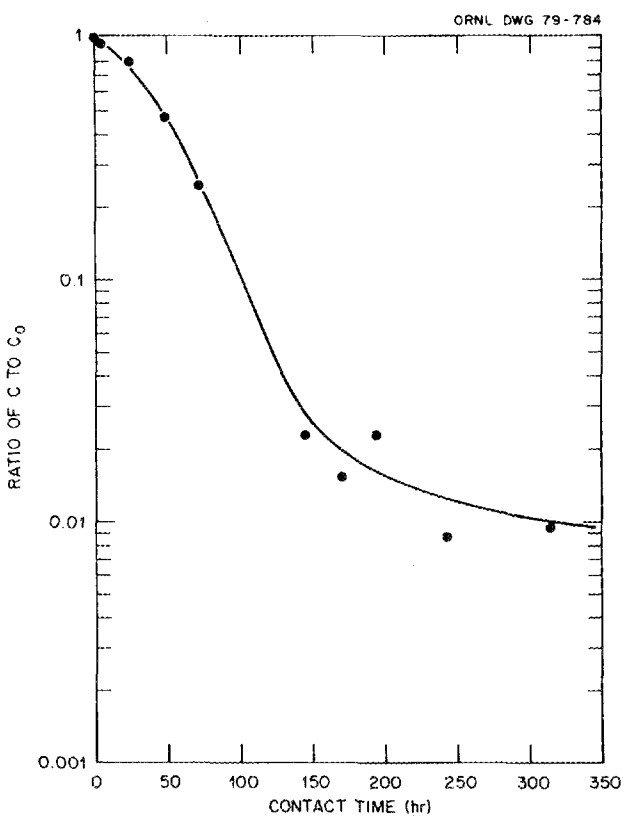

Fig. 5.23. Normalized tritium concentration in lithium as a function of contact time for yttrium sorber at 570 K.

function of the contact time. The apparent mass transfer resistance for contact times of <24 hr could be explained by an activation of the yttrium surface. A similar phenomenon occurred with the previous static tritium-sorption experiment.[40] Assuming that the driving force was the tritium concentration in the lithium, a mass transfer coefficient of 4×10^{-5} cm/sec was calculated. The ratio of the yttrium surface area to lithium volume was 0.19 cm^{-1}. This mass transfer coefficient from the forced convection of lithium is less than the mass transfer coefficient of 6×10^{-4} cm/sec that was determined from earlier static lithium experiments at 570 K.[39] This difference is currently being investigated.

The release rate of tritium from the yttrium samples contacted with tritiated liquid lithium is also being studied. The tritium recovery tests were made with the equipment used previously to study tritium removal from irradiated lithium-containing aluminum and sintered aluminum product.[41]

Tritium release rates were measured for four tritiated yttrium samples. The tritiated-yttrium coupons (surface area of each, 2.22 cm^2) contain ~8.8 to 10.9 ppm tritium. Figure 5.24 compares the tritium release rate data at temperatures of 780, 1070, and 1170 K (505, 800, and 900°C). The percentage of tritium released increased one order of magnitude from 780 K to 1070 K and another order of magnitude from 1070 K to 1170 K. All the tritium was released in 7 hr when a yttrium sample was heated to 1270 K. However, the sample could not be removed from the Hastelloy X sample chamber after the run because it had reacted with the inside of the tube. Yttrium forms a eutectic with both iron and nickel at ~1170 K. A molybdenum boat will be used in future experiments at high temperatures so that the yttrium will not alloy with the chamber wall.

The slope of each of the curves in Fig. 5.24 is equal to 0.5, which indicates diffusion-controlled release. The tritium release data do not follow this pattern exactly, but a diffusion coefficient was calculated from the initial gradient of the desorption data as a function of the square root of time. Estimated diffusion coefficients at 780, 1070, and 1170 K are 1.1×10^{-13}, 4.9×10^{-12}, and 9.3×10^{-10} cm^2/sec, respectively. From an Arrhenius relationship, the

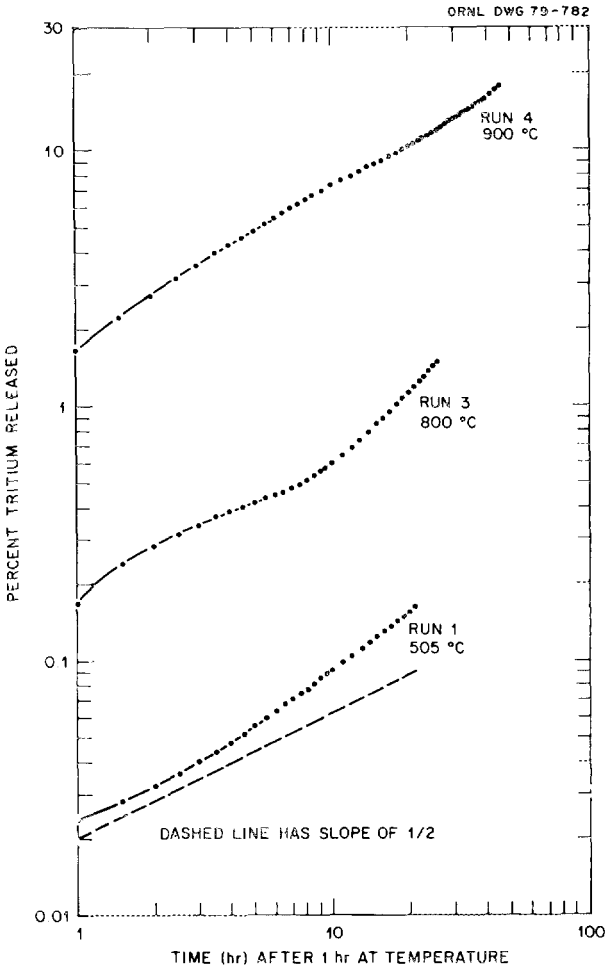

Fig. 5.24. Tritium release from yttrium at various temperatures.

dependence of the diffusion coefficient on temperature was found to be

$$D = 7.5 \times 10^{-4} \exp\left(\frac{-35{,}550}{RT}\right),$$

where

D = diffusion coefficient, cm^2/sec ;

R = gas constant, 1.987 cal K^{-1} g-$mole^{-1}$;

T = sample temperature, K.

Tritium release from yttrium will be investigated at higher temperatures. The effect of hydrogen addition to the argon sweep gas, which will provide a reducing atmosphere, will also be studied in future experiments.

40. C. D. Scott et al., *Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs) Mar. 1, 1975, to Aug. 31, 1975*, ORNL/TM-5291 (September 1976).

41. J. B. Talbot and F. W. Wiffen, "Recovery of Tritium from Solid Lithium-Sintered Aluminum Product (SAP) and Lithium-Aluminum Alloys," *J. Inorg. Nucl. Chem.* 41, 439–44 (1979).

6. Biotechnology and Environmental Studies

6.1 BIOENGINEERING TECHNOLOGY

Bioengineering technology, resulting from biochemical engineering research and development effort, can make important contributions to the field of energy. Processes based on biochemical action or materials will be utilized in energy production and conservation, resource recovery, and pollution control. The ORNL bioengineering projects that specifically address nuclear waste management are discussed in Sect. 4.3.

Research and development activities included studies on the following: (1) photobiological production of hydrogen using cell-free systems; (2) treatment of wastewater from coal conversion processes; (3) attachment of bacteria to solid surfaces in fixed-film bioreactors; and (4) the development of ANFLOW, a biological wastewater treatment process being investigated in an ORNL pilot plant.

Studies on the production of hydrogen using cell-free biological systems were continued, with emphasis on the chloroplast-ferredoxin-hydrogenase system. This system uses the light-driven reduction of ferrodoxin by chloroplasts instead of reduction by dithionite.[1] Measurements were made in a batch system containing ferredoxin, hydrogenase, and chloroplasts suspended in a buffer solution in a constant-temperature bath illuminated with incandescent lamps. An "oxygen trap" of glucose and glucose oxidase was frequently employed to prevent reoxidation of the reduced ferredoxin by any oxygen produced.

Parameters affecting the hydrogen production rate include light intensity, temperature, source and concentration of chloroplasts, ferredoxin, and hydrogenase. Conditions were optimized to give maximum hydrogen production rates. Chloroplasts from spinach gave higher hydrogen evolution rates than those from either turnip greens, romaine lettuce, or Swiss chard. Hydrogen evolution was measured at light levels of 3000 and 8800 lm/ft^2 (32,000 and 95,000 lux measured at 555 nm); the higher light intensity approximately doubled the hydrogen evolution rate (Fig. 6.1). The optimum temperature for continued maximum hydrogen evolution was ~25°C; at 35°C the hydrogen evolution rate slowly decreased after ~1 hr.

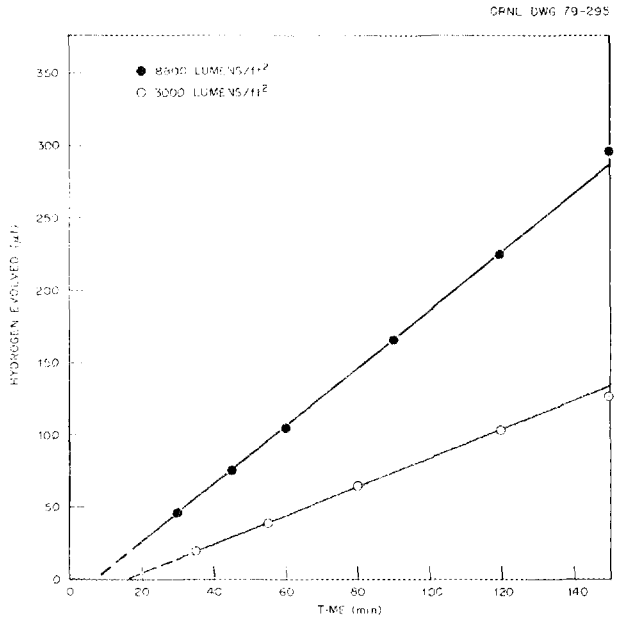

Fig. 6.1. Effect of light intensity on hydrogen evolution by the chloroplast-ferredoxin-hydrogenase system.

A technical assessment of a conceptual process[2] utilizing immobilized chloroplasts and hydrogenase was completed. This process would include two types of bioreactors, with chloroplasts immobilized in one reactor, and hydrogenase immobilized in the other.

1. B. Z. Egan and C. D. Scott, "Let Hydrogenase Do It," *Chem. Technol.* 8, 304 (1978).

2. B. Z. Egan and C. D. Scott, "Use of Cell-free Biological Systems for Hydrogen Production," *Biotechnol. Bioeng. Symp.* 8, 489–500 (1978).

Reduced ferredoxin would flow through the hydrogenase bed, where hydrogen would be generated. In the chloroplast bioreactor, oxidized ferredoxin circulating from the hydrogenase bed would be reduced by photosynthetic interactions and oxygen would be formed. The net reaction is the production of hydrogen and oxygen from water. The kinds and amounts of materials required, the reactions involved, the stability of the various components, the types and sizes of bioreactors, and the limitations and technical uncertainties associated with this process were considered.[3]

A major problem associated with the biochemical treatment of scrubber water from the ORNL Bench-Scale Hydrocarbonization Facility (BSHF) was encountered. The bacterial inoculum, a commercial preparation marketed as Phenobac which had been used successfully in previous tests, apparently lost its ability to adhere to fluidized particles—a characteristic essential for application in a fluidized-bed bioreactor. This problem dramatized the need for an understanding of the factors and mechanisms that mediate the attachment of microbial cells to solid surfaces in fixed-film bioreactors. A study of microbial attachment phenomena was begun, with emphasis on the Phenobac culture.

The ability of this preparation to attach to anthracite coal particles was observed in studies employing several different reactor configurations, including batch cultures in shake flasks, fed-batch cultures in shake flasks, percolation columns, and recirculating fluidized-bed bioreactors. The growth media employed in these studies included synthetic media in which phenol was the sole carbon and energy source, phenol-containing media supplemented with various concentrations of glucose or sucrose, and complex phenol-containing media (i.e., media supplemented with various concentrations of peptone, yeast extract, or peptone and beef extract).

Preliminary results indicate that when the Phenobac suspension is cultured in a synthetic medium containing phenol as the sole carbon and energy source, attachment of the cell population to the coal does not occur to any significant degree, regardless of the reactor configuration employed. Supplementation of the phenol-containing medium with the various organic sources mentioned above does not significantly improve the attachment of the microbial population to the coal when the population is grown in batch culture, fed-batch culture, or the recirculating fluidized bed. However, preliminary results from studies employing percolation columns, in which the medium was allowed to percolate down through a packed bed of anthracite coal, indicate that microbial attachment to the coal can be achieved in this configuration when a synthetic phenol-containing medium that is supplemented with either sucrose or peptone is intermittently fed to the columns. Studies are now under way to determine the feasibility of utilizing the percolation-column configuration, initially to achieve a rapid attachment of a phenol-oxidizing population to the coal and subsequently switching to an upflow fluidized-bed configuration to achieve rapid removal of phenol from phenol-containing wastes.

The observations mentioned above concerning the difficulty involved in obtaining an attached Phenobac population indicate that the attached population in the bench-scale, phenol-removing fluidized-bed bioreactor was not derived primarily from the Phenobac inoculum employed to seed the column. Further support for this belief comes from the observation that a large portion of the attached population is composed of filamentous fungi which have, to date, not been observed in "pure cultures" of the Phenobac preparation. Thus it would appear that the population found in the phenol-removing bioreactor was the result of an enrichment process.

The attached population contained in the phenol-removing bioreactor removed an average of 16 g of phenol per liter of reactor bed each day. The population appeared to be quite hardy in that it was able to withstand both a toxic increase in phenol (i.e., ~4000 ppm) which lasted for ~14 hr and a subsequent phenol starvation (i.e., 0 ppm) which lasted for ~12 hr. Both of these upsets to the system were due to mechanical problems, and each resulted in a reduction of the rate of phenol removal to 0 g phenol/day-liter. However, after proper operation was renewed and the inlet phenol concentration was returned to its usual operating level (~4000 ppm), the rate of phenol removal soon returned to normal (i.e., ~16 g/day-liter). Work is under way to further characterize the operating parameters of the phenol-removing bioreactors.

The development of anaerobic upflow (ANFLOW) bioreactors for advanced wastewater treatment systems was actively pursued in the biotechnology programs during the past year.

The ANFLOW system is based on continuous upflow feeding of an aqueous stream through a porous packed bed of solids, such as ceramic Raschig

3. *Advanced Technology Sect. Semiannu. Prog. Rep. Apr. 1, 1978 to Sept. 30, 1978,* ORNL/TM-6647/V1 (in preparation).

rings, to which anaerobic microorganisms are attached as a film. The attached microorganisms interact with the aqueous stream as it passes through the interstices of the packing. This particular system is being actively developed for several applications, including the treatment of municipal and industrial wastewaters and the processing of aqueous streams with high algae concentrations (as in eutrophic waters or waters from algae ponds used in solar-energy collection schemes).

The ANFLOW development for municipal wastewater treatment is in the later stages of a pilot-plant demonstration in which an on-line system has been operated for 2 years at the municipal wastewater treatment facility in Oak Ridge. The nominal treatment rate of this system is 18.9 m^3/day [5000 gallons/day (gpd)]. Except for an upstream comminuter that is responsible for reducing solids particle sizes, the pilot-plant treatment process consisted simply of the ANFLOW bioreactor followed by a single polishing step (sand-bed filtration). This system has demonstrated the ability to produce an effluent that meets the EPA secondary treatment requirements. It has also demonstrated, under ambient conditions, both long-term stability and simplicity of operation while treating municipal wastewater at flow rates essentially continuously. In addition, data on the basic phenomena of this innovative technology, including approximations of fermentation rates for soluble wastes and rates of accumulation and in situ digestion of solid wastes, have been made available. Essential design information on the response of ANFLOW units to varying hydraulic and organic loads has been generated, as has information on the temperature dependence of the overall process. The effects of various polishing processes on the bioreactor effluent have also been defined.

In anticipation of developing larger-scale demonstrations, we have performed a cost and energy comparison between the ANFLOW system and conventional wastewater treatment systems based on aerobic technology.[4] An industrial wastewater treatment firm, Associated Water and Air Resource Engineers, Inc. (AWARE), of Nashville, Tennessee, was also contacted and given the information obtained from our pilot-plant work to develop conceptual engineering designs for plants that treat 189 and 3780 m^3/day [0.05 and 1.0 million gallons per day (mgd)] and produce an effluent meeting secondary treatment requirements stipulated by the U.S. Environmental Protection Agency. Notably, ~86% of the wastewater treatment facilities projected for operation in this country in 1983 will treat 3780 m^3/day (1.0 mgd) or less.

Economic comparisons between ANFLOW and the aerobic technology (activated sludge) showed that ANFLOW offered savings in capital and labor costs as well as in energy consumption. In addition, we feel that the comparisons prepared by AWARE treated ANFLOW very conservatively. However, the AWARE comparisons of 3780-m^3/day (1-mgd) systems, based on ANFLOW or activated sludge, showed that ANFLOW used 40% less energy than conventional activated-sludge systems when weak wastewaters were treated and 70% less energy when strong wastewaters were treated. For 189-m^3/day (0.05-mgd) systems, ANFLOW used 45% less energy than activated sludge when weak wastewaters were treated and 53% less energy when strong wastewaters were treated.

The development of the ANFLOW system has progressed to the stage where a larger, more significant demonstration is warranted. We feel that a small commercial-sized unit [189,000 m^3/day (~50,000 gpd)] would probably be appropriate. The TVA has indicated a willingness to operate such a system near their development project in Hartsville, Tennessee, provided that installation can be arranged.

6.2 BIOANALYTICAL TECHNOLOGY

A basic understanding of biochemical systems is necessary in order to harness their tremendous potentials for energy conservation, energy production, and pollution abatement and control. New approaches to analytical biochemistry are required to aid in this understanding, with emphasis on selectivity, sensitivity, and rapid, high-throughput analyses.

Advanced Analytical Techniques

The development of a modular rotary electrophoresis system with potential for both high resolution and high sample throughput is in progress. Several techniques for measuring biomass in a denitrification reactor have been compared in order to test their relative capabilities for determining the viable biological activities.

4. W. L. Griffith, *Economics of the ANFLOW Process for Municipal Sewage Treatment*, ORNL/TM-6574 (March 1979).

Prototype electrophoresis system. A previous report[5] described the theoretical basis for acrylamide gel electrophoresis on gels of varying pore sizes. A single sample electrophoresed on several gels having different percentages of acrylamide yields both free electrophoretic mobility and the retardation coefficient for a protein when a regression of log R_f on percent acrylamide is performed. The slope of this linear function represents a so-called shape factor for the protein. The necessity for electrophoresing a single sample on four or more gels complicates the logistics of this type of analysis and provides a driving force for the development of the prototype rotary electrophoresis system described here.

The development prototype consists of four modular units: a gel-casting unit, an electrophoresis unit, a gel-scanning unit, and a destaining unit. The basic unit of the system is a two-layer plastic disc (18 cm in diameter) containing 12 gel channels (66.7 × 6.3 × 3.2 mm) spaced radially around the circular disc, as shown in Fig. 6.2. A stack of six rotors, each with a removable plastic top, is assembled and placed into the protective container on top of the rotatable unit shown in Fig. 6.3. The central nozzle is lowered into place, and an automated timing sequence is started. An acrylamide monomer is mixed with a catalyst and transferred to six measuring chambers by air pressure. Fluid volumes in the six chambers are equalized automatically by applying a vacuum through a timed solenoid valve. The liquid is then aspirated through six holes in the central nozzle (spaced vertically to match the rotor spacing in the stack) while the six-rotor stack is rotating at 600 to 800 rpm. In addition to its obvious advantage for rapid dynamic loading of 72 gel channels, centrifugation ensures the absence of bubbles in the gel and maintains a flat meniscus. Both a running gel and a capping gel are cast dynamically by the apparatus shown in Fig. 6.3. Coefficients of variation of 3% (variation in the length of a liquid loaded into the channels) were measured on a single-rotor and on a rotor-to-rotor basis.

The rotor stack containing polymerized gel columns is disassembled, and the samples are placed into cavities cast into the running gels. The rotors

5. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1978*, ORNL-5383, p. 55.

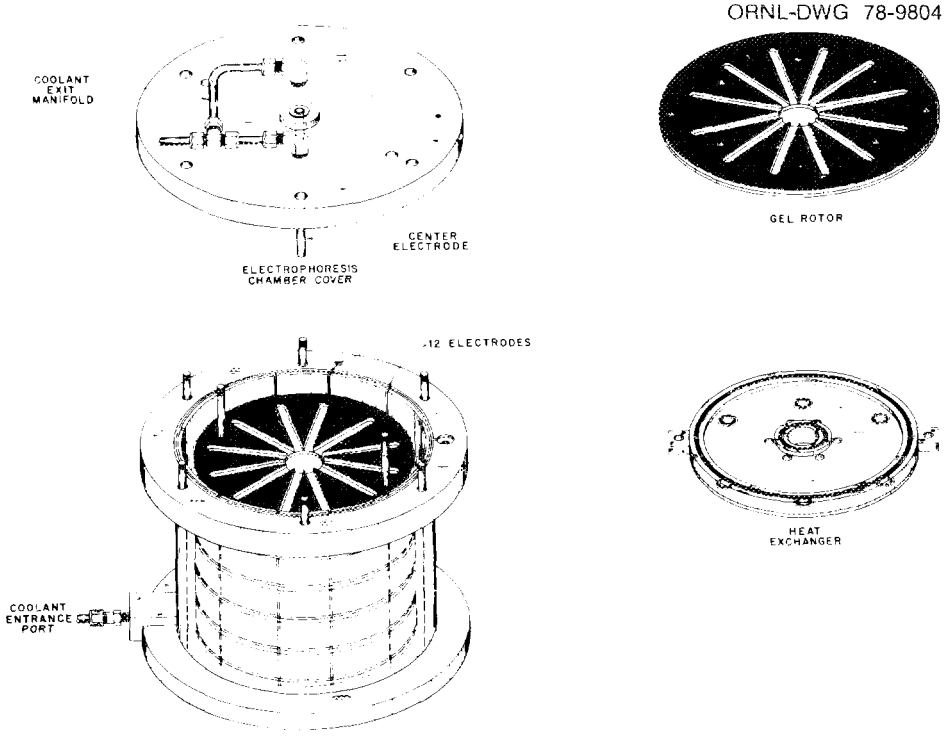

Fig. 6.2. Important components of the rotary gel electrophoresis system.

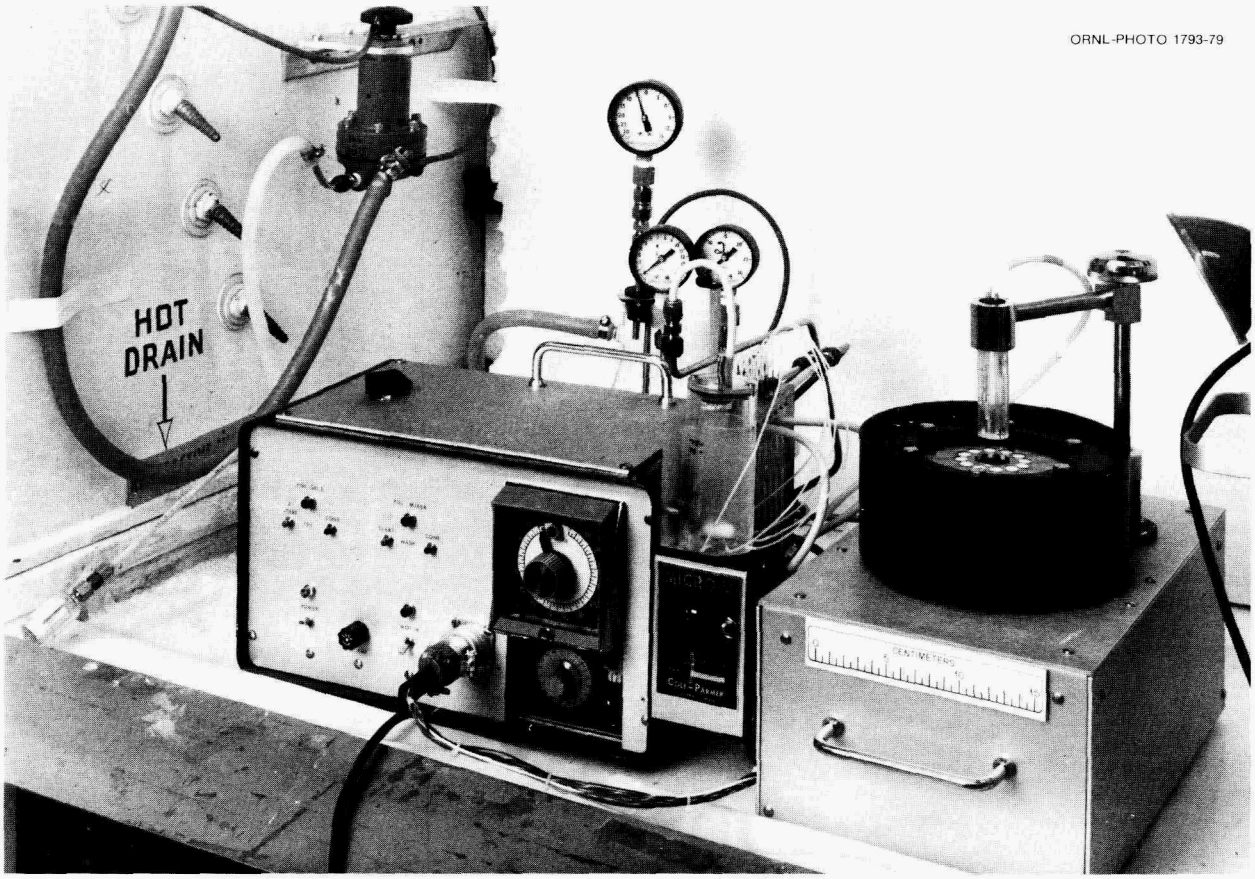

Fig. 6.3. Casting of acrylamide gel columns is performed by dynamic injection of acrylamide into the center of a six-rotor stack while it is rotated at 600 to 800 rpm.

are then reassembled into a stack by placing a heat exchanger (Fig. 6.2) between each rotor. The stack is inserted into the electrophoresis chamber and compressed to seal O-rings on both sides of the heat exchangers by tightening the chamber cover down using the thru bolts shown in Fig. 6.2. A single central electrode is inserted into the center chamber with an outer electrode chamber containing 12 electrodes spaced around the periphery of the vessel. Three separate fluids are maintained by this design: two electrode chamber fluids and a coolant fluid whose integrity is maintained by the O-rings on both sides of the heat exchangers. Forced circulation of the coolant maintains temperatures of ~5 to 6°C in the respective electrode chambers during electrophoresis at 260 V with currents of 50 to 60 mA for 2 hr. Smooth banding of samples at the interface between the capping and running gels has proven difficult to achieve apparently because the soft capping gel formulation deforms easily, thus affecting the cavity into which the sample is placed. This has led to nonuniform banding patterns which are not acceptable; however, direct injection of undiluted samples into the soft capping gel may solve this problem.

At the present time, staining and destaining of the disassembled rotors are performed conventionally. The top surfaces of the gel channels are exposed to a fixing and staining solution. Destaining is performed by placing the individual rotors between two electrodes with an impressed dc potential to enhance the migration of the anionic dye molecules from the gel. However, migration of the counterion is impaired since only the top surface of the gel is exposed to the destaining liquid. This has resulted in relatively slow destaining of the gel channels.

Scanning of all 12 channels in a single rotor is accomplished by rotating the 12-gel rotor on a platter between a light source and a detector contained in the fork-shaped optics head shown in Fig. 6.4. Every

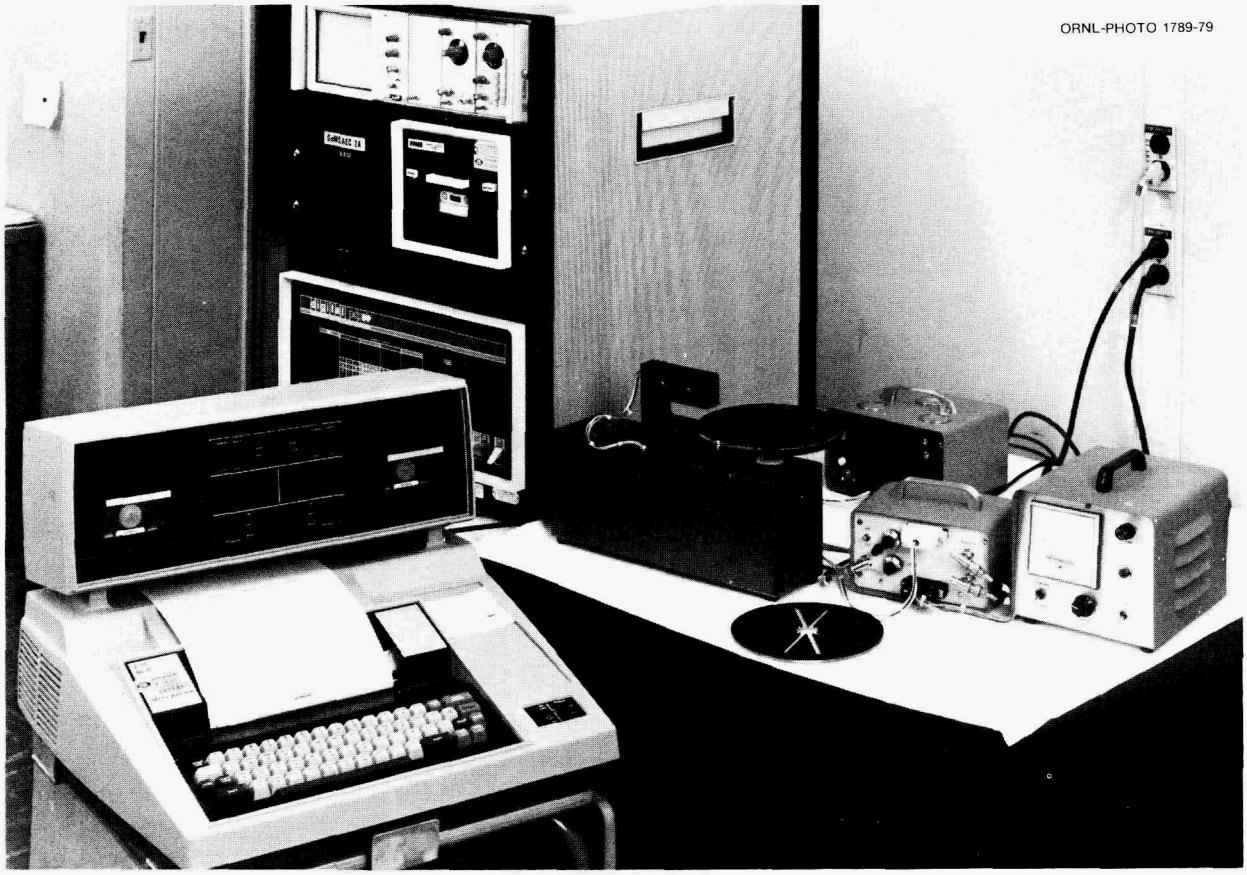

Fig. 6.4. Scanning of stained gels is performed by rotating the 12-gel disc through the fork-shaped optical head with approximately 40 transmission measurements acquired per centimeter of gel length by the PDP-8/e computer.

rotation of the platter moves the optics head 0.25 mm, or 100 transmission measurements are obtained for every 25 mm of travel for each of the 12 gels. Up to 195 data points are obtained and stored for the 12 gels within 1 min by the PDP-8/e computer shown in Fig. 6.4. The detector, which contains a beam splitter and two filters, is capable of monitoring two wavelengths. At the present time, the two wavelengths are only switch-selectable because the computer is not capable of obtaining both wavelengths simultaneously. The scanning system has demonstrated a resolution of 0.8 for two fine lines drawn 0.50 mm apart on a sheet of clear plastic. Computer software has been written in FOCAL language to identify peak maxima and the beginning and end of peaks, to integrate the area under a peak, and to display the data on a graphic scope.

Measurement of viable biomass. The increased use of bioreactors for the treatment of industrial waste requires an accurate and rapid assessment of microbiological activity and biomass in the system. We have compared three means of estimating biomass: (1) the level of mixed liquor volatile suspended solids (MLVSS), (2) the concentration of adenosine triphosphate (ATP), and (3) measured dehydrogenase activity. These measurements have been made with specific emphasis on nitrate removal in batch-type and continuous-flow, stirred-tank denitrification bioreactors.

The results of one study, using batch-type mini-bioreactors, are shown in Fig. 6.5. The MLVSS measurement, which gives the organic matter content of the nonfilterable residue, cannot discriminate between active and inactive biomass and therefore does not reflect sudden changes in metabolic activity.[6] Measurement of ATP does reflect viable

6. J. W. Patterson, P. L. Brezonik, and H. D. Putnam, "Measurement and Significance of Adenosine Triphosphate in Activated Sludge," *Environ. Sci. Technol.* **4**, 569 (1970).

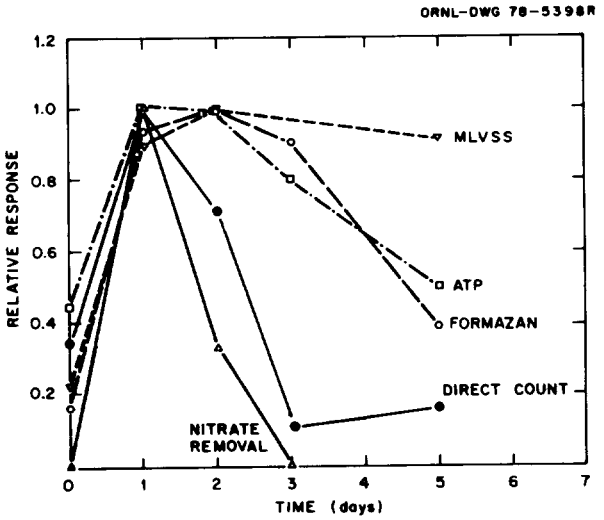

Fig. 6.5. Comparison of several methods for the measurement of biomass in a denitrification bioreactor. Both ATP and dehydrogenase measurements (via formazan dye) seem to relate to viable biomass, as indicated by the nitrate removal.

biomass; however, extraction difficulties[7,8] and inconsistency of data[9] have cast some doubt on its usefulness as a routine tool. Dehydrogenase activity measurement has been described as being a more accurate measurement of viable microbial activity and easier and less costly to use than other biomass measurements.[9,10]

The usual substrate for such assays is 2,3,5-triphenyltetrazolium chloride (TTC), which is sensitive to oxygen and requires very long incubation periods. However, we have used 2-(*p*-iodophenyl)-3-(*p*-nitrophenyl)-5-phenyltetrazolium chloride (INT) as a substrate and found it to have several advantages: (1) it is not affected by the presence of oxygen, (2) the reaction is rapid, and (3) only simple photometric equipment is required. The substrate intercepts electron transport in the cell, thus producing a cell-immobilized formazan product. The formation of this product is toxic to the cell, and the reaction terminates in as little as 10 min. This refractile crystalline product has an intense color and may be monitored by photometry between 500 and 600 nm; it is also useful as an indicator of viability in direct cell counting.[11,12] The methodology is particularly useful for estimating viable microorganisms attached to particulate material since the product is extractable with organic solvents and may be determined photometrically by its light-absorption band at 490 nm.

Development of the Centrifugal Fast Analyzer

Efforts on the portable Centrifugal Fast Analyzer (CFA) were primarily focused on the fabrication of additional systems; three systems were completed and delivered during this report period. Some work was also done on the application of the instrument to fast chemiluminescent reactions and the addition of an external photomultiplier tube (PMT) to monitor low-level signals.

Engineering development. The current design of the optical system for the portable CFA places the PMT ~2.5 cm below the center of the cuvet. This factor and the restriction placed on the high voltage to the PMT (~500 V) were limited by the sensitivity of the instrument when it was used to detect low-level chemiluminescence signals. To alleviate these problems, an external PMT was mounted in the metal rotor cover which, when closed, placed it within ~6 mm of the center of the cuvet, and an external high-voltage source made it possible to apply up to 1500 V to the PMT. This modification enabled the portable CFA to detect ATP concentrations of 0.07 ppm by means of the chemiluminescent luciferin-luciferase reaction. This was an improvement over that which could be measured by the regular optical system by at least two orders of magnitude.

Fabrication. A complete portable CFA system, which incorporates the PDP-11V03 microcomputer, graphics oscilloscope, automated rotor-loading station, and rotor-washing station, was delivered to the Department of Human Genetics at the University of Michigan. New computer software was provided

7. B. S. Ausmus, "The Use of ATP Assay in Terrestrial Decomposition Studies," *Bull. Ecol. Res. Comm. (Stockholm)* **17**, 223 (1973).

8. E. A. Paul and R. L. Johnson, "Microscopic Counting and Adenosine 5'-Triphosphate Measurement in Determining Microbial Growth in Soils," *Appl. Environ. Microbiol.* **34**, 263 (1977).

9. F. G. Pohland and S. J. Kang, *Measurements of Active Biomass Concentrations in Biological Waste Treatment Processes*, EPA-60012-75-029 (1975).

10. J. Skujins, "Dehydrogenase: An Indicator of Biological Activities in Arid Soils," *Bull. Ecol. Res. Comm. (Stockholm)* **17**, 235 (1973).

11. R. Zimmerman, R. Hurriaga, and J. Becker-Birch, "Simultaneous Determination of the Total Number of Aquatic Bacteria and the Number Thereof Involved in Respiration," *Appl. Environ. Microbiol.* **36**, 926 (1978).

12. D. M. DeSha and B. J. Dozier, "A Direct Counting Method for Assessing the Performance of Bioreactors," accepted for publication in *Developments in Industrial Microbiology*, 1979.

with this system to take advantage of the massive storage capacity (512K) of the dual floppy discettes. The software was designed to assay and store hemoglobin assays for families consisting of four individuals (two parents and two children), together with identification data. Subsequent enzyme assays and kinetic data on thermally denatured protein samples processed on the portable CFA are then stored according to family identification, and these results are all automatically converted to units of activity per unit of hemoglobin concentration, thus placing all data on a uniform basis. Editing capability was provided so that errors could be corrected.

Two self-contained portable CFA instruments were fabricated. One is for our use here at ORNL; the other was delivered to the National Aeronautics and Space Administration accompanied by a complete engineering documentation package, which included 43 engineering drawings and operational and trouble-shooting manuals. A software program was developed especially for this instrument to enable the analysis of a series of unknown samples using a minimum standard curve. The standards are fit automatically by regression to both a linear and a quadratic model. The best fitting model is then selected, and the parameters from this model are used to compute the concentration of the remaining unknown samples.

Applications. The clutch/brake assembly that is incorporated into the rotor drive of the portable CFA enables discretely loaded samples and reagents to be transferred into their respective optically transparent cuvets within 60 msec. To demonstrate the ability of this instrument to measure fast reactions the chemiluminescent reaction between hypochlorite and luminol was investigated using a reaction that has potential utility. This reaction was considered to be a good model since the decay of luminescence is known to obey pseudo-first-order kinetics over a range of reaction conditions, and the light emission is of very short duration.[13] Both chlorine and ClO_2 are used extensively in the disinfection of water and in the bleaching of paper pulp, and the rapid determination of these compounds is of considerable interest.[14]

Chlorine in aqueous solution yields hypochlorite, which oxidizes luminol to 3-aminophthalic acid accompanied by the emission of light at 430 nm. The addition of peroxide enhances the luminescence response of the reaction.[13] Chemiluminescent reactions, serving as independent light sources, overcome the problems associated with the measurement of light transmission through a mixture of solution and air bubbles during the critical first two revolutions of the rotor.

Figure 6.6 (*a*) illustrates the chemiluminescence response for hypochlorite and luminol. At a rotor speed of 3500 rpm, as many as 50 observations may be taken for each cuvet in <1 sec. Hypochlorite may be quantitated by either measuring peak height or integrating light emission over a selected time interval. In Fig. 6.6 (*b*), the data are plotted semilogarithmically to illustrate the first-order decay of the light emission. As illustrated here, reactions with half-lives as short as 40 msec may be accurately measured. In general, rate constants may be determined with a precision of 3 to 5%, which compares favorably with the precision of 10% or higher that was reported when these reactions were monitored by the stopped-flow technique.[13] The dual-condition data-acquisition capabilities of the portable CFA[15] permit both the fast and slow reaction phases to be

13. U. Isacsson, J. Kowalewska, and G. Wettermark, "Kinetic Investigation of Reactions Between Inorganic Chlorine Compounds and Luminol," *J. Inorg. Nucl. Chem.* **40**, 1653 (1978).

14. R. L. Jolley, H. Gorchev, and D. H. Hamilton, Jr. (eds.), *Water Chlorination: Environmental Impact and Health Effects*, vol. 2, Ann Arbor Science, Ann Arbor, Mich., 1978.

15. J. E. Mrochek et al., "A New Portable Centrifugal Analyzer with Expanded Versatility," *Clin. Chem.* **23**, 1416 (1977).

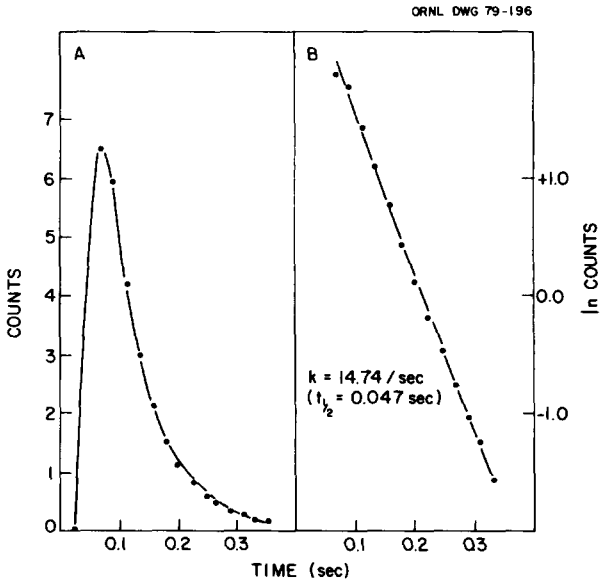

Fig. 6.6. Chemiluminescence data for the hypochlorite-luminol reaction acquired by the portable CFA. (*a*) Peak light intensity was observed ~70 msec after the initial rotor movement. (*b*) First-order decay of the light intensity is illustrated with a reaction half-life of 47 msec.

followed in the same run, thus enabling differential kinetic analysis. The use of the external PMT (as described earlier) makes it possible to measure hypochlorite concentrations of <1 ppm by this procedure.

6.3 ENVIRONMENTAL AND PERSONNEL MONITORING

The programs described in this section deal with two aspects of the problem of monitoring and controlling worker exposure to polynuclear aromatic hydrocarbon (PNA) compounds in the work areas. The common objective of the program is to develop technology that is useful to the environmental and industrial hygiene monitoring requirements of fossil energy conversion.

Portable Fluorescence Spotter Development

Development of the portable spotter for detecting PNA contamination on work area surfaces was continued during this report period. The spotter, which consists of an optics unit connected to a battery-powered electronics module (both units are hand held), monitors PNAs on surfaces by exciting and detecting PNA fluorescence. The instrument employs excitation beam modulation and phase-sensitive fluorescence detection to isolate weak fluorescent signals from intense background illumination. Optical filters for both the excitation and emission bands can be selected to enable monitoring for various classes of aromatic hydrocarbons.

The advanced optics unit (Fig. 6.7) is basically a compact version of the prototype optics unit that was described previously [16,17] This unit uses a single-lens reflex illumination/collection system incorporating a dichromatic beam splitter. This technique ensures that the fields of the illuminator and the fluorescence detector coincide. A reference photodiode, mounted in the illuminator, provides a signal which is used

16. *Advanced Technology Sect. Semiannu. Prog. Rep. Apr. 1 to Sept. 30, 1977,* Sect. 3.4, ORNL/TM-6238/V1 (in preparation).

17. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1978,* ORNL-5383, pp. 57–58.

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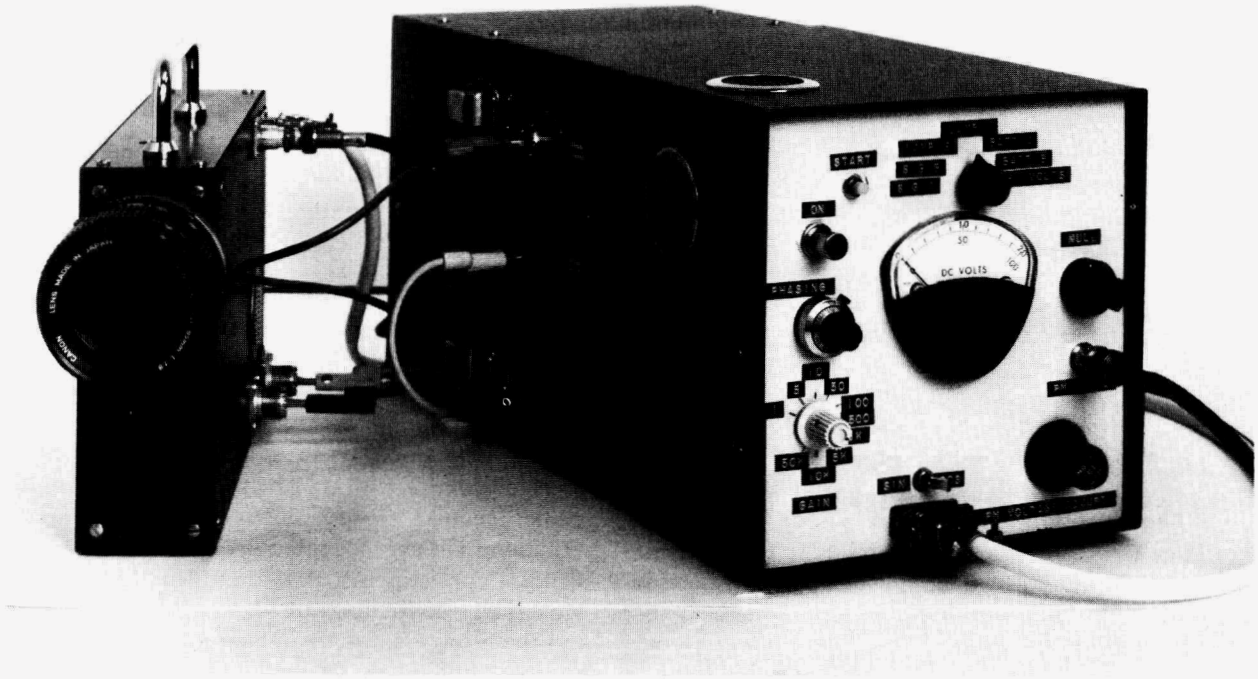


Fig. 6.7. Portable fluorescence spotter.

to offset the background fluorescence of the dichromatic beam splitter and output lens. The optics unit measures 32 × 6 × 20 cm and weighs 2 kg.

Table 6.1 lists the specific fluorescence of several fossil-energy conversion products as measured by the spotter. From a distance of 1 m, the spotter can detect 1 μg of perylene in dilute solution in illuminated work areas and submicrogram amounts in darkened areas.

Table 6.1. Specific fluorescence of coal liquefaction and oil shale products

Sample	Specific fluorescence[a] (units/mg)
COED syncrude	6.3
Hydrotreated coal distillate	3.4
Product distillate	11.3
Centrifuged shale oil	4.8
ORNL hydrocarbonization oil (HC-12)	0.2
SRC-II fuel oil blend	7.7
SRC-I recycle solvent (raw)	4.6
SRC-I wash solvent	0.9
SRC-I light organic liquid (raw)	0.1
SRC-I process solvent	3.7
SRC-I light oil	*b*

[a]One unit of fluorescence is defined as the equivalent fluorescence of 1 μg of perylene in dilute solution in cyclohexane.
[b]Not detectable.

The prototype portable electronics unit (Fig. 6.7) contains the electronic circuitry required to power the optics unit and to process and read out the fluorescence signal. These circuits include a uv lamp regulator and igniter, a printed-circuit phase-sensitive demodulator, a chopper driver, various power supplies, and signal output circuitry. The fluorescence is read out on the panel meter shown in Fig. 6.7 and also as an audio signal produced by a voltage-controlled oscillator coupled to a small speaker. The audio output enables the operator to locate contaminated areas, while the meter readout provides a measure of the level of PNA contamination.

The entire instrument is powered from two 12-V rechargeable lead-acid gel cells which provide power for 1 hr of continuous operation. The electronics module weighs 7 kg and measures 17 × 19 × 40 cm.

Field testing of two complete spotter units in selected coal liquefaction facilities is scheduled to begin during FY 1979.

Cell Microfluorometry for Personnel Monitoring

The purpose of this program is to develop methods by which fossil-energy conversion plant personnel can be monitored for exposure to or uptake of PNAs. Several PNAs, such as 1,2-benzopyrene (BP), are procarcinogens; that is, they are metabolized to intermediates which bind to cellular constituents including DNA and may cause cellular neoplastic transformation. Others, such as benz[*a*]anthracene (BA), are cocarcinogenic in that they enhance the carcinogenic potential of the parent carcinogens.

Cells from many mammalian tissues such as lung, kidney, intestine, skin, and liver and also white blood cells (lymphocytes) contain the cytochrome P-450 mixed-function oxidase (MFO) enzyme system, which metabolizes PNAs such as BP to various active intermediates. These active intermediates are rearranged or further metabolized to such products as phenols, quinones, dihydrodiols, and epoxides. The epoxide intermediates of the metabolism of PNAs have been tentatively identified as the ultimate carcinogens. Many of the phenolic products are further metabolized to make them more water soluble as glucuronide and sulfate conjugates and are subsequently excreted. Prior exposure of the cells to PNAs caused enhancement of various P-450 system constituent enzymes including aryl hydrocarbon hydrolase (AHH), which produces 3-hydroxybenzopyrene (3-BPOH). This induction of enzyme activity in cells varies with the type and amount of PNA to which the cells have been exposed and therefore can be used to monitor cellular exposure. Thus by periodically assaying lymphocytes, skin cells, and lung cells (such as pulmonary macrophages) in plant personnel, one can presumably monitor their short- and long-term exposure to PNAs.

The initial work on this project was begun with the assistance of personnel from the Biology Division using hamster embryo fibroblast (HEF) cultures. Tertiary cultured HEFs are exposed to BA for 24 hr and are then harvested and assayed for AHH activity. The harvested cells are homogenized and separated by centrifugation into a cell homogenate and a nuclear pellet. The homogenate, which contains the major cellular P-450 locus, the endoplasmic reticulum, is then incubated for 0.5 hr at 37°C in a medium consisting of BP with added NADPH and Mg^{2+}. The reaction mixture is extracted with hexane, and the hexane extract is mixed with 1 *N* NaOH in

order to extract polar metabolites such as 3-BPOH, which are measured fluorometrically.

The specific activity of HEFs incubated with various concentrations of BA is plotted against the BA concentration in Fig. 6.8. As can be seen, the AHH activity rises sharply for increasing BA concentrations from 0 to 6 *M*. The activity then decreases gradually with further addition of BA, which may be due to second-order BA-induced effects on cell metabolism or to cytotoxicity.

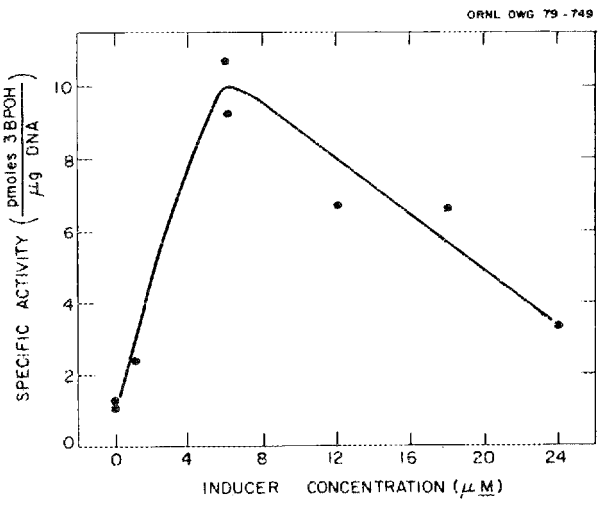


Fig. 6.8. Specific activity of hamster embryo fibroblasts as a function of benz[*a*]anthracene concentration.

6.4 ENVIRONMENTAL STUDIES

During this period, in collaborative work with the Biology Division, we determined that disinfection of wastewater effluents with either ozone or chlorine produces mutagenic constituents. We are also organizing the Third Conference on Water Chlorination: Environmental Impact and Health Effects. A major effort continues to be placed on instrumental development and research on the characterization and identification of organics in coal conversion process and waste treatment stream.

Chemical Effects of Disinfectants

The objective of this program, funded by the U.S. Environmental Protection Agency, is to characterize the nonvolatile organics in wastewater effluents that have been disinfected with either chlorine, ozone, or uv light. Both concentrates of the disinfected wastewater effluents and constituents separated from the concentrates are screened for mutagenic activity. Constituents that are determined to possess mutagenic activity are subsequently characterized chemically and identified when possible. This is a cooperative program with the Biology Division,[18] in which the mutagenesis testing is conducted by the Biology Division and the chemical processing and identification efforts are conducted by the Chemical Technology Division.

It was previously reported that although disinfection of wastewater effluents with either chlorine or ozone destroys some nonvolatile constituents, it produces other constituents. It appears, however, that disinfection with uv light has relatively little chemical effect, as determined by high-performance liquid chromatography (HPLC).[19-21] In addition, tests have shown that concentrates of chlorinated primary effluent from the Oak Ridge West Wastewater Treatment Plant are highly mutagenic to bacterial tester strain TA-1535 but are negative to other strains used. Mutagenic activity was detected in eluate fractions separated by HPLC from one of the active primary concentrates; however, the total activity in the separated fractions was much less than the activity of the concentrate.[20,22]

Most of the concentrates of secondary effluent, except the unchlorinated effluent (control), have given negative mutagenic activity tests. Nevertheless, mutagenic constituents have been separated by HPLC from both undisinfected secondary effluents and those disinfected by chlorine and ozone. This phenomenon of mixtures giving negative mutagenic

18. R. B. Cumming, Mammalian Genetics Section, Biology Division.

19. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979*, ORNL-5383, pp. 57–62.

20. R. L. Jolley et al., *Characterization of Nonvolatile Organics in Disinfected Wastewater Effluents: Interim Report*, ORNL/TM-6555 (February 1979).

21. R. L. Jolley et al., "Effects of Chlorine, Ozone, and Ultraviolet Light on Nonvolatile Organics in Wastewater Effluent," *Progress in Wastewater Disinfection Technology*, Cincinnati, Ohio, Sept. 18–20, 1978, ed. by A. D. Venosa, EPA 60019-79-018 (June 1979).

22. R. B. Cumming, L. R. Lewis, R. L. Jolley, and C. I. Mashni, "Mutagenic Activity of Nonvolatile Organics Derived from Treated and Untreated Wastewater Effluents," *Progress in Wastewater Disinfection Technology*, Cincinnati, Ohio, Sept. 18–20, 1978, ed. by A. D. Venosa, EPA 60019-79-018 (June 1979).

tests and constituents separated from the mixture giving positive tests has been observed by other investigators and is being studied further.

Two mutagenic fractions were separated from the unchlorinated secondary effluent (control), and nine mutagenic fractions were separated from the chlorinated secondary effluent (1.5 ppm chlorine residual) of the Lyons Bend Wastewater Treatment Plant in Knoxville, Tennessee, which mainly treats domestic residential wastewater (Figs. 6.9 and 6.10). Tables 6.2 and 6.3 give the identified constituents in these mutagenic fractions. It should be emphasized that these identified constituents may not be the mutagenically active compounds in the fractions.

Similarly, seven mutagenic fractions were separated from the unchlorinated secondary effluent (control), and nine mutagenic fractions were separated from the chlorinated secondary effluent (1.0 ppm chlorine residual) of the Moccasin Bend Wastewater Treatment Plant in Chattanooga, Tennessee, which treats wastewater composed of ~60% industrial and 40% commercial and residential wastewater. Four of these fractions were common to both chlorinated and unchlorinated effluents. It also appears that ozonation of secondary effluents produces mutagenic constituents. For example, ten mutagenic fractions were separated from the unozonated secondary effluent (control), and 16 mutagenic fractions were separated from the ozonated secondary effluent (~6 ppm ozone dosage) of the Upper Thompson Sanitation District Wastewater Treatment Plant in Estes Park, Colorado. Six of these fractions were common to both the control and ozonated effluents. Identification and characterization of the mutagenic constituents in the HPLC fractions will be emphasized in the next phase of this program.

National Chlorination Conference

The Third Conference on Water Chlorination: Environmental Impact and Health Effects will be held in Colorado Springs, Colorado, October 28 to

ORNL DWG 78-21597R

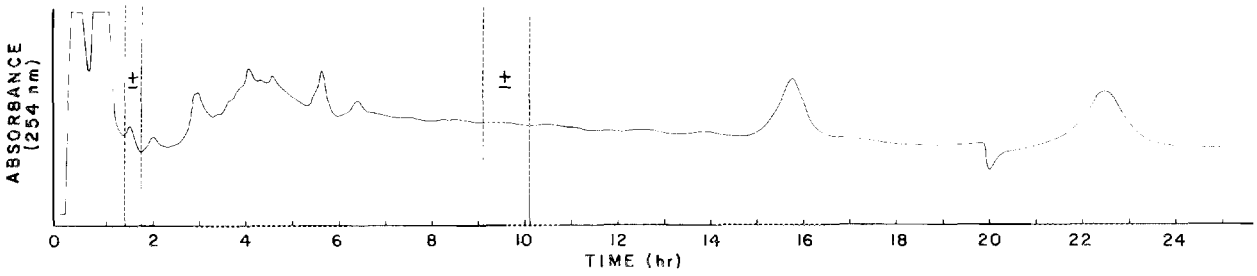


Fig. 6.9. High-performance liquid chromatogram of the uv-absorbing constituents in the unchlorinated secondary effluent (control) of the Lyons Bend Wastewater Treatment Plant, Knoxville, Tennessee. The mutagenic fractions are indicated by the symbol ±.

ORNL DWG 78-21599R

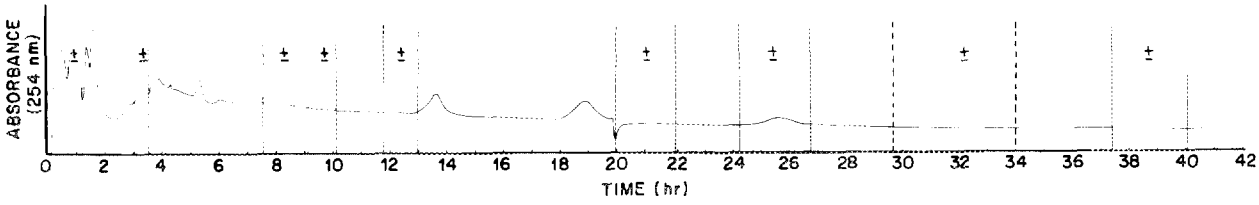


Fig. 6.10. High-performance liquid chromatogram of the uv-absorbing constituents in the chlorinated secondary effluent (1.5 ppm chlorine residual) of the Lyons Bend Wastewater Treatment Plant, Knoxville, Tennessee. The mutagenic fractions are indicated by the symbol ±.

Table 6.2. Identified constituents in mutagenic fractions of unchlorinated secondary effluent (control) from the Lyons Bend Wastewater Treatment Plant, Knoxville, Tennessee

Constituent	Liquid chromatography fraction	Identification method[a]
Caffeine	19–22	AC, MS
Phosphate	111–122	GC, MS
Ethylene glycol	111–122	GC
Phenol	111–122	GC
Glycerol	111–122	GC
Adenosine	111–122	GC

[a]AC—anion chromatography; MS—mass spectrometry; GC—gas chromatography.

Table 6.3. Identified constituents in mutagenic fractions of chlorinated secondary effluent from the Lyons Bend Wastewater Treatment Plant, Knoxville, Tennessee

Constituent	Liquid chromatography fraction	Identification method
Propylene glycol	10–15	AC, GC, MS
Uracil	10–15	AC, GC, MS
Phenylalanine	10–15	AC, MS
Phosphate	38–43	GC, MS
3,4-Dideoxypentonic acid	38–43	GC, MS
L-α-Glycerophosphate	38–43	MS
Palmitic acid	38–43	GC, MS
Ethylindan	111–112	MS
Phosphate	111–112	GC, MS
4-Chlorobenzoic acid	143–146	AC, GC, MS
6-Dimethyladenosine	143–146	GC
Phosphate	310–318	GC, MS

November 2, 1979. Staff personnel of ORNL have lead roles in the planning and organization of this conference. Several objectives of the conference are to (1) improve communication between scientists and practitioners in water chlorination fields, (2) present important research and developments that have taken place since the 1977 conference, (3) review current chlorination practices, (4) learn how and to what extent health and environmental consequences of chlorination are being evaluated, and (5) thoroughly discuss and analyze the risks and benefits of chlorination practices and develop an understanding of the factors that lead to regulations. Conference sessions and workshops will include such topics as chlorination processes, practices and effects of biofouling control, health effects, chemistry and chemical methods, freshwater and marine aquatic ecosystems, human and ecological effects, and risk assessment and regulations. Cosponsoring agencies are the Department of Energy, the U.S. Environmental Protection Agency, the National Cancer Institute, the Nuclear Regulatory Commission, the Tennessee Valley Authority, and Oak Ridge National Laboratory.

Characterization and Identification of Organics in Coal Conversion Process and Waste Treatment Streams

Three complete liquid chromatographic (LC) systems have been developed and applied to the aqueous waste streams of a number of coal conversion processes. These systems will be briefly described here with their respective applications. Glass-capillary gas chromatography for high-resolution gas chromatographic confirmation of organics following LC fractionation and separation methods development prior to gas chromatographic/mass spectrometric (GC/MS) analysis, particularly for coal liquefaction and gasification product oils, has become well established in our laboratory.

Two ion exchange LC screening systems, consisting of multiple detectors in series, have been used extensively for monitoring coal liquid streams. Both an analytical (1.23-ml maximum sample volume) system and a preparative (11-ml maximum sample volume) screening system are presently in use. The former is used primarily for methods development and initial sample screening, whereas the latter is optimized for chromatographing large sample volumes for fraction collection and subsequent capillary GC/MS identification. A schematic of such an anion exchange system is shown in Fig. 6.11.[23] These systems are capable of monitoring an LC effluent stream with five discrete detectors, which include the following: uv absorbance at 254 and 280 nm, cerate oxidimetric detection (monitors oxidizable constituents in solution via a $Ce^{4+} \rightarrow Ce^{3+}$ reduction, $\lambda_{Ex} = 254$ nm and $\lambda_{Em} = 360$ nm), and native fluorescence using ORNL-type fluorometers ($\lambda_{Ex} = 254$ nm, $\lambda_{Em} \geqslant 305$ nm; and $\lambda_{Ex} = 360$ nm, $\lambda_{Em} \geqslant 405$ nm). These detectors

23. M. S. Denton and S. R. Dinsmore, Sect. 10.5.2 in *Fossil Energy Program Quarterly Progress Report for the Period Ending June 31, 1978,* ORNL-5444 (November 1978).

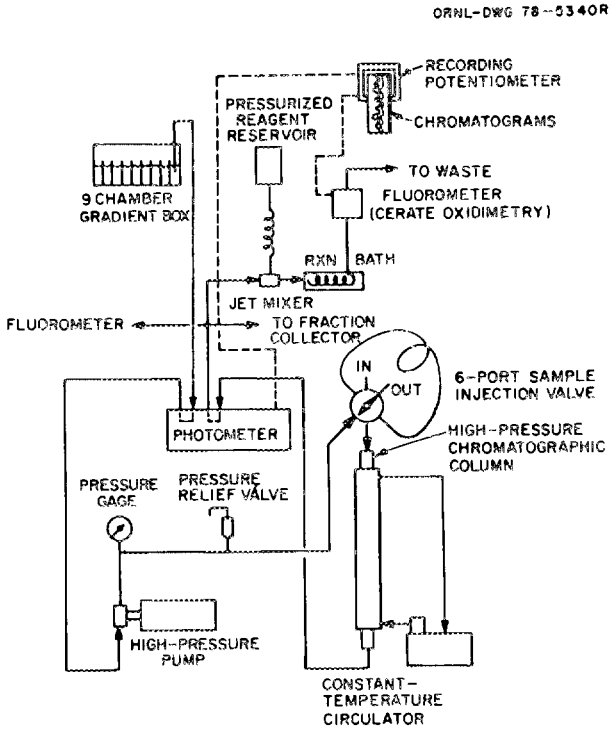


Fig. 6.11. Schematic of characterization system.

have been described in detail previously. Native fluorescence is the most recent addition.[23-25]

The capabilities of the analytical system are illustrated in Fig. 6.12, in which a synthetic aqueous coal waste was chromatographed. The novelty of the system, beyond the uv-absorbance ratioing capabilities, is that it offers series uv and fluorescence detection for selectivity enhancement. The latter has found routine usage in our laboratory and was reported as early as June 1978.[23] As can be seen from the figure, such multidetector capability and absorbance ratioing can greatly aid in the characterization and identification of specific organic components, or at least offer information concerning the compound classes in which they fall.

Sampling and chromatographing profile samples from the various coal conversion processes serve a twofold purpose: (1) to provide process development feedback, and (2) to determine which compounds are refractory to, removed by, or produced in the subject wastewater process train. In order to accomplish these goals within a reasonable time, a new, high-speed, high-resolution system (Fig. 6.13) has been developed by modifying a commercial liquid chromatograph that was manufactured by Waters Associates, Inc. The dual-pump system with variable-gradient generator has allowed us to separate a synthetic aqueous coal waste, similar to the one chromatographed in 18 hr (Fig. 6.12), in ~15 min (Fig. 6.14). Since most aqueous coal wastes are somewhat more complex than a synthetic standard such as this, a longer run time has been adopted for the sake of resolution. A 40-min linear gradient from distilled water (DW), with a 2-min initial hold, to 100% ethanol containing 1% glacial acetic acid was used. The separation is novel in that pure grain alcohol (190 proof) was used rather than methanol or acetonitrile, which is conventionally used in reverse-phase chromatography (RPC). The 190-proof ethanol demonstrates distinct advantages for coal waste separations in that it is a superior solvent for the typical compounds that are encountered, and it is extremely pure (i.e., it demonstrates few of the absorbing or fluorescing impurities typically found in LC solvents). Table 6.4 compares the elution orders and volumes obtained on the RPC and ion exchange screening systems. The former has the obvious advantage of speed, whereas the latter clearly demonstrates the ability to class fractionate the compounds into one- and two-ring nitrogen heterocyclics, aromatic amines, phenols, indoles, etc.

Both systems have been applied to a number of samples from different coal conversion process streams and have been coupled with our multicomponent analytical scheme for organic characterization and identification. This scheme consists of LC, GC, and GC/MS, allowing confirmed identifications.

Three aqueous waste streams were thoroughly investigated after undergoing a myriad of cleanup steps. These streams included wastes from a coal gasifier [University of Minnesota, Duluth (UMD)], a coal liquefaction process [ORNL Bench-Scale Hydrocarbonization Experiment (BSHE)], and a full-scale coal-tar chemical plant waste treatment facility. In addition to process aqueous streams, product oils are being characterized from a Solvent Refined Coal process and subsequent class fractionation liquids (benzene-solubles, oils, resins, etc.).

The BSHE samples from hydrocarbonization (HC) runs HC-21 through HC-26 have been chromatographed, and conclusions have been drawn

24. M. S. Denton and S. R. Dinsmore, Sect. 10.5.2 in *Fossil Energy Program Quarterly Progress Report for the Period Ending September 30, 1978*, ORNL-5487 (January 1979).

25. M. S. Denton and S. R. Dinsmore, Sect. 9.5.2 in *Fossil Energy Program Quarterly Progress Report for the Period Ending December 31, 1978*, ORNL-5520 (April 1979).

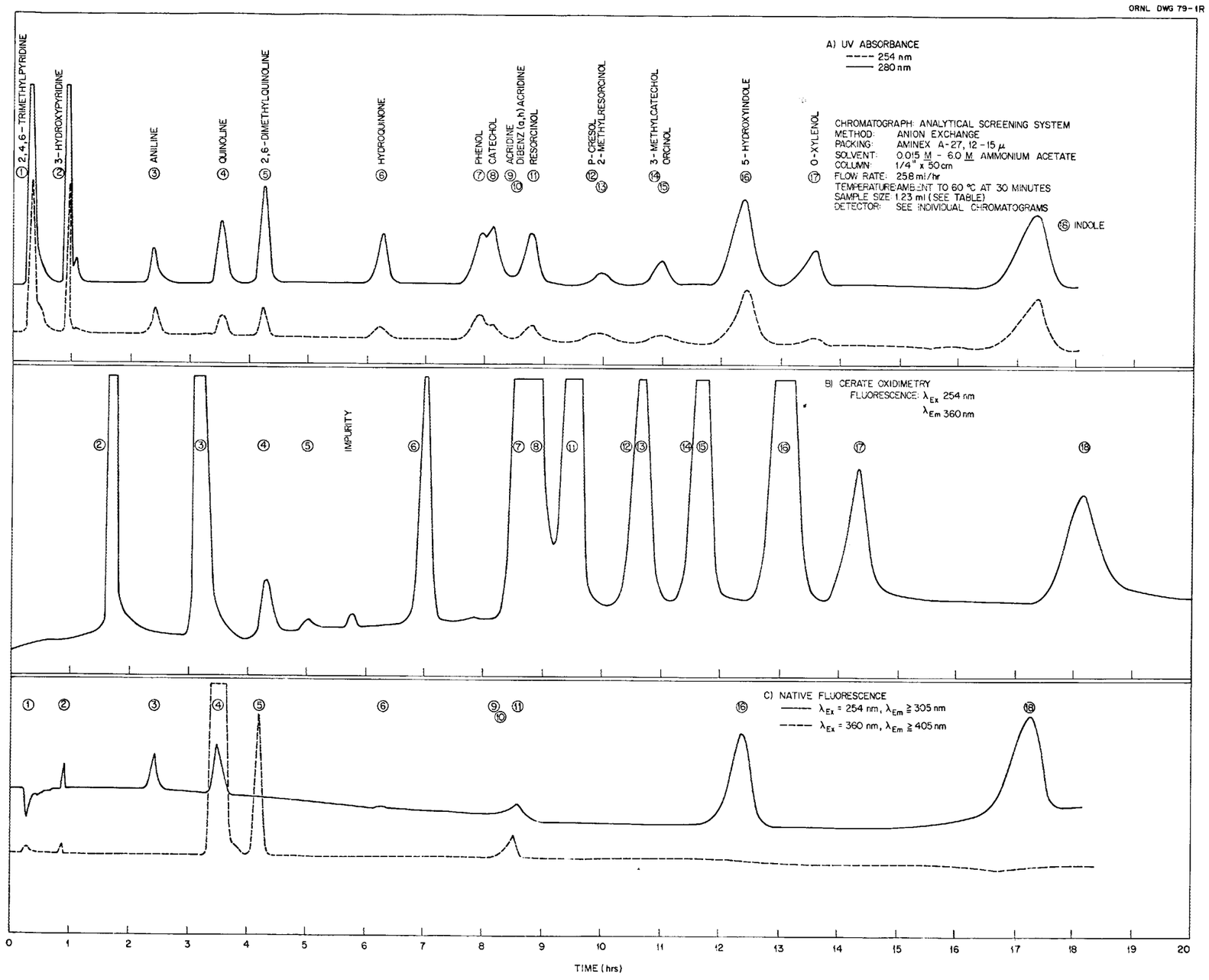


Fig. 6.12. Synthetic coal conversion wastewater.

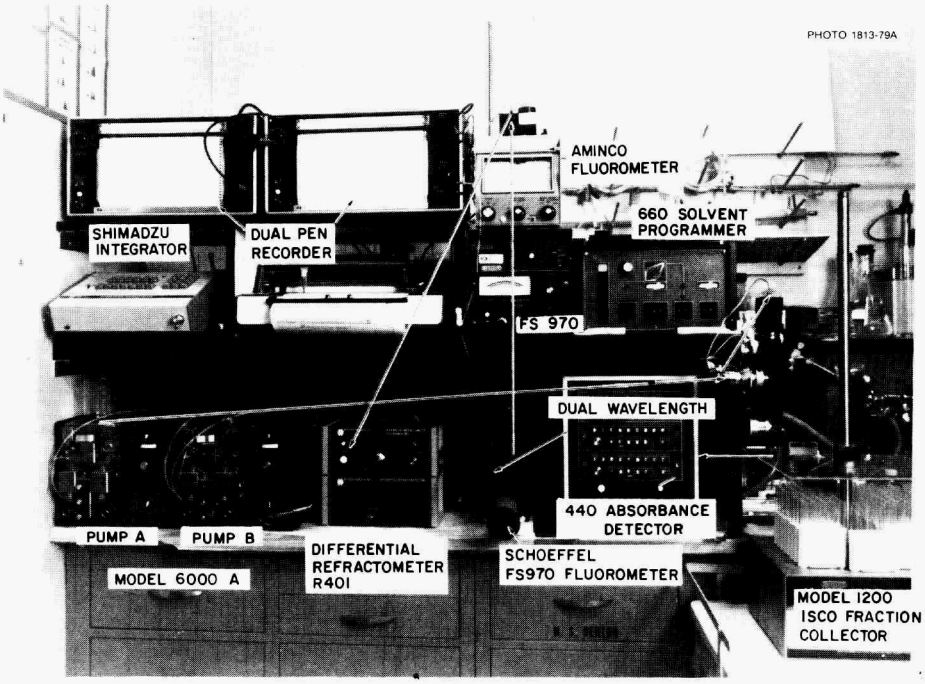


Fig. 6.13. Multidetector, high-performance liquid chromatograph for coal-conversion effluent characterization.

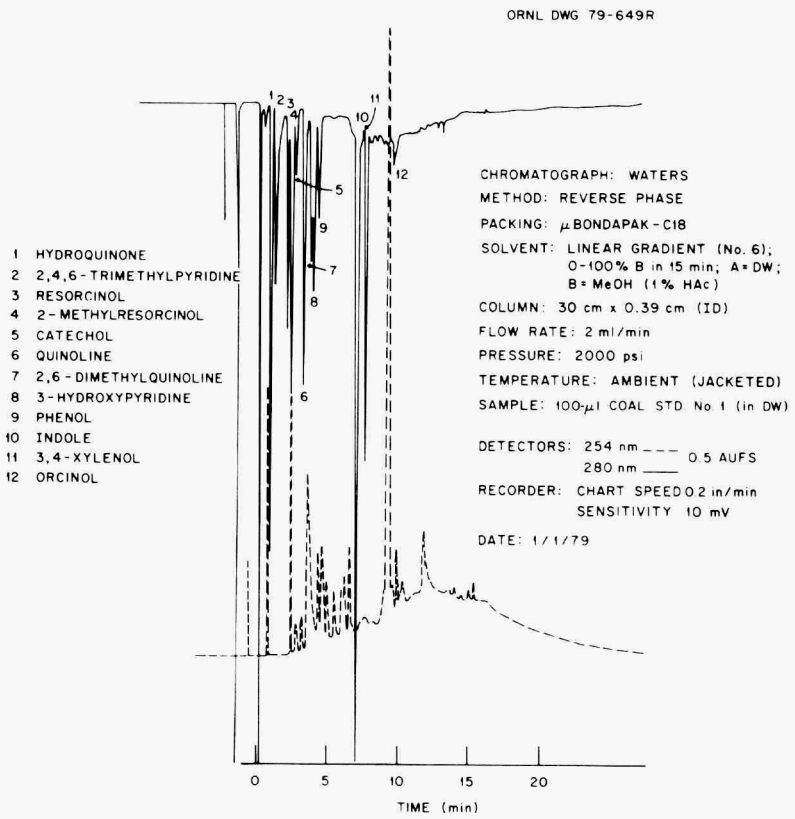
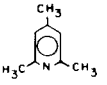
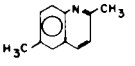
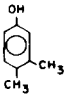


Fig. 6.14. Reverse-phase chromatographic separation of synthetic coal conversion wastewater.

Table 6.4. Elution orders and volumes obtained on the reverse-phase and ion exchange screening systems[a]

Reverse-phase chromatography		Ion exchange chromatography	
Compound	Structure	Compound	Class
1. Hydroquinone (11.46 ml)		2,4,6-Trimethylpyridine (8.6 ml)	Pyridines
2. 2,4,6-Trimethylpyridine (11.85 ml)		3-Hydroxypyridine (24.1 ml)	
3. Resorcinol (13.63 ml)		Quinoline (91.8 ml)	Quinolines
4. 2-Methylresorcinol (14.79 ml)		2,6-Dimethylquinoline (110.3 ml)	
5. Catechol (14.83 ml)		Hydroquinone (161.7 ml)	Phenols
6. Quinoline (15.60 ml)		Phenol (205.1 ml)	
7. 2,6-Dimethylquinoline (15.83 ml)		Catechol (210.0 ml)	
8. 3-Hydroxypyridine (15.92 ml)		Resorcinol (227.2 ml)	
9. Phenol (19.35 ml)		2-Methylresorcinol (256.7 ml)	
10. Indole (25.79 ml)		Orcinol (283.8 ml)	
11. 3,4-Xylenol (26.79 ml)		3,4-Xylenol (350.0 ml)	
12. Orcinol (33.67 ml)		Indole (447.0 ml)	Indoles

[a]Elution volumes are given in parentheses. These values were measured at the first detector in series (uv at 254 nm) for both chromatographic systems.

concerning the effect of various coal types (bituminous Illinois No. 6 and subbituminous Wyodak coals) and different coal treatments (caking prevention steps).[23,24,26-28] Aqueous wastes from the UMD gasifier (e.g., ash pan) have been investigated, in addition to background studies done on the Duluth landfill site (where spent ash will be dumped) and nearby Miller Creek.[25] The most detailed studies have been made on aqueous profile samples from a waste treatment facility located downstream from a coal-tar chemical facility.[23-25,27] These samples were chosen for degradation and sample-handling protocol studies since they are well defined and representative of a typical coal conversion waste.[25] These studies are subsequently being applied to all incoming samples. Figure 6.15 represents a typical profile study on this aqueous waste. As an example, the following peaks have been identified by LC retention times and verified by GC/MS: quinoline at ~4 hr, phenol at ~7.5 hr, cresol at ~10 hr, *m*- and *p*-xylenol at ~11 hr, and *o*-xylenol at ~13 hr. Further work is being conducted on characterizing the above-mentioned waste treatment streams as well as other streams from several treatment methods being developed in-house, including activated sludge, tapered fluidized-bed bioreaction, lignite adsorption, activated charcoal adsorption, ozonation, and combinations of these methods.[28]

26. R. L. Jolley, W. W. Pitt, Jr., J. E. Thompson, and M. S. Denton, Sect. 10.5.2 in *Fossil Energy Program Quarterly Progress Report for the Period Ending December 31, 1977*, ORNL-5387 (May 1978).

27. M. S. Denton and S. R. Dinsmore, Sect. 10.5.2 in *Fossil Energy Program Quarterly Progress Report for the Period Ending March 31, 1978*, ORNL-5421 (July 1978).

28. M. S. Denton and S. R. Dinsmore, in *Fossil Energy Program Quarterly Progress Report for the Period Ending June 30, 1979*, ORNL-5574 (in preparation).

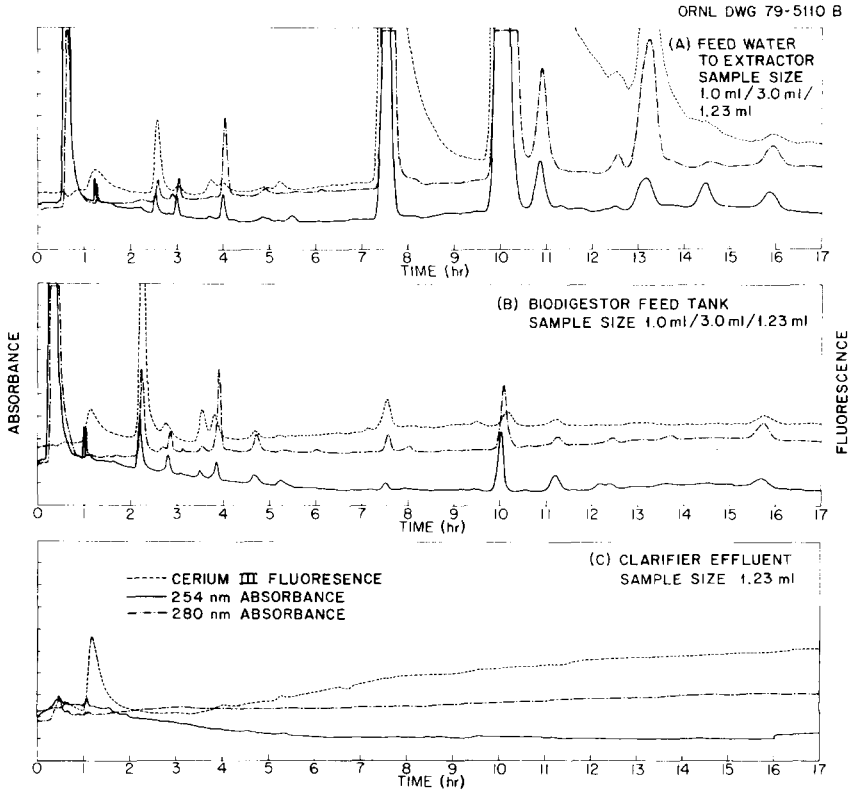


Fig. 6.15. Chromatographic profiles of aqueous effluents. Run conditions: column—50-cm × 0.64-cm stainless steel; resin—Biorad A-27, 12- to 15-μ diam; gradient—0.015 to 6 *M* ammonium acetate, pH 4.45; elluent flow—25.8 ml/hr; temperature—ambient to 60° C at 0.5 hr.

7. Special Isotope Production and Separations

7.1 TRANSURANIUM-ELEMENT PROCESSING

The Transuranium Processing Plant (TRU) is the production, storage, and distribution center for the heavy-element research program in the United States. At TRU, target rods irradiated in the High Flux Isotope Reactor (HFIR) are processed for the separation, recovery, and purification of the heavy actinide elements, which are distributed to laboratories throughout the country for their research work with these elements. Products are usually highly purified prior to shipment and are frequently provided in special chemical forms and/or in special devices required by the experimenter.

TRU Operations

The purposes of this section are to report the production and disposition of transuranium materials and to describe recent changes in the processes and equipment being used in TRU. More detailed information is presented in a series of progress reports on production, status, and plans.[1]

Production, shipment, and fabrication. During this report period, 13 HFIR targets were processed to recover the transuranium elements. Table 7.1 provides a comparison of the amounts of key isotopes obtained this year with the total amounts produced at TRU in 12 years of previous operation. In addition to the target processing, several steps were taken toward increasing the supply of feed material (curium and americium) for HFIR targets. About 360 g of curium (93% ^{244}Cm) was received from the ORNL Fission Product Development Laboratory (FPDL) in five canisters. The canisters were cut open, and about 250 g of the curium was transferred to smaller containers for shipment to the Savannah River Plant (SRP). This is the first stage of an exchange of two batches (approximately 250 to 300 g each) of curium between ORNL and SRP. Because of the particular isotopic compositions involved, this exchange will be advantageous to both parties. The remainder of curium from FPDL was purified from the ^{240}Pu daughter and converted to the oxide form for subsequent shipment to researchers. Approximately 85 g of americium oxide that was received from SRP was processed and converted to americium oxide microspheres for use in HFIR targets.

During product finishing operations this year, we recovered and purified 75 μg of ^{253}Es, 38 mg of ^{249}Cf, and 104 mg of ^{248}Cm; these are the daughter products of ^{253}Cf, ^{249}Bk, and ^{252}Cf respectively. Fifty-five product shipments were made to researchers throughout the country. Eight HFIR targets were fabricated.

Processes and equipment. The dissolver off-gas system that was installed last year[2] to demonstrate the Iodox process for removing radioiodine was operated during Campaign 56 using mercuric nitrate [0.4 *M* $Hg(NO_3)_2$–10 *M* HNO_3]. The decontamination factor achieved for ^{131}I was 500. This factor is not as good as that obtained while using the Iodox process (scrubbing with hyperazeotropic nitric acid), but it is sufficient to remove the bulk of the ^{131}I and leave only a few millicuries to be sorbed on the secondary (Hopcalite-charcoal) system.

The nine mineral oil–filled, lead-glass bulk shielding windows in the main cell bank were partially dismantled and cleaned internally. This was the first time since the windows had been installed that any of the mineral oil or glass plates had been removed. Cleaning involved draining the mineral oil, removing the hot-side cover glass and the 8-in. (20.3-cm)-thick lead-glass plate in four of the windows, wiping internal surfaces with ethanol and lint-free cheesecloth to remove a hazy soap film that contained some lead carbonate, reassembling the window using new

1. L. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Report of Production, Status, and Plans for the Period January 1, 1978–September 30, 1978*, ORNL-5531 (June 1979).

2. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1978*, ORNL-5383, pp. 68–69.

Table 7.1. Amounts of materials recovered in the Transuranium Processing Plant

Time period	April 1978 to March 1979	August 1966 to March 1978
Number of years	1	12
Number of target campaigns	1	38
Number of targets processed	13	435[a]
Amounts of key isotopes recovered:		
^{242}Pu	0	141 g
^{243}Am	3 g	249
^{244}Cm	21 (60) g[b]	1831 g
^{249}Bk	32 mg	424 mg
^{252}Cf	322 mg	3809 mg
^{253}Es	0.8 mg	17.5 mg
^{257}Fm	0.6 pg	9.4 pg

[a]Number of targets includes 238 HFIR targets, 176 SRP slugs and targets, and 21 SRP Pu-Al tubes.
[b]Value in parentheses is total curium.

gaskets, and filling the window tank with fresh mineral oil. The two 6-in. (15.2-cm)-thick lead glass plates and the cold-side cover glasses were not disturbed in any of the windows. The glass surface had not been etched. Light transmittance measurements indicated that the old mineral oil was only very slightly inferior to the new oil.

Special Projects

The facilities available at TRU are used for a variety of purposes in addition to those associated with the main-line production and distribution of transuranium elements. These special projects include nonroutine productions, special preparations, special irradiations in the HFIR, and fabrication of neutron sources from ^{252}Cf.

Fabrication of neutron sources from ^{252}Cf. Some of the californium recovered at TRU is incorporated into neutron sources, which are loaned to researchers. Four sources containing 5 μg to 2.6 mg of ^{252}Cf were fabricated this year; three of these were doubly encapsulated in type 304L stainless steel in a standard TRU configuration (NSD).[3] One source was prepared for the National Bureau of Standards in a special point-source configuration.[4]

Sources returned. Neutron sources are returned to TRU when the projects for which they were requested are completed or when replacement sources are ordered to make up for decay of the ^{252}Cf. These sources are available for reassignment until the appropriate time for reprocessing to recover the ^{248}Cm daughter. During the report period, three sources were returned and five were reassigned. In addition, a small neutron source was received from Oak Ridge Associated Universities and placed in the TRU inventory of sources available for reassignment. This source had been fabricated at SRP. Ninety-two sources are now on loan, and five sources (including the SRP source), which contain from 2 μg to 1.8 mg of ^{252}Cf, are available for reassignment.

Purification of ^{243}Am. The project to prepare multigram amounts of highly purified ^{243}Am (for use in neutron cross-section studies, for capture gamma studies, and as an analytical standard) was completed during this period. Ion exchange techniques were used to reduce the concentration of ^{244}Cm in the ^{243}Am to less than 1 ppm. Approximately 32 g of ^{243}Am was purified and then converted to the oxide form by calcining the oxalate. Another batch, containing 2 g of ^{243}Am, was purified further using new equipment and special care to prevent recontamination; this product contained $\leqslant$25 ppb of ^{244}Cm.

Enrichment of ^{244}Pu. A project to enrich the ^{244}Pu concentration in approximately 100 mg of plutonium for use in biomedical studies was completed during this report period. During April 1977, the plutonium was irradiated in the HFIR to burn out the lighter

3. J. E. Van Cleve, Jr., L. C. Williams, J. B. Knauer, and J. E. Bigelow, "Fabrication of ^{252}Cf Neutron Sources at Oak Ridge National Laboratory," p. 25 in *Applications of Californium-252, Proceedings of an American Nuclear Society National Topical Meeting*, CONF-720902 (1972).

4. L. C. Williams, J. E. Bigelow, and J. B. Knauer, Jr., "Equipment and Techniques for Remote Fabrication and Calibration of Physically Small, High Intensity ^{252}Cf Neutron Sources," pp. 165–72 in *Proceedings of 24th Conference on Remote Systems Technology* (1976).

isotopes. Subsequently, it was chemically processed to isolate the irradiated plutonium, which was stored to await decay of ^{246}Pu (half-life = 10.85 days). A final purification run (nitrate anion exchange) has now been made. The final product, containing 54.3 mg of ^{244}Pu, read only 2 mR/hr at contact. The specific alpha activity of the product was about three times that of pure ^{244}Pu but only 1/1200 that of pure ^{239}Pu; most of the excess activity came from the ^{242}Pu. The isotopic analysis and the contributions to alpha activity are shown in Table 7.2.

Table 7.2. Isotopic analysis of enriched ^{244}Pu

Nuclide	At. %	Alpha emission (%)
^{238}Pu	0.000033[a]	11.11
^{239}Pu	0.0021[a]	2.60
^{240}Pu	0.0016	7.20
^{241}Pu	0.0013	0.07
^{242}Pu	0.572	43.62
^{244}Pu	99.423	35.40

[a]Values adjusted to agree with observed alpha pulse-height analysis.

Production of ^{254}Cf. Californium-254 was prepared by irradiation of 14 μg of isotopically pure ^{253}Es in the HFIR Hydraulic Rabbit Facility to produce 39 hr of ^{254m}Es. A small fraction (0.078%) of this material decays by electron capture to ^{254}Cf. (The majority of the ^{254m}Es decays by beta emission to ^{254}Fm, which in turn decays by alpha emission to ^{250}Cf.) When ^{254}Cf is produced in this manner, it is sufficiently enhanced with respect to ^{252}Cf to permit studies of the spontaneous fission properties of ^{254}Cf without interference from the fission of ^{252}Cf.

The irradiated rabbit was transferred by means of the hydraulic transfer system from the HFIR basin to TRU cave B where it was dissolved and chemically processed. A high-pressure ion exchange run was made to separate the einsteinium from the initial californium daughter. After an interval of 5 days, a second high-pressure ion exchange run was made to separate the newly ingrown californium. The product of the second run is the premium ^{254}Cf; however, the product of the first run was also of sufficient quality to be of some value. The isotopic compositions of the californium products are listed in Table 7.3.

Purification of ^{240}Pu. Two multigram lots of aged ^{244}Cm were processed this year to remove the ingrown ^{240}Pu. The crude ^{240}Pu product was saved for later recovery and purification because of its unusual isotopic composition. The first batch contains 21 g of ^{240}Pu; the second batch contains about 11 g. We have received several requests for portions of the material and have further processed decigram amounts of the crude material in a glove box using the standard plutonium nitrate–anion exchange process in a 7-ml column. Although more than the usual difficulty was experienced in adjusting the valence of the plutonium in feed (possibly due to organic residues from the in-cell operations), the ion exchange went smoothly once the adjustment was accomplished. The first lot was converted to oxide by oxalate precipitation, followed by calcination. This material is being used to prepare flux monitors for measuring fast-neutron spectra. The second lot is radiochemically very pure; it will be used in studies of ^{240}Pu capture gammas and

Table 7.3. Isotopic compositions of ^{254}Cf products

Nuclide	First-run product		Second-run product	
	At. %[a]	Percentage of fissions	At. %[a]	Percentage of fissions
^{249}Cf	7.2	5×10^{-8}	≤2.4	~0
^{250}Cf	86.4	2.7	99.91	1.10
^{251}Cf	3.6	0	≤3.2	~0
^{252}Cf	2.8	16.7	≤0.91	≤1.9
^{254}Cf	0.0263[b]	80.6	0.0914[b]	98.9
Amount of ^{254}Cf shipped:				
First-run product		237 pg		
Second-run product		181 pg		

[a]Estimated from alpha pulse-height analysis.
[b]Estimated from gross neutron counts with known corrections.

in studies of the lesser-known decay modes of the ^{236}U daughter. The isotopic compositions of the two lots and the amounts purified are shown in Table 7.4.

Table 7.4. Isotopic compositions of ^{240}Pu products

Nuclide	Lot No. 5H111Pu-OX (at. %)	Lot No. 5H136Pu-Prod (at. %)
^{238}Pu	0.095	0.014
^{239}Pu	0.018	0.020
^{240}Pu	99.866	99.936
^{241}Pu	≤0.001	0.001
^{242}Pu	0.020	0.029
^{244}Pu	≤0.001	≤0.001
^{240}Pu recovered	0.134 g	0.292 g

7.2 ISOTOPIC SEPARATIONS

The current separations program has two primary objectives. The first is to maintain viable sales and Research Materials Collection (RMC) inventories for use in fundamental neutronics research and in diverse medical, commercial, and applications research such as nuclear medicine, analytical instrumentation, atomic clocks, and lasers. Sixty new loans, amounting to approximately 2.9 kg of enriched electromagnetically separated isotopes, were made from the RMC during the past fiscal year. During the same period, 1886 sales accounted for more than 1.2 kg of separated isotopes whose value was more than $1.4 million. Recent experience has shown that approximately 60% of the sales revenue has come from foreign sales.

The second objective of the program is to develop a basic understanding of high-throughput ion sources, ion beam dynamics, and isotopic receiver concepts. The systematic investigation and improvement of the performance of electromagnetic separators through the development of alternate component design and modifications of operational parameters assist in providing higher-assay isotopes at greater production rates.

Isotopic separations of five different elements were completed, two of which (mercury and thallium) were in progress at the beginning of the reporting period Throughout this period, only one segment of separators (eight beta-type units) was utilized at any given time for production separation. These units were operated on a 5-day/week, 24-hr/day basis. Table 7.5 lists these elements and the approximate percentage of effort expended for each separation, the isotope of primary interest, the recovered quantity, and the isotopic purity of the isotope of interest. Four of the five nuclides are precursors for the production of radioisotopes currently being used in nuclear medicine; the fifth (^{62}Ni) is also the precursor of a radioisotope, but it is used in an industrial application. The remaining isotopes of each element, which could be collected concurrently, will be available for potential sales or RMC inventories.

In addition to the production separations, three research and development (R&D) enrichment programs were completed by utilizing specialized equipment or special charge materials. These were ^{96}Ru, $^{192,194}Os$, and ^{208}Pb.

The ruthenium separation, whose purpose was to recover 100 mg of ^{96}Ru enriched to ~98%, made use of a special nickel-lined arc chamber, a nickel ion exit slit, normal ruthenium-metal charge material, and chlorine triflouride as the fluorinating agent. Three short runs were involved with a total ion reception time of 43 hr. The recovered product consisted of

Table 7.5. Summary of stable isotope production

Element	Percent of total annual effort	Major isotope	Quantity (mg)	Assay (%)
Mercury	6.4	196	505	40.61[a]
Thallium	6.4	203	464,484	96.28
Nickel	27.1	62	65,337	96.64
Chromium	27.1	50	30,370	96.40
Calcium	33.0	46	53[b]	>35[c]

[a]Average isotopic purity of two inventory samples.
[b]Estimated from monitored ion currents.
[c]Estimated.

142 mg of 98.56% ^{96}Ru. This is the highest-purity ^{96}Ru separated in the ORNL calutrons.

Osmium-194, a radioactive isotope with a half-life of 6 years, is a beta emitter with a decay energy of 97 keV. This nuclide, which is produced by neutron irradiation, is considered a valuable mass spectrometry "spike" for measuring the ^{187}Os daughter from the decay of the extremely long-lived (5×10^{10} years) nuclide, ^{187}Re. Because ^{187}Re is a naturally occurring radionuclide, the precise determination of its half-life would permit its use as a "clock" for determining the age of the universe.

The charge material supplied for the isotopic enrichment of ^{194}Os consisted of ~1 g of moist osmium powder containing a calculated 5.4 μg of ^{194}Os. The one run involving osmium had an ion reception time of 11 hr. The ion source, as in the ruthenium separation, had a nickel-lined arc chamber and a nickel ion exit slit; the osmium was vaporized through the use of chlorine trifluoride. Graphite pockets were used to catch the separated ^{192}Os and ^{194}Os. Activity measurements made on the two collected samples and the original charge, along with peak-to-valley ratios acquired through the run, indicated that the enrichment was successful.

The special high-purity ^{208}Pb enrichment effort was made for the purpose of obtaining gram quantities of ~99.9% product for a specific customer. To attain the requested purity, 82.7 g of lead that had been preenriched to 98.17% in ^{208}Pb by a prior calutron separation was used as the feed. The lead, which was in the form of oxide, was dissolved and converted to anhydrous lead chloride, the preferred charge compound. Special equipment involved in the separation included a two-part water-cooled collector pocket, a source oven that was slightly modified for better temperature control, and partial side shields in the liner. The separation consisted of one run with an ion reception time of 86 hr, which yielded a monitored equivalent weight of 16.5 g of ^{208}Pb. Following chemical recovery and refinement, 14.245 g of 99.97% ^{208}Pb was recovered from the back part of the collector, 0.703 g of 99.81% from the front part, and 0.547 g of 99.59% from the face plate. The process efficiency, which from previous separations was expected to be between 12 and 15%, was a very excellent 20% for this enrichment program.

The 180° sector separator was used to prepare ion-implanted and surface-deposited targets for physics research. Two ^{204}Hg-ion implanted targets were prepared using an accelerating potential of 38 keV and 65-μg/cm^2 carbon foils as substrates. The monitored ion current was maintained at 4 μA/cm^2, and the deposition was continued until the integrated ^{204}Hg ion current corresponded to an area density of 15 μg/cm^2. Two sets of isotopically enriched ^{178}Hf and ^{180}Hf targets were made. The first set, consisting of two targets of each isotope, was prepared using 5×10^3-μm nickel foil substrates, and the ion beam was decelerated to ~200 eV at the target. The estimated thickness, based on integrated ion current, was >500 μg/cm^2. The second set, also consisting of two targets of each isotope, was prepared using 75-μg/cm^2 carbon foil substrates with the Hf^+ beams decelerated to ~200 eV. The estimated isotopic purity of all of these targets was >99.9%.

During the year, 31 new lots of separated isotopes were added to the inventory to fill sales and/or loan requirements. These new lots, comprised of eight different elements, represented a total weight of 888 g; however, the sales program for approximately the same time interval (fiscal year ending September 30, 1978) involved 1256 g. It thus becomes obvious that a steady-state inventory cannot be maintained by using an eight-tank operation. Fifty-two samples, which had been on loan from the RMC, were reprocessed and returned to the loan pool.

Separator Research and Development

In addition to active participation in the three special collections (^{96}Ru, ^{194}Os, and ^{208}Pb) and in certain in-process development runs, the separator R&D group was involved in the following studies: (1) development of an ion source and operating parameters to permit the use of mercury metal as charge material in the collection of mercury isotopes; (2) development of a high-temperature ion source capable of vaporizing and ionizing metallic charges such as the lanthanides or actinides; and (3) development of a system that provides high process efficiency, efficient ion collection, and a charge-recovery technique for processing gaseous feed materials such as the rare gases.

In analyzing separator operations for mercury, it is apparent that startup and achieving and maintaining acceptable beam focus are the problem areas. Although ~10 mA of total ion output is usually possible with mercury metal or with various mercury compounds (monochloride, dichloride, or sulfide), the isotopic purity of the products, notably ^{196}Hg, is limited by poor focus. A systematic study, primarily using mercury metal as a charge, was initiated to evaluate the effect of the various calutron components on focus. After obtaining reliable vapor control

in the ion source, changes were made to improve liner conductance, the ion exit slit sizes were altered, miniplates that border the beam were substituted for full-boundary plates, changes were made in the ion source, different arc-support gases were used, and an attempt was made to increase spacing between collector pockets. The use of a multifilament ion source, which was a major change, was also attempted in an effort to improve focal conditions. To date, more than 25 changes have been made in calutron parameters, and no single change affects the separation of mercury isotopes as much as providing a perfectly clean system for the operation.

The development of an ion source with the capability of processing high-temperature feeds continued. The M-16 ion source, with the filament position behind the ion exit slit, operated at an oven temperature of ~1500°C using Dy_2O_3 charge material chlorinated with a controlled flow of CCl_4. Following some difficulties with this source, which seemed to be related to the porosity of the graphite components, a P-2 type of arc chamber and oven assembly was fitted to an M-12 source assembly for testing. The P-2 equipment was designed for high-temperature operations in the radioactively controlled area. A test run with the P-2 assembly, which also used $Dy_2O_3 + CCl_4$ as the charge system, gave an output of 3.2 mA of $^{164}Dy^+$ at an applied power of 2.5 kW. A postrun inspection of the source showed that the lava heater insulators had fragmented at the operating temperature. The P-2 subassembly was then fitted with the high-temperature version of the oven-arc assembly. With a restrictive vapor baffle placed inside the charge bottle, the modified source consistently gives twice the output of the M-16–type source. Maximum output is attained with a power input of ≥3.2 kW. The differences in source geometry responsible for this increase in ion output have not yet been identified.

In the past, the efficient separation of rare-gas isotopes in an electromagnetic isotope separator was complicated by the difficulty of retaining the isotopically enriched product in a conventional collector pocket. The potential requirement of using an expensive preenriched feed would make it necessary to add a feed recovery system. A development program was initiated in an effort to resolve some of the past difficulties so that the xenon isotopes could be enriched.

A new concept of collecting separated rare-gas isotopes on a continuously renewed metallic surface has proved to be a reasonably efficient method of retaining isotopically enriched products. Following futile efforts to vaporize and uniformly deposit aluminum on a 5- by 8-in. (12.7- by 20.3-cm) plate at ≥1 g/hr, antimony was chosen as a substitute material. Deposits were formed from antimony vapors in a prototype receiver, and the orifice configuration of the oven was altered until a uniform deposit was achieved. A monitored 21-cm^3 (STP) collection of $^{40}Ar^+$ yielded an unpurified 16 cm^3 (STP) of recovered gas from the 16.8 g of antimony deposited on the plate. The actual ion impact area was ~130 cm^2 with a current density of ~4 $\mu A/cm^2$. Approximately one-half of the deposited antimony flaked off the plate as a result of ion bombardment, and these flakes were included in the product recovery. Essentially no gas was found trapped in the antimony not hit directly by the ion beam.

In a subsequent collection of ^{131}Xe from normal feed, the area impacted was smaller than with the argon beam, and the calculated current density was 10 $\mu A/cm^2$. Even though flaking occurred again and the current density was higher, >50% retention was achieved.

The possibility of feeding the ion source directly with gas exhausted from the diffusion pumps was discounted when it was verified that the system would probably initiate a gaseous discharge when it was connected to the 35-kV source potential.

As an alternative to a total feed recovery system, attempts are being made to increase the process efficiency to a level such that feed recovery can be omitted. With continued source modifications and the use of helium as a support gas, it is estimated that an efficiency of 15 to 20% can be attained. Previously, a process efficiency of 5% was typical in a separation; currently, the output has reached 10 mA, with beam quality ranging from 30:1 to 80:1. The recently made changes may well eliminate the necessity of feed recovery.

8. Nuclear Regulatory Commission Programs

8.1 REACTOR SAFETY RESEARCH

Fission Product Release from LWR Fuel

The primary objectives of this program are to determine the quantities and characteristics of radiologically significant fission products released from defected fuel rods in steam and air in the temperature range 500 to 1600°C. The experiments are not intended to simulate specific hypothetical accidents but rather to duplicate the general conditions of a spent-fuel transportation accident (SFTA), a controlled loss-of-coolant accident (LOCA), and a LOCA with partially deficient emergency cooling.

The series of experiments has included tests of apparatus efficacy using individual chemical species anticipated in accident situations,[1] tests in which simulated fission products were implanted in unirradiated fuel rods,[2] and release tests with segments of both low- and high-burnup fuel rods.[3] Preliminary models[4] for the release of cesium and iodine in steam were formulated for 500 to 1200°C, the temperature range anticipated for a controlled LOCA. The models assume that the release is the sum of the "burst release" (that carried out with vented plenum gas at the time of rupture) and the "diffusional release" (that which diffuses from the gap space as a function of time at constant pressure).

During this reporting period, the gap inventories of cesium and iodine in high-burnup fuel rods removed from the H. B. Robinson-2 reactor were measured to be ~0.3% of the total inventory[5,6] as compared with the fission gas release in-reactor of ~0.25%. Four tests were performed with this fuel in the temperature range 1300 to 1600°C to explore diffusional release from defected fuel rods at higher temperatures. For these tests, the cladding was first expanded by internal pressure to form a uniform radial pellet-to-cladding gap of 0.38 mm. This gap width, combined with a hole drilled through the cladding, produced a defect equivalent to that expected to result from pressure-rupturing of the cladding.

The results of subsequent heating of these fuel rod segments and previous results normalized to 10-min release from a ruptured rod configuration are shown in Fig. 8.1. Cesium and iodine that were released within this time period originated from the initial gap inventory for temperatures ≤1200°C. A large release of cesium and iodine occurred rather rapidly when the fuel rod segments were heated to between 1300 and 1600°C. This is believed to have resulted from the coalescence of small fission gas bubbles, iodine, and cesium that had previously accumulated at grain boundaries. The large bubbles that were formed linked in tunnel fashion to obtain access to the gap space.[7,8]

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1. R. A. Lorenz, M. F. Osborne, J. L. Collins, S. R. Manning, and A. P. Malinauskas, *Behavior of Iodine, Methyl Iodide, Cesium Oxide, and Cesium Iodide in Steam and Argon*, ORNL/NUREG/TM-25 (July 1976).
2. R. A. Lorenz, J. L. Collins, and S. R. Manning, *Fission Product Release from Simulated LWR Fuel*, NUREG/CR-0274 (ORNL/NUREG/TM-154) (October 1978).
3. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, O. L. Kirkland, and R. L. Towns, *Fission Product Release from Highly Irradiated LWR Fuel*, NUREG/CR-0722 (ORNL/NUREG/TM-287) (in preparation).
4. R. A. Lorenz, J. L. Collins, and A. P. Malinauskas, *Fission Product Source Terms for the LWR Loss-of-Coolant Accident: Summary Report*, NUREG/CR-0091 (ORNL/NUREG/TM-206) (June 1978).
5. A. P. Malinauskas et al., *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period January–March 1978*, NUREG/CR-0116 (ORNL/NUREG/TM-208) (June 1978).
6. A. P. Malinauskas et al., *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period April–June 1978*, NUREG/CR-0370 (ORNL/NUREG/TM-242) (September 1978).
7. A. P. Malinauskas et al., *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period July–September 1978*, NUREG/CR-0493 (ORNL/NUREG/TM-280) (December 1978).
8. A. P. Malinauskas et al., *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period October–December 1978*, NUREG/CR-0682 (ORNL/NUREG/TM-308) (April 1979).

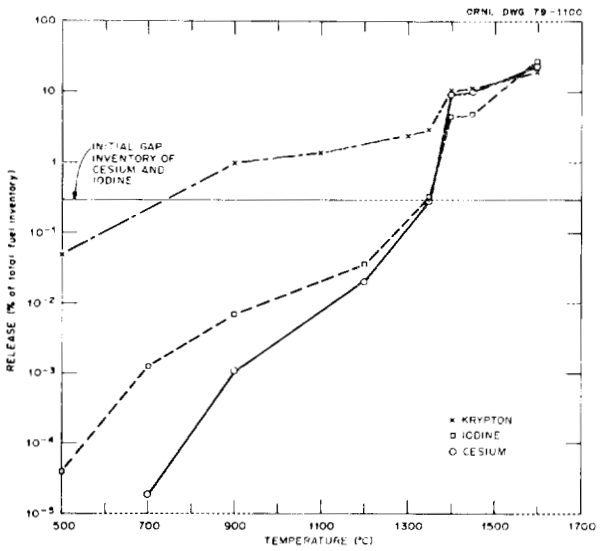

Fig. 8.1. Release of krypton, iodine, and cesium from 15.2 cm of H. B. Robinson-2 fuel: 10 min in steam with ruptured cladding.

In addition to releases of the initial gap inventory and grain boundary accumulations, diffusion from the UO_2 matrix occurs slowly above ~1000°C. The diffusion coefficient, D, for cesium from high-burnup fuel was measured to be 7×10^{-12}/sec at 1100°C.[6]

One experiment was conducted in the Boiling Water Reactor Test Series. This series tests fuel from the Peach Bottom-2 reactor irradiated to 13,000 MWd/MT (metric ton of initial uranium) at a linear heat rating high enough to have released approximately 15% of the fission gas from the peak burnup region of the fuel rod. One fuel rod segment was pressure-ruptured at 970°C, and it was determined that 1.71% of the total cesium inventory was released with the vented "plenum" gas. This compares with ~0.03% of the total cesium released in a similar test conducted at 900°C an H. B. Robinson-2 fuel rod segment irradiated at a low-heat rating. The difference is explained by a similar ratio of cesium gap inventories.

Transient Release from LMFBR Fuel

The objective of the Aerosol Release and Transport (ART) experimental program in the Chemical Technology Division, sponsored by NRC, is the characterization of aerosols resulting from a fast reactor accident. It is intended to provide data and analytical techniques for the assessment of the containment behavior and release of radionuclides and fuel particles to the environment as a result of postulated hypothetical core-disruptive accidents (HCDAs).

The initial phase of the program emphasized the development of a nonnuclear high-energy transient simulator technique which used a capacitor discharge; this was successfully demonstrated and later integrated with the Fuel Aerosol Simulator Test (FAST) project in the Engineering Technology Division. Descriptive material is contained in several summary reports.[9,10]

A second phase of the program initiated last year required the development of alternative techniques for generating fuel-simulant (LMFBR mixed oxide) aerosols on a continuous basis for U_3O_8 or UO_2 concentrations approaching 100 g/m^3. The first of these new techniques was the dc electric-arc method.[11] This technique generates a somewhat crystalline type of pure UO_2 aerosol composed of primary particles that exhibit vapor-condensation crystal growth as a result of the extended time of residence in the high-temperature zone of the furnace. The method, however, was found to be limited to the production of relatively low maximum aerosol concentrations (<20 g/m^3) in the 4.5-m^3 test vessel.

Fast reactor fuel aerosol generation by the metal-oxygen process. A new method, based on the continuous combustion of finely divided metallic uranium in an oxygen atmosphere preheated by a 40-kW dc plasma electric arc, was developed as a second alternative this year. This generator was simpler to scale up and was recently adopted for use by the tenfold-larger ART companion facility, the Nuclear Safety Pilot Plant, as their primary fuel-aerosol generation technique. A modification of the dc plasma torch has been fitted with a larger array of 16 capillary metal-powder feeder tubes to increase the burning rate. A further modification, with larger-diameter feeder tubes that will double the present burning rate of 120 g/min, is under development. Aerosol concentrations above 50 g/m^3 of U_3O_8 have

9. M. J. Kelly, G. W. Parker, and J. M. Rochelle, *Development of the Capacitor Discharge Vaporization Technique to Produce Aerosols Formed under Conditions Postulated for Hypothetical Core Disruptive Accidents*, NUREG/CR-0226 (ORNL/NUREG/TM-160) (July 1978).

10. A. L. Wright et al., *Effect of Energy Density on Aerosol Yield and Primary Particle Sizes Produced by the Capacitor Discharge Vaporization (CDV) of UO_2*, NUREG/CR-0120 (ORNL/NUREG/TM-163) (October 1978).

11. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977*, ORNL-5295, pp. 69–72.

been generated in the 4.5-m^3 CRI-II containment vessel for detailed characterization in terms of deposition rate, particle size, and nitrogen-adsorption (BET) surface area.

Size distribution analysis by the spiral duct centrifuge. One unique method of measuring size distribution of the chain-agglomerate type of aerosol is the fractional deposition of the aerosol on the foil liner of a spiral-duct aerosol centrifuge. After the foil has been cut into multiple short segments and the segments have been analyzed for uranium, size distributions can be determined in the conventional way. A typical set of distribution curves, shown in Fig. 8.2, illustrates the remarkable reproducibility of this method of size analysis. When this method is used to compare sizes with those from cascade impactors, it is confirmed that impactors,[11] as well as all high-velocity orifice devices, give erroneous (smaller) size distributions for chain agglomerate particles because of agglomerate fragmentation.

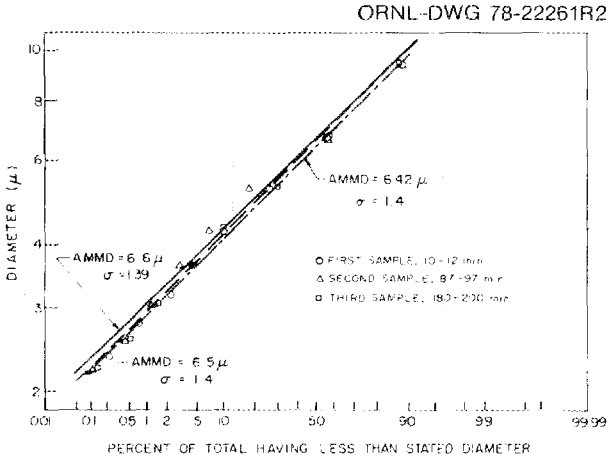

Fig. 8.2. Aerodynamic sizes of plasma-torch-generated U_3O_8 agglomerates at three interval.

By combining (1) the average primary particle size derived from the BET surface area, (2) the average number of agglomerates (condensation nuclei) per unit volume, and (3) the total airborne weight of oxide per unit volume, the number of primary particles in an average branched-chain agglomerate can be calculated; this is illustrated in Table 8.1 for an example of each type of fuel aerosol. Photomicrographs of agglomerates taken at similar intervals show similar numbers of primary particles in the agglomerates.

The next phase of our program will investigate the aerosol behavior of mixed oxides (UO_2, U_3O_8, Na_2O_x). A recent version of the plasma torch with the mixer head is shown in Fig. 8.3.

Table 8.1. Number of primary particles per agglomerate

Time (min)	Type of aerosol: Capacitor-discharge UO_2, CDV-16	Plasma-torch U_3O_8, PT-20	Arc-furnace UO_2, AF-10
20	6,600	1,882	280
40	12,400	3,103	440
60	10,300	3,311	500
80	9,200	3,065	530
100	8,900	2,671	550
150		1,774	580
200		1,292	610
250		1,064	570
300		957	510

8.2 AUTOMATED STORAGE VAULT STUDY

The objectives of the safeguards work for NRC in the Chemical Technology Division include the study and development of the requirements, criteria, and operating characteristics of vaults that offer a high degree of protection for special nuclear materials (SNM) storage. Results of this study have been presented in a series of three reports[12–14] that will assist the Materials Protection Standards Branch of NRC in the preparation of standards, guides, and criteria for vault storage systems within the licensee fuel cycle sector.

The first report[12] evaluated concepts of various degrees of vault automation and established their feasibility and desirability. The second report established the safeguards value and the cost of vault automation.[13] The third report discussed design criteria developed by applying the safeguards worth–evaluation methodology to various vault concepts and the establishment of a basis for comparison of the options.[14]

12. W. R. Hamel and L. B. Shappert, *Desirability and Feasibility of Vault Automation in SNM Storage*, NUREG/CR-0318 (ORNL/NUREG-20) (October 1977).

13. W. T. McDuffee and W. R. Hamel, *Value Impact of Vault Automation in Special Nuclear Material Storage*, NUREG/CR-0019 (ORNL/NUREG-33) (August 1978).

14. W. T. McDuffee, W. R. Hamel, L. B. Shappert, and A. S. Pruitt, *Design Criteria for Vault Automation in Special Nuclear Material Storage*, NUREG/CR-0372 (ORNL/NUREG-44) (November 1978).

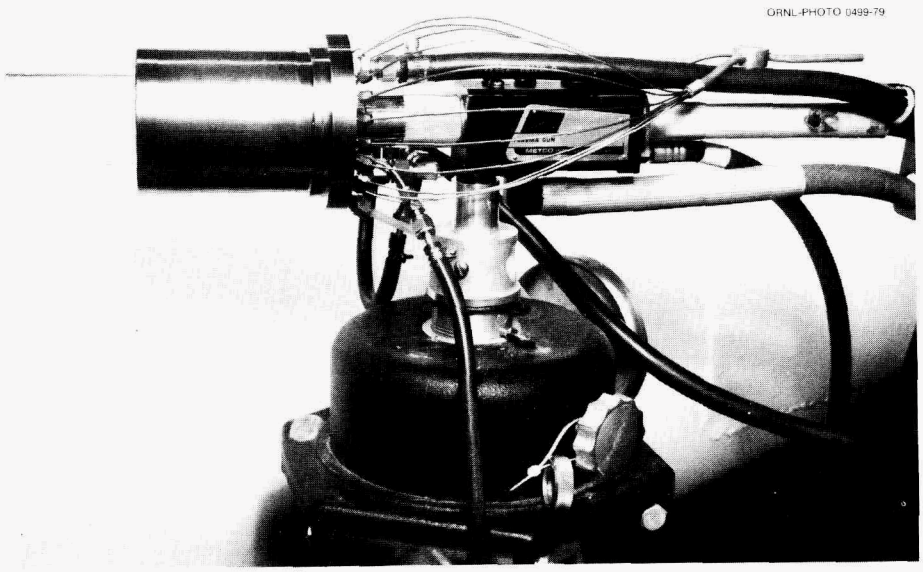

Fig. 8.3. Plasma torch with mixer head.

A quantitative evaluation must be made of the safeguards-related performance before vault storage design options can be determined. To evaluate the vault storage effectiveness, it is first necessary to identify the vault design parameters that can affect the basic safeguards functions. After the design parameters have been identified, they can be evaluated by using a numerical technique that would permit a designer to perform trade-off studies. This evaluation methodology should be sufficiently well structured to ensure repeatability by different designers; however, the concept is difficult because of the inherent complexity and subjectivity of safeguards functions and design parameters.

The evaluation methodology is built on a standard set of vault safeguards performance factors that have been defined in terms of the basic safeguards functions. Generally, these performance factors are assigned a numerical value of 0 to 10 based on the attributes of the particular vault concept being considered. To alleviate some of the subjectivity associated with the process of assigning values, each factor has been assigned a specific value that lies between a "standard" lower and upper bound. The purpose of establishing these performance standard bounds is to provide all design personnel with the same reference points. Under the assumption that all evaluations are made with sound engineering judgment, the numerical safeguards values become a reasonable basis for universal comparison of designs.

Once values are assigned to each of the safeguards performance factors, combined performance values for the basic safeguards functions and the overall safeguards value can be calculated using weighted arithmetic averages. Weighting factors are introduced to emphasize or deemphasize certain groups of performance factors.

When the evaluation process is complete, the performance values obtained for each of the safeguards functions would be allowable minimum-value criteria, which can also be considered as "acceptance criteria." A minimum overall allowable value ensures a suitably effective integrated safeguards capability.

8.3 DEVELOPMENT OF "AS LOW AS REASONABLY ACHIEVABLE" (ALARA) GUIDES FOR THE NUCLEAR FUEL CYCLE

Engineering survey studies were conducted to provide the Office of Standards Development with the technical information required to formulate appropriate ALARA guidelines for the release of

radioactive materials from various segments of the nuclear fuel cycle. A report on the conversion of yellow cake to UF_6 by the solvent extraction–fluorination process is in preparation.[15] This will be the final report in the ALARA series. The engineering reports (1) present incremental capital and operating costs for changes and additions to systems and (2) develop corresponding source terms for radioactive emissions and noxious effluents. The systems examined range from those in use to those that may be developed within the foreseeable limits of available technology on the basis of expected operation during the lifetime of the facilities. Estimates of errors inherent in the development of these data are stipulated. The environmental aspect of each study describes the behavior of radionuclides and other noxious materials in the environment and qualitatively estimates the radioactive exposure to the public.

8.4 SAFETY REVIEW OF NUCLEAR FACILITIES

The Chemical Technology Division continued to provide technical assistance to the Office of Nuclear Material Safety and Safeguards in connection with the licensing of nuclear facilities and the preparation of related generic reports. Safety reviews were completed and evaluation reports were prepared for the proposed expansion and operating license renewal, respectiviely, of General Electric's Morris Fuel Storage Operation.

Other significant activities included (1) participation with NRC and Los Alamos Scientific Laboratory in an evaluation of the effects of a tornado on the ventilation system in Nuclear Fuel Services' West Valley Fuel Reprocessing Plant, and (2) a determination of decontamination and exposure costs resulting from the accidental release of radioactive materials from radioisotope processing and fuel fabrication facilities.[16]

8.5 WASTE MANAGEMENT GENERIC STUDIES

The waste treatment operations at all large nuclear and many nonnuclear installations are quite similar. Contemporary reviews of the current state of the art for each waste treatment operation are therefore of value to all segments of the nuclear fuel cycle in evaluating the role of a particular operation. Generic reports on evaporation, ion exchange, and solid waste treatment were prepared and issued in 1973 and 1974. These reports have been updated,[17–19] and a new report on the use of filtration to treat radioactive liquids in light-water-cooled nuclear power plants has been prepared and issued.[20]

15. M. B. Sears, E. L. Etnier, G. S. Hill, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle—Conversion of Yellow Cake to Uranium Hexafluoride, Part II. The Solvent Extraction-Fluorination Process,* ORNL/NUREG/TM-7/P2 (in preparation).

16. J. P. McBride, *Economic Consequences of Accidental Releases from Fuel Fabrication and Radioisotope Processing Plants,* NUREG/CR-0222 (ORNL/NUREG/TM-240) (January 1979).

17. H. W. Godbee and A. H. Kibbey, *The Use of Evaporation to Treat Radioactive Liquids in Light-Water-Cooled Nuclear Reactor Power Plants,* NUREG/CR-0142 (ORNL/NUREG-42) (September 1978).

18. W. E. Clark, *The Use of Ion Exchange to Treat Radioactive Liquids in Light-Water-Cooled Nuclear Reactor Power Plants,* NUREG/CR-0142 (ORNL/NUREG/TM-240) (January 1979).

19. A. H. Kibbey, H. W. Godbee, and E. L. Compere, *A Review of Solid Radioactive Waste Practices in Light-Water-Cooled Nuclear Reactor Power Plants,* NUREG/CR-0144 (ORNL/NUREG-43) (October 1978).

20. A. H. Kibbey and H. W. Godbee, *The Use of Filtration to Treat Radioactive Liquids in Light-Water-Cooled Nuclear Reactor Power Plants,* NUREG/CR-0141 (ORNL/NUREG-41) (September 1978).

9. Miscellaneous Programs

9.1 CONVERSION OF CONSOLIDATED EDISON URANIUM FROM A NITRATE SOLUTION TO U_3O_8

A total of 1047 kg of uranium (76.5% ^{235}U, 9.67% ^{233}U, 1.40% ^{234}U, 5.63% ^{236}U, 6.84% ^{238}U, and 120 parts of ^{232}U per million parts of total uranium) is stored as a nitrate solution in an 18,900-liter (5000-gal) vessel in the Building 3019 facility. The solution has been stored in the present steel vessel for 10 years. It appears unattractive for use as reactor fuel because of the high ^{236}U content and the requirement for remote fabrication into fuel even if interest were evinced in using it.

The solution is maintained subcritical with two soluble neutron poisons (gadolinium and cadmium). Although the vessel was packed with borosilicate glass rings prior to introduction of the solution, neither the integrity nor the boron poison content of these rings can be verified. In addition, the pit housing the vessel does not contain borosilicate rings; therefore, we must rely on soluble poisons to prevent criticality in the event of leakage from the vessel into the pit. The measured concentrations of the poisons have varied widely over the 10-year storage period. However, at no time did the sum of the measured gadolinium and cadmium poison concentrations drop below values adequate to ensure criticality control. We do not have evidence of significant corrosion in the vessel, as determined by analyzing samples of the solution for stainless steel constituents. However, localized corrosion could have occurred, and would present a problem since the vessel walls are only 0.53 cm (0.21 in.) thick. Both DOE-ORO and ORNL Safety Committees have stated that continued storage for longer than an additional 5 years may be unwise.

We have completed the conceptual design of a facility for converting the uranium to U_3O_8, using a demonstrated technique of concentration and nitrate removal followed by solidification in the primary storage can. After being sealed in a second can, the unit is to be placed in one of our recently installed earthquake-proof storage wells.

The high cost ($12 million) of the conversion facility has prompted us to study a number of alternatives for continued storage of this material. Although several alternatives are less expensive, we feel that our solidification proposal is the only one capable of eliminating the long-term storage problems. We will continue the detailed design of this facility at least through FY 1979. Our present schedule calls for solidification of the uranium in FY 1983.

9.2 $^{233}U_3O_8$ PACKET LOADING FOR ARGONNE NATIONAL LABORATORY

We are presently preparing approximately 2000 packets of $^{233}U_3O_8$ powder, each containing 33 g of U_3O_8 converted from freshly purified ^{233}U nitrate solution. These packets will be used to perform criticality experiments in the Zero Power Reactor in Idaho. A single packet (Fig. 9.1) measures $5.08 \times 7.62 \times 0.64$ cm ($2 \times 3 \times {}^1/_4$ in.). The packets are vibrated during loading, sealed by fusing the end-cap to the body via programmed welding, leak-tested under vacuum in an ethylene glycol solution, decontaminated in an ultrasonic bath, plated with nickel to reduce direct alpha contamination, and then counted for alpha contamination. A line of stainless steel glove boxes (Fig. 9.2) containing the operations required to perform these tasks was installed and placed in service during the past year.

We have prepared 615 packets to date which meet all of the specifications required by Argonne National Laboratory (ANL). These packets were prepared from four lots of material that had been purified and converted immediately prior to packet loading. Four hundred packets are packaged for shipment; the remaining 215 packets can be shipped in mid-April.

We are operating at a yield of ~75% (packets produced/packets loaded). Our principal source of

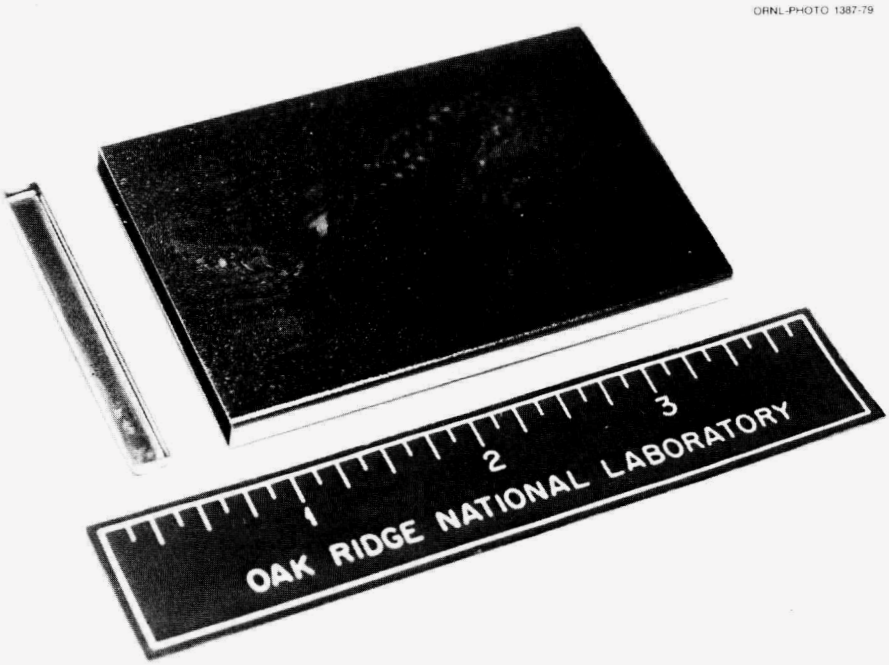

Fig. 9.1. Stainless steel packet for Zero Power Reactor Experiment.

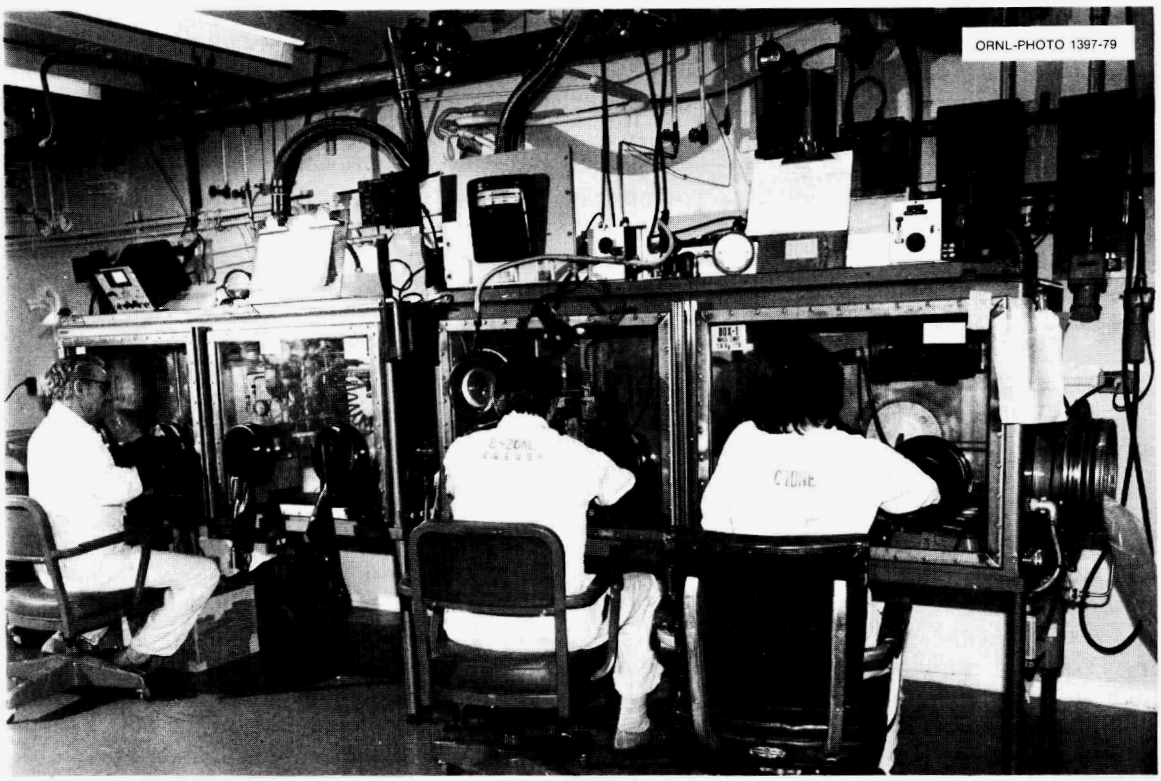

Fig. 9.2. Packet loading facility in Building 3019.

rejection is leakage due to poor welding. The welding problem is difficult to resolve because of the following factors: (1) the precision required of the tracking mechanism, (2) the changes in welding current due to heat buildup in the programmer, and (3) the length and taper of the welding rods.

9.3 URANIUM-233 PROCESSING

The Oak Ridge National Laboratory serves as a national distribution center for ^{233}U. The facility includes shielded wells for storing up to 454 kg of ^{233}U in solid form (density = 1 g/cm^3) and tanks (containing borosilicate glass rings for neutron poisoning) that can store 900 kg of ^{233}U in the form of uranyl nitrate solution at ^{233}U concentrations up to 250 g/liter. An adjacent vault, constructed to withstand the earthquake and tornado criteria, can be used to store up to 200 kg of fissile material.

Installed remotely operated purification facilities include (1) a single-cycle solvent extraction system with a capacity of 35 kg of ^{233}U per week, and (2) a high-pressure ion exchange process with a capacity (including regeneration) of 25 kg per day. A conversion system contained in glove boxes can be operated to convert ^{233}U to UO_2 or U_3O_8 at the rate of 25 kg of ^{233}U per week.

During this report period, four dissolution cycles were performed to convert 16.3 kg of ^{233}U from aged UO_2 and U_3O_8 to nitrate solution. Four additional dissolution cycles were performed to dissolve 4.0 kg of ^{233}U and 200 kg of thorium contained in UO_2-ThO_2 pellets.

One solvent extraction run was made to recover 21.0 kg of ^{233}U. Eight ion exchange runs were made to purify 75.9 kg of ^{233}U suitable for conversion to UO_2 or U_3O_8.

Eight conversion runs were made to convert 8.0 kg of ^{233}U from nitrate solution to UO_2. An additional eight runs were made to convert 48.9 kg of ^{233}U to U_3O_8.

Receipts during this report period include 300 kg of ThO_2-UO_2 pellets from the Light-Water Breeder Reactor Fuel Fabrication Program. This material contained 6.2 kg of ^{233}U, which is presently being processed in the facility.

Upgrading of the system is currently under way to provide better operational efficiency. Much of the equipment installed 25 years ago in the solvent extraction plant is being replaced.

9.4 SAFEGUARDS IMPROVEMENTS TO BUILDING 3019

The physical security system in Building 3019 was updated to meet the latest requirements of the Department of Transportation (DOT). Modifications include new fencing, perimeter lighting, and a "hardened" guard post.

An area inside the building was remodeled to house the Facility Integrated Computer System, and the computer was installed. The ultimate goals of this system are (1) to maintain near-real-time accountability of uranium, plutonium, and thorium, and (2) to survey personnel movements in the facility as well as the physical protection system. Installation of the electrical transmitters, which will transmit signals from the in-cell vessels to the computer, is nearing completion. Checkout of the computer is under way.

The system will provide an instantaneous volume balance in the plant and, later, an almost instantaneous fissile mass balance. It is expected that technology developed in this program will be useful in fuel recycle facilities.

9.5 SHIPPING-CASK TEST PROGRAM

Full-scale destructive tests of spent fuel casks have been carried out at ORNL. The purpose of these tests is to develop improved methods for assessing the adequacy of environmental and public safety controls provided by DOE shipping-container systems for nuclear materials.

In this test series, the 20-metric ton Knapp Mills spent fuel cask (equipped with a balsa impact limiter fitted over the cask closure) was drop-tested at the Tower Shielding Facility from a height of 9 m. A drain valve was sheared off, which had been anticipated, but there was no discernible damage to the cask. Instrumentation recorded an impact loading on the cask that was four times the force measured in a similar cask involved in a 96-km/hr (60-mph) collision between a truck and an abutment at Albuquerque, New Mexico.

In a second test, the same cask loaded with an unirradiated 300-kg pressurized-water reactor (PWR) fuel element was dropped at a 35° angle onto the nonclosure end from a height of 9 m. The upper (closure) end was unprotected in this test. While the cask had a velocity of 48 km/hr (30 mph) at the time of initial impact on the bottom end, subsequent rotational motion caused the closure end

to reach a velocity of 32 km/hr (20 mph) at the time of the secondary impact. The secondary impact forced the closure end tie-down trunnion into the body of the cask, splitting the weld between the end of the cask and the inner liner. Lead was extruded through the 30-cm-long crack, and the closure plug was forced askew. The fuel element was badly bent, but no fuel rods were ruptured.

In a different set of experiments, three successive oblique-angle drop tests of a 10-ton, thin-walled UF_6 cylinder were made from heights of 3, 6, and 9 m. The cylinder was filled to 95% of capacity with water, and the void space was pressurized to 0.5 MPa (75 psig) with nitrogen. Examination showed that considerable deformation of the cylinder had occurred in each of the three drop tests, but no leaks were found. These tests were part of a program to develop cylinder protection during in-plant handling.

9.6 ENGINEERING SAFEGUARDS PROGRAM

The principal objective of the Engineering Safeguards Program (ESP) is to demonstrate process monitoring as it might be accomplished by inspectors of a nuclear fuel recycle facility. A multiphase work plan, covering the five fiscal years from now through 1984, has been developed for ESP. The four major contributions to the program are as follows: (1) analytical development, which will generate the instrumental capability; (2) computer system safeguards, which will provide a balanced, overall process view of accountability, internal security, physical protection, and external surveillance; (3) project support, which will comply with the external program function requirements such as operator training and nuclear materials documentation; and (4) microscopic process monitoring, which will supplement the internal security, physical protection, and external surveillance with a partial, element-by-element evaluation of the separate system components.

Improved instrumentation and computer interfaces will initially permit the solvent extraction system operations conducted in the Building 3019 Pilot Plant to be monitored as an accurate, but passive and static, volume balance. Subsequently, the volume balance will be made as an active, dynamic method of almost-instantaneous process monitoring. Appropriate concentration instrumentation, to be added to the Pilot Plant later, will permit an active, dynamic, fissile-material mass balance to be determined within ~15 sec.

The technology developed by ESP will be applied directly to the detailed design of the Consolidated Fuel Recycle Program Hot Experimental Facility. Future technological upgrading, and subsequently increased demonstrational capability in the Pilot Plant, will be applied to new, yet-to-be-designed nuclear fuel recycle facilities. All technology developed within the Pilot Plant will be of a generic nature. Any reprocessing/refabrication facility using any nuclear fuel cycle should be able to implement our design technology.

9.7 NUCLEAR SAFETY ASSISTANCE

The Chemical Technology Division has continued to assist the Nuclear Safety Information Center (NSIC) by providing editorship for the Plant Safety Features section of *Nuclear Safety*. This bimonthly technical journal, which recently completed its 20th year of publication, is sponsored by the U.S. Nuclear Regulatory Commission and the U.S. Department of Energy. The journal is divided into six major sections: General Safety Considerations, Accident Analysis, Control and Instrumentation, Plant Safety Features, Environmental Effects, and Operating Experiences.

The Plant Safety Features section covers a broad subject area that encompasses the following: the anticipation and mitigation of hazards of all types within plant boundaries, including containment and handling of hazardous materials; the management of wastes, including the cleaning of air and water; engineered safety systems; and the nature of hazardous phenomena and effects on plant structures and systems. All phases of the fuel cycle are represented.

The following articles have appeared in the Plant Safety Features section of *Nuclear Safety* during the past year:

"The Sodium Loop Safety Facility"

"Recent Advances in Alternate ECCS Studies for Pressurized-Water Reactors"

"Letter to the Editor: Comments on 'Effect of Engineered Safety Features on the Risk of Hypothetical LMFBR Accidents' in Vol. 19, No. 2"

"Author's Response to Preceding Letter"

"Handling and Storage of Spent Fuel from Light-Water Power Reactors"

"The Fifteenth DOE Air-Cleaning Conference"

"Failures in Nuclear Air Monitoring, Ventilation, and Cleaning Systems"

Nuclear Safety won first place for the fourth consecutive year in the annual competition sponsored by the Society for Technical Communication.

9.8 MODELING SOLID HYDROGEN STORAGE BEDS

A model is being developed to predict the behavior of metal hydride beds that are used for hydrogen storage. The first embodiment of this model assumes that (1) hydrogen is always in equilibrium with the metal hydride, and (2) no pressure drop occurs in the bed. Under such conditions, heat transfer controls performance. Heat transport and thermodynamic properties are represented in the model as functions of temperature, pressure, and composition whenever possible. The model is being tested by comparing the results obtained for it with data reported by Strickland and Yu[1] from a cylindrical bed containing 38.1 kg (84 lb) of iron-titanium alloy. In their experiments, hydrogen was introduced at the center line of the vessel through a porous metal tube, and heat was transferred to and from the system by water flowing in an annular shell around the test bed. Each run consisted of a period during which the feed (or withdrawal) rate was held constant at some value between 20 and 40 std liters/min, and a period during which the pressure was held constant at either 3.45 or 0.11 MPa (500 or 16 psia). This model, which contains no empirical constants, reproduces all the qualitative aspects of the data, but events (such as temperature and pressure maxima) occur at the wrong times. Model development is continuing in order to obtain a more acceptable fit to the experimental data. Two approaches are being pursued; the first involves altering some of the uncertain experimental parameters used in the present model, while the second involves including reaction kinetics and pressure gradients in the model. Tests with higher feed rates (and desorption runs) and alternative geometries are also planned.

1. G. Strickland and W. S. Yu, *Some Rate and Modeling Studies on the Use of Iron-Titanium Hydride as an Energy Storage Medium for Electric Utility Companies*, BNL-50667 (Apr. 26, 1977).

9.9 REMOVAL OF HAZARDOUS RADIONUCLIDES FROM URANIUM ORES AND/OR TAILINGS

It has been recognized for some time that improved waste management of uranium mill tailings might result if the long-lived uranium daughters were leached out, recovered from the leach liquor, converted to solids, and stored in a manner similar to reactor fuel reprocessing wastes. The specific objective of this study is to determine the technical feasibility of removing the long-lived daughters ^{230}Th, ^{226}Ra, and ^{210}Pb, whose decay half-lives are 80,000, 1622, and 19.4 years respectively. Studies thus far have emphasized the use of nitric acid to solubilize uranium and its long-lived daughters from uranium ore, and quantitative data have been obtained for ^{226}Ra.

About 99% of the ^{226}Ra was leached from a typical western ore after six successive, stirred-contact, batch leaching stages (crosscurrent) with fresh 3 *M* HNO_3 solution at 60°C. A 4-hr contact time and a 30% concentration of solids were employed in each stage. The percentages of radium leached from the original ore after stages 2, 4, and 6 were 95.5, 98.1, and 98.6% respectively. The effectiveness of HNO_3 leaching diminishes rapidly after the second stage. Nitrate ion present in the residues as either nitric acid or nitrate salts could be readily removed by water washing. The radium activity in the final leach residue was 9 pCi/g. Barium sulfate was shown to be an effective carrier for radium. Radium recoveries of >99% are attained by $BaSO_4$ precipitation after diluting leach liquors to 0.3 *M* HNO_3 concentrations and adding 0.025 mole of barium nitrate and 0.025 mole of sulfuric acid per liter of diluted leach liquors. Studies are in progress to determine the minimum amounts of barium and sulfate ions that are necessary for good radium recovery.

9.10 HYDROGEN ISOTOPE SEPARATION USING BIPOLAR ELECTROLYSIS

Hydrogen isotope separation from aqueous systems is an important technology for both heavy-water production and tritium recovery from fission and fusion reactor coolant streams. Bipolar electrolysis is a commonly used process for the production of hydrogen and oxygen from water. Bipolar electrolysis with hydrogen-permeable electrodes (BEPE) for isotope separation differs from ordinary bipolar electrolysis because the bipolar electrode is made of a metal that is highly permeable to hydrogen.

Both electrolysis and permeation favor enrichment of the lighter isotope; therefore, this process promises to combine the best attributes of electrolysis, gas permeation, and multistage operation into a single cell.

An analysis of data supplied by Ramey, Petek, and Kobisk (ORNL Solid State Division) showed that accurate separation factors can be determined from BEPE experiments using a McCabe-Thiele type of approach.[2] Two experiments were analyzed, and a separation factor of 5 (for all stages) provided an adequate representation of the data for D_2O in H_2O at a current density of 250 mA/cm^2. A separation factor of 6.53 gave an adequate representation for T_2O in H_2O at 300 mA/cm^2. Interstage concentrations for the latter experiment confirm that using the same separation factor for bipolar and terminal electrodes is a good assumption. Analysis of hydrogen and deuterium permeation rates indicates that maximum current densities for this process will be ~1.27 A/cm^2 for H_2O and 0.16 A/cm^2 for D_2O.

9.11 FUEL CYCLE EVALUATION STUDIES

During this report period, the Chemical Technology Division participated in three different studies in support of fuel cycle evaluations. These evaluations have both domestic and foreign components and reflect the concern of the United States over the spread of technologies involving materials suitable for nuclear weapons. The first activity was to supply information for the Alternative Fuel Cycle Evaluation Program. The information supplied consisted of detailed technical and cost evaluations of fuel fabrication and reprocessing[3] and, more recently, waste management. This work has been substantially completed and forms part of the basis for the final, overall evaluation of alternative fuel cycles.

The second activity was our participation in the Nuclear Alternative Systems Assessment Program (NASAP), which is the domestic program to evaluate alternative fuel cycles in an overall sense. Our principal activities have been to review the fuel-cycle-related sections of successive drafts of the final NASAP report for technical completeness and accuracy.

The third activity of the Division was to provide technical support to the International Fuel Cycle Evaluation (INFCE). This support consisted of reviewing fuel-cycle-related INFCE documents and attending INFCE Working Group 4 (reprocessing, plutonium handling, and recycle) meetings to provide technical backup.

9.12 CHEMICALS AND SPECIALTY FUELS FROM SOLAR ENERGY

Studies on the use of solar energy as a heat source by industry for the production of chemicals and specialty fuels have been made for (1) short-term application to existing industry, and (2) longer-range scoping studies of innovative processes which may become viable alternatives to existing processes after about 1990. The first category has included studies on the calcining of gypsum and drying of gypsum wallboard, the calcining of limestone to produce lime, and both the dehydration of bauxite and the production of steam for use in the Bayer alumina process. Studies on the longer-term applications that will depend on further development of solar energy technology to achieve temperatures of up to 2100°C have included: (1) direct fixation on nitrogen from air by the presently unused Wisconsin process where solar heating would substitute for natural gas, (2) thermal splitting of water by thermochemical cycles using iron oxides (Fe_2O_3 and Fe_3O_4), and (3) thermal splitting of carbon dioxide either directly or by use of thermochemical cycles to produce carbon monoxide and oxygen.

All of these studies have involved preparation of material and heat balances and the formulation of preliminary flowsheets. In addition, the short-range studies have also included the preparation of cost estimates to determine whether the use of solar energy is economically competitive with existing energy sources. Data indicate that solar energy is too costly, without at least some government subsidies, tax incentive, or other government assistance.

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2. J. S. Watson and S. D. Clinton (compilers), *Advanced Technology Sect. Semiannu. Prog. Rep. Apr. 1, 1978 to Sept. 30, 1978. Volume 2: Engineering Science Programs*, ORNL/TM-6647/V2 (in preparation).

3. A. R. Olsen, R. R. Judkins, W. L. Carter, and J. G. Delene, *Fuel Cycle Cost Studies—Fabrication, Reprocessing and Refabrication of LWR, SSCR, HWR, LMFBR, and HTGR Fuels*, ORNL/TM-6522 (March 1979).

9.13 MIDEAST STUDIES

As a result of the Egyptian-Israeli peace discussions at Camp David in the fall of 1978, the White House requested that the U.S. Department of State obtain as many proposals as possible for projects that would aid and abet peace between these two nations. The Department of State immediately sought assistance from about 20 other government agencies, universities, national laboratories, private foundations, and consultants on a broad range of topics. One of these was the Office of Water Research and Technology, Department of the Interior (former Office of Saline Water), who requested that former ORNL studies on desalination and agro-industrial complexes and Mideast studies made in the period between 1967 and 1971 be reviewed and updated. Additionally, ORNL was asked to provide any new ideas that could be generated on a short time schedule. This effort involved the Engineering Technology Division, the Energy Division, the Program Planning and Analysis Office, and the Chemical Technology Division during October and November 1978.

The work in the Chemical Technology Division included preparation of a report on various studies and proposals that might lead to better economic use of the Sinai area. Included in these proposals were (1) a survey of the amount of groundwater in Wadi el Arish to determine how much natural water is available for agricultural, municipal, and industrial use before seawater desalination is required; (2) a determination of the potentials for solar and geothermal energy; (3) an assessment of the potential for hydroelectric development using subsea-level basins; (4) a plan that would use the Sabkhet el Bardawil embayment in the northwest Sinai for production of solar salt and other seawater chemicals; and (5) the development of light industries in the El Arish area to utilize regional raw materials for production of chemicals and products for domestic use and export. The main purpose of such activities would be to provide a basis for moderate- to large-scale settlement of the Sinai as a means of promoting peace in the area.

Administrative Summary

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2. Battelle Columbus Laboratories, Columbus, Ohio.
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4. University of Tennessee, Knoxville; consultant to Chemical Technology Division.

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6. Hanna Mining Co., Nashwauk, Minn.
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8. U.S. Environmental Protection Agency, Washington, D.C.
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34. Roane State Community College, Harriman, Tenn.; formerly with the Chemical Technology Division.
35. Deceased.
36. Georgia Institute of Technology, Atlanta.
37. Sargent and Lundy Engineers, Chicago.

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43. Solid State Division.
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April 5	*Dissolution of Breeder Fuels*	
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	Gasifiers in Industry Program	C. H. Brown, Jr.
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	Pyrolysis of Bituminous Coal Blocks Under UCG Conditions	P. R. Westmoreland
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March 21	The Separations Systems Data Base	J. W. Roddy
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	System Development	C. W. Hancher
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DIVISIONAL PERSON-POWER AND FINANCIAL SUMMARY
FY 1979

	Funding (in thousands)	Person-years
DOE PROGRAMS		
Coal	$ 3,694	21.5
Fusion	28	0.5
Fission	23,595	132.0
Physical Research	6,194	78.0
ANFLOW	178	2.5
Biology and Environment	1,308	15.0
Biomedical Applications	69	0.5
TRUST and ^{233}U Dispensing Facility	2,656	18.0
TOTAL DOE PROGRAMS	**$37,722**	**268.0**
WORK FOR OTHERS PROGRAMS		
Nuclear Regulatory Commission	$ 872	8.5
Pacific Northwest Laboratory	1,350	12.5
Office of Nuclear Waste Isolation	2,468	17.5
Other federal agencies	788	8.0
Miscellaneous	326	4.0
TOTAL WORK FOR OTHERS	**$ 5,804**	**50.5**
TOTAL FINANCIAL PLANS	**$43,526**	**318.5**

CHEMICAL TECHNOLOGY DIVISION AUTHOR INDEX

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