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**CHEMICAL TECHNOLOGY DIVISION
ANNUAL PROGRESS REPORT
for Period Ending March 31, 1978**

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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, 1977-March 31, 1978. 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 consists of about 380 staff members who occupy space in 12 buildings located at the ORNL, Y-12, and HFIR-TRU sites. Of these, approximately 230 are engineers or scientists and 110 are technicians or draftsmen; the remainder are primarily secretaries or administrative personnel. These individuals comprise a versatile, mobile work force that may be deployed in various jobs, within the Division or throughout the Laboratory, 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).

There were no major changes in the programs during the past year, although significant redirection was experienced in some of them and shifts of emphasis were necessary in others. Both the Advanced Fuel Recycle Program and the Alternate Fuel Cycle Technologies/Thorium Fuel Cycle Technology Programs received additional support in the areas of alternate fuel cycles. The scope of these programs was enlarged to include the use of thorium in both breeders and light-water reactors (LWRs). The proposed pilot plant for the Advanced Fuel Recycle Program has been delayed indefinitely, and the conceptual planning was generalized to make it possible to adopt any fuel recycle scheme which may be selected in the future. Studies of the high-temperature gas-cooled fuel cycle continue to occupy 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 been successful in broadening the base of the engineering development aspect of our coal

conversion programs. Several new experimental efforts have been initiated in general support of emerging coal liquefaction technology. These include investigations of the effects of chemical and physical properties of process streams on equipment design, new chemical approaches to liquefaction, and others. Our engineering analysis activities continue to be primarily supportive of the Department of Energy program management, with additional emphasis on process modeling.

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.

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 are carrying out substantial reactor safety research and are contributing to NRC "As Low As Reasonably Achievable" Guides for the Nuclear Fuel Cycle and related studies.

Other highlights of this report period include:

1. Reinstitution of the sol-gel program for reactor fuel preparation (jointly with the Metals and Ceramics Division).
2. Demonstration of the removal of heavy metals from waste streams, using microorganisms.
3. Development of a method for fixation of waste iodine as barium iodate in concrete with leach rates as low as 10^{-5} cm²/sec. Samples of concrete that were set and cured at elevated temperatures

and pressures show good resistance to leaching by superheated brine.

4. Development and application of a computer-based logistics model capable of optimizing the shipments of radwaste or spent fuel from the point of generation to a final destination.
5. Development of a sinter-leach method for recovering aluminum and other metal values from fly ash.
6. An investigation using thermodynamic calculations that explain evaporative losses of plutonium during carbothermic reduction of the oxide and their minimization by increasing the temperature or by allowing oxygen to remain dissolved in the carbide.
7. Inauguration of a new symposium series, "Biotechnology in Energy Production and Conservation."
8. Receipt of an I-R-100 award, which was granted by *Industrial Research* for our development efforts on the portable Centrifugal Fast Analyzer.
9. Development of a process for the preparation of ^{243}Am containing less than 1 ppm ^{244}Cm .
10. Production of gram quantities of high-purity ^{122}Te containing less than 0.2% ^{123}Te for use in the manufacture of ^{123}I for nuclear medicine application.
11. Development of a high-temperature ion source capable of operating at an oven temperature of about 1500°C.
12. Development of semiempirical models for the release of cesium and iodine from failed LWR rods. Results from these models are lower by factors of 200 and 60 for cesium and iodine releases, respectively, than those assumed in the Reactor Safety Study (WASH-1400).
13. Preparation of a design study and preliminary cost estimate for conversion of a uranium nitrate solution containing 1047 kg of uranium (76.5% ^{235}U , 9.7% ^{233}U , 1.4% ^{234}U , 5.6% ^{236}U , 6.8% ^{238}U , and 120 parts of ^{232}U per million parts of total uranium) to U_3O_8 and its subsequent storage in an earthquake-proof, safeguarded facility.
14. Completion of the management and technical coordination of the Barnwell Nuclear Fuel Plant Applicability Study for DOE.

2. Fission Energy

2.1 ADVANCED FUEL RECYCLE AND ALTERNATE FUEL CYCLE TECHNOLOGIES PROGRAMS

Fuel cycle studies concerned with the development of aqueous processes for both LWR and advanced reactor fuels are not reported here, in compliance with regulations which stipulate that such information must be distributed only through limited, controlled lists. All work with breeder fuels is now included under the Advanced Fuel Recycle Program. The results of these studies are reported in topical reports and in a series of quarterly progress reports, the most recent of which is the *Advanced Fuel Recycle Program Progress Report for the Period January 1 to March 31, 1978*, ORNL TM-6306 (in preparation). These reports are distributed under category UC-79c—Liquid-Metal Fast Breeder Reactors.

The associated efforts in LWR fuel reprocessing, now done under the Alternate Fuel Cycle Technologies Program, are reported in a separate series of quarterly progress reports with a similar controlled distribution. The most recent is the *Alternate Fuel Cycle Technologies/Thorium Fuel Cycle Technology Programs Quarterly Report for the Period January 1 to March 31, 1978*, ORNL TM-6307 (in preparation). Task areas in the two programs are closely related; in some cases, they are partially funded from both programs. Major emphasis has been the examination of some of the schemes that increase the nonproliferation characteristics of the fuel cycles.

2.2 HTGR FUEL RECYCLE DEVELOPMENT PROGRAM

The Chemical Technology Division's activities under the HTGR Fuel Recycle Development Program include development efforts in head-end reprocessing, fuel fabrication, off-gas cleanup, waste

treatment, and generic studies of thorium fuel cycles. Work was done at both laboratory and engineering scales, as well as at the hot laboratory scale (i.e., remotely in hot cells). This work 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 summarized separately in topical reports, in monthly program reports (ORNL GCR T documents), and in annual progress reports, the most recent of which is the *Gas-Cooled Reactor Programs, HTGR Fuel Recycle Development Program Progress Report for the Period October 1, 1976, through September 30, 1977*, ORNL-5423 (in preparation).

2.3 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 monthly GCR documents and in annual reports, the most recent of which are the *Gas-Cooled Reactor Programs, HTGR Base Technology Program Progress Report for the Period July 1, 1975, through December 31, 1976*, ORNL-5274 (November 1977) and *Gas-Cooled Reactor Programs, HTGR Base Technology Program Progress Report for the Period January 1, 1977, through December 31, 1977*, ORNL-5412 (in press).

2.4 FUEL FABRICATION STUDIES

In the early 1970s, development work on fuel fabrication was suspended at ORNL. At that time, pellet fuels were already well developed, and funding was not available for studies of alternative methods such as the ORNL Sol-Gel process. Interest and support for the Sol-Gel Sphere-Pac method of

fabricating metal-clad fuel elements have now been renewed because this method is amenable to remote operation, which would be required for gamma-active fuels such as ^{235}U or plutonium-uranium spiked with fission products.

As presently conceived, the Sol-Gel Sphere-Pac process consists in utilizing nitrate solutions of plutonium, uranium, and/or thorium to prepare dense, ceramic microspheres that can be loaded into fuel tubes to a smear density of 81 to 88% by low-energy vibration. The lower-density (81%) loading can be obtained by filling the tube with a spherical product whose diameter is about one-tenth of the tube diameter and infiltrating the packed tube with a smaller-size product, whose diameter is about one-tenth that of the large spheres. The higher-density (88%) loading can be obtained by using two sizes of coarse spheres followed by infiltration of fines with an average diameter about one-seventh that of the small, coarse spheres. The nominal sphere diameters required for 88% smear density are 800, 200, and 30 μm for most metal-clad fuels presently proposed.

Survey of Methods for Preparing Fuel Microspheres

The first step in reactivating studies of the Sol-Gel Sphere-Pac process was to make a literature search to update our knowledge of developments in technology. Several European countries have continued vigorous research efforts and have reported successful, attractive alternatives to the original sol-gel processes that were developed at ORNL. The newer methods utilize chemical gelation agents (usually ammonia) in place of the water extraction method of forming the spheres. This eliminates the need for making true sols having low nitrate contents; in fact, a sol is not required in most cases. Nitrate solutions of heavy metal are usually made acid deficient by extraction of nitrate or partial neutralization with ammonia. Water-soluble polymers may be added to give support to the gels. The adjusted feed solution is commonly called a broth.

Two methods of gelation of broth by ammonia precipitation of heavy metal are: (1) external, in which gel spheres are prepared by allowing drops of broth to fall through ammonia as a gas or dissolved in an immiscible liquid; and (2) internal, in which gelation is effected by allowing drops of broth containing an ammonia donor to fall through a hot, immiscible liquid, which causes rapid internal generation of ammonia. In contrast to gelation by water extraction, the gel spheres formed by gelation in ammonia contain ammonium nitrate and other

products of neutralization which must be leached by immersion of the gel spheres in dilute ammonium hydroxide. The ammonium hydroxide also serves to complete the precipitation of the heavy-metal oxides. Drying, calcining, and sintering of the spheres must be performed under controlled conditions to prevent cracking and to ensure the production of strong, dense ceramic spheres.

Pure UO_2 microspheres have been prepared by at least three methods: (1) dehydration of UO_2 sols, (2) gelation of UO_2^{2+} broths by ammonia gas, and (3) gelation of UO_2^{2+} broths by internal generation of ammonia. Preparation of spheres from UO_2 sol involves protection of the sol against oxidation and is generally limited to sintered spheres of diameters less than 500 μm because the characteristically small crystallites tend to cause cracking. Preparation of spheres from broths with ammonia gas appears simple but produces soft gel spheres which must be handled carefully during washing and drying and must be calcined to oxidize the support polymer before being sintered to a dense product. Use of internal gelation produces a firm gel sphere which is easily handled, but it requires the use of an immiscible liquid (as the dispersion medium), which must be removed before sintering.

Pure ThO_2 spheres have been prepared from ThO_2 sol formed by peptization of thermally denitrated thorium nitrate or by a series of solvent extraction contacts and thermal digestions to denitrate thorium nitrate solutions. ThO_2 sols are very stable and are easily formed into spheres either by water extraction with an immiscible alcohol or by gelation in ammonia gas. Spheres have also been formed by gelation of thorium nitrate broths with ammonia gas.

Mixed ThO_2 - UO_2 spheres have been prepared from sols formed by peptizing steam-denitrated ThO_2 with uranyl nitrate, or by solvent extraction and thermal digestion to denitrate a mixed thorium-uranyl nitrate solution. ThO_2 - UO_2 spheres have also been produced from broths prepared by partial neutralization of a mixed thorium-uranyl nitrate solution. Gelation of the mixed sols and the broths has been accomplished by using water extraction and ammonia gas respectively. Gel spheres prepared from broths by treatment with ammonia must be washed thoroughly to remove ammonium nitrate before drying and sintering.

Mixed PuO_2 - UO_2 spheres have been prepared by (1) mixing low-nitrate PuO_2 and UO_2 sols and forming them into spheres by water extraction, and (2) mixing plutonium nitrate and uranium nitrate with organic stabilizers to form a broth which is

gelled either internally or externally with ammonia. Broths can be prepared according to many different recipes, most of which are designed to avoid the formation of plutonium polymers. From a chemical standpoint, the preparation of $\text{PuO}_2\text{-UO}_2$ spheres is generally easier than the preparation of pure UO_2 spheres because of the stabilizing effect of plutonium.

Experimental Studies

Preparation of UO_2 spheres. Experimental studies have been initiated, with primary emphasis on UO_2 spheres. Our objective is to examine the various processes so that a selection can be made before proceeding into cold engineering studies and preparation of irradiation test material. Processes utilizing UO_2^{2+} as opposed to U^{4+} have been evaluated first because of instability problems with reduced uranium in nitrate medium, which was used in the original ORNL water extraction processes. Work with UO_2^{2+} broths is under way to test the processes described in the literature.

For external gelation, a solution of uranyl nitrate ($\sim 0.5\text{ M}$) is modified by addition of a water-soluble polymer such as methyl cellulose or polyvinyl alcohol to produce a broth with a viscosity of about 100 cSt. Microspheres are formed by pumping the broth through a nozzle into ammonia gas, which forms a skin of ammonium diuranate precipitate at the surface of the drops. The precipitation is completed by aging in an aqueous ammonium hydroxide solution. The size of the microspheres can be controlled very precisely by imposing a vibration on the broth as it is pumped through the nozzle. After the microspheres have been formed, they are washed thoroughly in ammonium hydroxide to remove ammonium nitrate and soluble organic materials which would cause cracking during the drying step. The drying is usually carried out in a moist atmosphere to prevent damage to the spheres. Calcination in air to remove the remaining organic compounds is followed by reduction with 4% hydrogen (in argon) to produce UO_2 , which is then sintered at approximately 1450°C to obtain dense microspheres.

For internal gelation, the uranyl nitrate is made about 25% acid deficient and concentrated to about 3 M so that a solution of hexamethylenetetramine and urea can be added to produce a broth that is about 1.3 M in uranium and contains 1.5 moles of nitrate, 1.3 moles of hexamethylenetetramine, and 1.3 moles of urea per mole of uranium. Microspheres are formed

by pumping the broth through a nozzle into a hot (70 to 95°C) immiscible liquid, which causes initial gelation within a few seconds due to the ammonia released via hydrolysis of the hexamethylenetetramine. The spheres are usually held at an elevated temperature for about 1 min. The washing, drying, and sintering steps are similar to those used for spheres prepared by external gelation.

At the present stage of testing, internal gelation appears to be the most effective process for preparing pure UO_2 microspheres. Large and medium-size microspheres (200 to 1100 μm) have been formed by using a pulsed nozzle. Fines ($<40\text{ }\mu\text{m}$) have been produced using a two-fluid nozzle with turbulent flow. The excess reactants and waste products (ammonium nitrate and formaldehyde) are easily removed from the spheres by washing with 0.5 M ammonium hydroxide. Drying either in air at ambient temperature or in steam at 200°C produces a stable material without cracking. Calcining in air to oxidize residual organic compounds to CO_2 has not been necessary because of the thorough washing. Sintering in 4% hydrogen argon to 1450°C has yielded high-density spheres of the three desired diameters (800, 200, and 30 μm) with very little cracking or clustering. The sintered microspheres are characterized by high ($>98\%$ of theoretical) density, good sphericity, and structural integrity.

Preparation of uranyl-plutonium nitrate. Studies have been initiated to evaluate methods for preparing concentrated acid-deficient solutions of $\text{UO}_2(\text{NO}_3)_2\text{-Pu}(\text{NO}_3)_3$ from mixed solutions of plutonium and uranium. If stable feed solutions that are about 3 M in total metal concentration and have NO_3^- metal mole ratios of about 1.8 can be prepared, they can be used to form $\text{UO}_2\text{-PuO}_2$ microspheres by internal gelation procedures.

Initial work will involve vacuum distillation at 40°C of mixed uranium-plutonium nitrate solutions and partial neutralization or removal of nitrate from the concentrated product. Procedures employing these techniques have been successfully used to prepare highly concentrated, acid-free solutions of $\text{Pu}(\text{NO}_3)_3$, which could then be mixed with concentrated $\text{UO}_2(\text{NO}_3)_2$ solution and used to produce uranium-plutonium carbide microspheres.¹ Successful application of this procedure to the mixed-metal

1. K. Bischoff, M. H. Lloyd, and H. Schumacker. *Sol-Gel Processes for Carbide Preparation, Status Report from Switzerland*, EIR-Bericht Nr. 236 (May 1973).

system requires: (1) maintaining plutonium in the tetravalent state, (2) avoiding plutonium polymerization, and (3) adjusting the nitrate concentration to substoichiometric values.

Experimental Engineering Facility

Modifications and additions are being made to Building 3503 in order to provide a facility for

carrying out experimental engineering studies of the processes developed for fuel fabrication. This facility will contain work areas with filtered off-gas needed to handle unirradiated thorium and uranium compounds. Equipment will be installed to accomplish the major steps of sol or broth preparation, sphere formation, washing, drying, calcining, and sintering to dense spheres.

3. Coal Conversion and Utilization

3.1 COAL CONVERSION PROCESS DEVELOPMENT

During this report period, the activities related to coal conversion process development encompassed four areas: (1) continuing effort on the hydrocarbonization of coal, (2) continuing effort on the pyrolysis of coal blocks to provide supporting data for in situ gasification, (3) completion of our investigation of carbonization of liquefaction residues, and (4) three preliminary investigations supporting coal liquefaction.

Hydrocarbonization Research

Fluidized-bed pyrolysis processes constitute an important part of coal conversion technology. In the hydrocarbonization process, coal is pyrolyzed under hydrogen pressure in a fluidized bed to produce hydrocarbon liquids, substitute natural gas (SNG), and solid char. The relative yields and the quality of these products may be controlled by adjustment of the operating conditions.

Bench-scale hydrocarbonization experiment. In bench-scale experiments, hydrocarbonization of coal is being studied in a 4-in.-ID (10-cm) fluidized bed capable of operating at a hydrogen pressure of 315 psia (2170 kPa) and at temperatures to 1200°F (649°C). An axial draft tube is used to provide recirculation of the fluidized bed and to reduce the gas residence time in the reactor. During the first phase of operation, experiments were performed to provide yield data on the hydrocarbonization of Wyodak coal, which is a low-sulfur, western subbituminous C coal.¹ During this reporting period, the system has been used to determine operability and to obtain yield data for an agglomerating bituminous coal (Illinois No. 6). Agglomerating coals tend to

cake when heated and are therefore more difficult to process. Chemical pretreatment was studied as a means of reducing the caking tendencies of the coal, and of improving the liquid yield from hydrocarbonization.

Significant results obtained from the experiments are summarized below. Additional details of these results have been reported elsewhere.²⁻⁵

1. Hydrocarbonization [at 315 psia (2170 kPa) and 1060°F (571°C)] of Illinois No. 6 coal pretreated with sodium carbonate has produced the highest liquid yield obtained thus far [24% based on moisture- and ash-free (maf) coal]. This is higher than the maximum yield obtained from the hydrocarbonization of Wyodak coal under the same operating conditions, as shown in Fig. 3.1. The yield is also significantly higher than the 14% yield achieved using Illinois No. 6 coal pretreated with calcium oxide-sodium hydroxide. The sodium carbonate and calcium oxide-sodium hydroxide pretreatments were accomplished by heating aqueous slurries in an autoclave at 200 to 300°C. The process is similar to that used by Battelle Memorial Institute for desulfurization of coal.⁶

2. A process which effectively eliminates agglomeration during hydrocarbonization was developed to chemically pretreat Illinois No. 6 coal at atmospheric pressure. In this process, coal is treated with an aqueous mixture of calcium oxide and sodium

1. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5295.

2. Coal Technology Program Quarterly Progress Report for Period Ending June 1977, ORNL-5327.

3. Coal Technology Program Quarterly Progress Report for Period Ending September 1977, ORNL-5357.

4. Coal Technology Program Quarterly Progress Report for Period Ending December 1977, ORNL-5387.

5. Coal Technology Program Quarterly Progress Report for Period Ending March 1978, ORNL-5421.

6. E. P. Stambaugh et al., "Environmentally Acceptable Solid Fuels by the Battelle Hydrothermal Coal Process," Second Symposium on Coal Utilization, Louisville, Ky. (October 1975).

Fig. 3.1. Liquid hydrocarbon yield at 315-psia hydrogen pressure as a function of temperature.

carbonate at 80°C. This process is simpler and is expected to be less expensive than those processes requiring the use of higher pressures. A hydrocarbonization experiment using coal treated by this method proceeded smoothly, and a significant oil yield was obtained, but complete yield data are not yet available.

3. Seven experiments were performed with untreated Illinois No. 6 coal to determine the operability of the system at temperatures ranging from 850 to 1100°F (454 to 593°C) and at a hydrogen pressure of 300 psig (2170 kPa). The coal feed was diluted with char in coal:char ratios ranging from 1:3 to 1:6. The system operated satisfactorily at 850°F (454°C), but at the higher temperatures [~1000°F (538°C)] needed to achieve maximum liquid yields, caking occurred at the reactor wall above the draft tube; this prevented proper recirculation of the fluidized bed.

For future experiments, the length of the reactor will be increased to give coal particles a longer residence time in the draft tube. In a later run, the draft tube will be connected directly to a cyclone to give rapid disengagement of the solids and quenching of the hydrocarbon vapor, which will prevent cracking.

Engineering Support for In Situ Gasification Process Development

Over 90% of the U.S. coal resources are estimated to be economically inaccessible by present surface- and deep-mining techniques. Much energy from this otherwise inaccessible coal may be recoverable by in situ gasification, a technology in which coal is gasified within the seam. At three field sites in Wyoming and West Virginia, DOE is sponsoring U.S. development of processes to be used for different coals under different geological conditions. Research at ORNL on the pyrolysis of large coal blocks has provided useful data for modeling, planning, and interpretation of field-test results.

In experiments that began in 1975, 6-in.-diam (15-cm) right circular cylinders of lignite, subbituminous coal, and bituminous coal have been pyrolyzed by heating the blocks at 0.3, 3, or 14°C/min (surface temperature) from ambient to maximum temperatures of 500 to 1000°C. An inert (argon) or reducing (hydrogen) purge gas is used to sweep gas- and vapor-phase reaction products from the reactor into a water-cooled condenser. Water and organic liquids are collected, and the noncondensable gases are metered, sampled, and analyzed. In many of the experiments, radial temperature profiles have been measured by thermocouples inserted into the block.

Block pyrolysis of low-rank coals. Important effects of internal heat and mass transfer resistances on yields have been observed in subbituminous coal, and similar mechanisms seemed to be operating in a recent lignite test. From temperature profiles within coal blocks, drying of the high-moisture, low-rank coals (30% H₂O in Wyodak subbituminous, 40% in Wilcox formation lignite) proceeded at high heating rates by a shrinking-core mechanism. Because the 100°C wet core could still be present when the pyrolyzed surface of the block reached 1000°C, steep temperature gradients could exist within the block. In subbituminous coal, steam from the drying core was observed to react with the hot outer bank of char, producing significant amounts of carbon monoxide and hydrogen in 3°C/min experiments; this compares with pyrolysis of dry powders, of dried coal blocks, and of as-received blocks heated at 0.3

7. P. R. Westmoreland, R. C. Forrester III, and A. P. Sikri, "In Situ Gasification: Recovery of Otherwise Inaccessible Coal Reserves," in *Proceedings of the Miami International Conference on Alternative Energy Sources*, Miami Beach, Fla., Dec. 5-7, 1977.

$^{\circ}\text{C}/\text{min}$. In the last case, heating was slow enough to allow complete drying before pyrolysis began.

Block pyrolysis of bituminous coal. Research during the past year has emphasized block pyrolysis of bituminous coal from the Pittsburgh seam. Morgantown Energy Research Center (MERC) will conduct a field test in this seam near Pricetown, West Virginia, during the summer of 1978. In planning for that test, data describing swelling, yield structures, and tar physical properties are especially important. As in pyrolysis of subbituminous coal blocks, the effects of internal heat and mass transfer resistances can become important.

Differences in coal swelling may be explained as resulting from temperature profiles within the block. This explanation is based on a simplified concept of coal plasticity being a function of temperature, so that as the coal is heated to T_1 its structure becomes molten and plastic, but the structure resolidifies into coke as it reaches T_2 . Swelling occurs because bubbles of pyrolysis gases form and foam within the plastic region.

In this model, a uniform block temperature (from slow heating rates) would cause the entire block to become plastic at T_1 and considerable swelling would occur. Blocks heated at $0.3^{\circ}\text{C}/\text{min}$ have behaved in this manner, swelling by as much as 50%. Likewise, a steep, radial temperature gradient (from high surface heating rates) would create a narrow zone of plastic coal between temperatures T_1 and T_2 , permitting little swelling as the narrow plastic zone moved inward. In an experiment at $14^{\circ}\text{C}/\text{min}$, very little swelling was observed, but the block surface did become glazed. Block behavior at $3^{\circ}\text{C}/\text{min}$ was intermediate between these cases (Fig. 3.2): lava-like flow of the block surface and small amounts of swelling would result from a wider plastic zone between T_1 and T_2 .

Secondary cracking of pyrolysis products may account for certain changes in the product yield structure from hydrogen-purged experiments. As temperature gradients become steeper (higher surface heating rates), an increase is observed in char yield, gas yield, and water evolution, but the yield of organic condensables decreases. The decreased yields of reactants for secondary cracking and increased yields of products support this hypothesis.

Such an increase in secondary cracking could result from heat and mass transfer resistances within the coal block. Because of internal mass transfer resistances, pyrolysis products do not escape immediately from the block interior but must negotiate some outward path by convection or diffusion.

Fig. 3.2. Char block after experiment BP2-37 ($3^{\circ}\text{C}/\text{min}$ to 870°C).

Because of internal heat transfer resistances, block temperatures are nearly uniform at $0.3^{\circ}\text{C}/\text{min}$; however, at higher heating rates, steeper thermal gradients can exist between the hot block surface and the cooler center. A simultaneous effect of these resistances could be secondary cracking of pyrolysis products from the block center as the products move outward through the hotter surface regions. Less effect of heat transfer resistance would be present at slower heating rates, although internal mass transfer might be slowed by the increased plastic deformation of the block structure.

Carbonization of Coal Liquefaction Residues

Most coal liquefaction processes produce a by-product liquid residue stream (i.e., underflow from solid-liquid separation) containing a large amount of solid materials (ash, unreacted coal, abraded catalyst). This residue also contains significant quantities of valuable light liquids. The Energy Research and Development Administration (now DOE) requested that the Chemical Technology Division evaluate the process feasibility of residue carbonization operations proposed by two of their contractors: Fluor Engineers and Constructors, Inc.,⁸ and the Ralph M. Parsons Corporation.⁹ The objectives of pressurized

8. Fluor Engineers and Constructors, Inc., *Conceptual Design for Advanced Coal Liquefaction Commercial Plant Annual Technical Progress Report*, April 21, 1976-April 30, 1977, FE-2251-28 (June 1977).

9. J. B. O'Hara, N. E. Jentz, H. T. Syverson, G. H. Hervey, and R. V. Teeple, *Project POGO, Total Coal Utilization, COG Refinery Design Criteria, R&D Report No. 114 Interim Report No. 5*, FE-1775-31 (August 1977).

carbonization of coal liquefaction residue as a unit operation are (1) to recover valuable liquid and gaseous components from the residue, and (2) to produce a solid, free-flowing (granular) char to be overlaid to a gasifier for hydrogen production. Although carbonization of coal liquefaction residue has been studied previously near atmospheric pressure, this is the first study at high pressure.

An experimental fluidized-bed carbonization system was assembled; it consisted of four major pieces of equipment: (1) a gas preheater, (2) a fluidized-bed carbonizer, (3) a condenser, and (4) a condensate receiver. In addition, an activated carbon trap was used to recover any vapors passing the condenser, a wet-test meter measured effluent gas flow, and grab samples of effluent gas were taken at intervals during an experimental run.

Task I. Carbonization of hydroextraction residue. The Fluor concept¹ involves the fluidized-bed carbonization of settler or hydroclone underflow at 415 psia and 950 to 1100°F (593°C). The residue is a liquid at room temperature with a large amount of suspended solids and significant amounts of light liquid (50% boiling, <350°C). Also used as feed in these experiments was the <700°F (371°C) boiling fraction of the residue, called solvent. The solvent is a light, solids-free liquid and is similar to the recycle hydrogen donor solvent used for liquefaction. The feed for each experiment was pumped into the fluidized bed, using a packed-plunger, positive

displacement pump. The fluidized solids were alumina and hydrocarbonization char fluidized with preheated argon. Experiments were performed at two pressures [65 and 415 psia (4.6 and 30 MPa)] and two temperatures [900 and 1050°F (482 and 566°C)]. Results are summarized in the upper portion of Table 3.1. It was concluded that (1) settler or hydroclone underflow residue can be carbonized in a fluidized bed with significant recovery of light liquids, (2) solvent losses are 3 to 7%, and (3) coking of the heavier liquid is increased at higher pressures.

Task II. Rapid pyrolysis of vacuum-still bottoms. The Parsons concept² involves the rapid pyrolysis of vacuum-still bottoms (VSB) in an entrained-flow reactor at 1100°F (593°C) and 500 psia (36 MPa). At room temperature, VSB is a solid, but it is fluid at about 400°F (204°C). Feeding of the VSB was accomplished by using several small lock-hoppers to simulate continuous feed. Experiments were performed at 1100°F (593°C) and 415 psia (30 MPa), using methane as the fluidizing gas and alumina as the fluidized solid. Illinois No. 6 coal, VSB, and a 1:1 mixture of VSB and coal were used as feed for the experiments, the results of which are summarized in the lower portion of Table 3.1. The VSB proved to be a very intractable material to pyrolyze, since the nonvolatile materials were liquid at reactor conditions. It was concluded that (1) carbonization of VSB does not produce a solid char, and (2) only a small amount of liquid, which is of low quality, is

Table 3.1. Summary of pressurized carbonization results

Run No.	Bed material	Pressure (psia)	Temperature		Fluidizing gas	Feed material	Char yield (wt %)	Liquid yield (wt %)	Gas yield (wt %)
			(°F)	(°C)					
7	Alumina	415	900	482	Argon	Residue-1	43	34	1
8	Alumina	65	900	482	Argon	Residue-1	30	38	1
9	Alumina	15	900	482	Argon	Solvent	7	55	0
10	Alumina	65	900	482	Argon	Solvent	7	62	0
13	Alumina	15	900	482	Argon	Residue-2	19	47	0
14	Alumina	65	900	482	Argon	Residue-2	16	58	0
15	Alumina	65	1050	566	Argon	Solvent	1	77	0
17	Alumina	65	900	482	Argon	Solvent	3	68	1
21	Char	65	900	482	Argon	Residue-2	5	60	2
22	Char	415	900	482	Argon	Residue-2	5	71	5
28	Alumina	415	1100	593	Methane	Coal	58		13
29	Alumina	415	1100	593	Methane	50% coal, 50% VSB	57	5	21
30	Alumina	415	1100	593	Methane	VSB	61	11	19

¹Two residues were used, designated as residue-1 and residue-2; solvent denotes the <700°F (371°C) boiling fraction of residue-2.

recovered. Experimental work on this project has been completed, and a final report is being prepared.

Coal Liquefaction Development Studies

In order to develop innovative liquefaction technologies or to improve existing technology, three areas were studied during this reporting period: supercritical extraction of coal, rapid hydrocarbonization, and measurement of physical properties for coal liquids at high temperatures and pressures.

Supercritical extraction. Researchers at the Coal Research Establishment (United Kingdom) have produced attractive extraction yields from coal by using treatment with supercritical toluene.¹⁰ Specifically, toluene at 350°C and 100 atm was reported to have produced more tar than could be produced from pyrolysis processes. For example, when British coals of 18 to 45% volatile matter (maf) were extracted with toluene, 8 to 25% (maf basis by weight) of extract was produced along with small gas and liquor yields and a devolatilized char. Based on promising estimates of process economics at these yields,¹¹ a 14-kg/hr pilot plant was constructed, and testing was scheduled to begin in 1977.¹²

Batch experiments were conducted at ORNL to examine applicability of the British results to American coals. Because its composition was similar to a British coal that has yielded ~25% extract, bituminous coal from the Illinois No. 6 seam was chosen for these experiments.¹³ Toluene and methanol were tested as solvents; potassium hydroxide and sodium hydroxide were tested as possible catalysts for hydrogen donation. Solvent and additive were first measured into a 1400-cm³ autoclave, and a fine-mesh basket containing 30 g of dried, powdered, and sized coal was suspended in the autoclave. After sealing and purging, the reactor was heated for about 2.5 hr to reach extraction temperature (340°C for toluene, 270°C for methanol). Following 1.5 hr of extraction, the system was cooled to room temperature (2 to 3 hr). Yield is defined as the weight loss of the vacuum-dried, char-containing basket expressed as a percentage of the maf coal weight.

Extraction yields of 43% were obtained in experiments using toluene at 341 to 343°C and 232 to 269 atm. Satisfying theoretical limitations, these yields do not exceed the 48.1% volatile matter content of coal. Such high yields suggest the viability of a supercritical "skimming" process in which oil and a useful high-carbon residue would be produced. When methanol was used (273°C, 141 atm), the yield was 12%. In tests using potassium hydroxide and sodium hydroxide additives, little change in yield was observed.

Rapid hydrocarbonization. Despite promising high conversion of coal on a laboratory scale, a successful reactor concept for rapid hydrocarbonization must be developed before those yields can be realized commercially. Process engineers at ORNL have proposed a rapid hydrocarbonization reactor based on recirculating fluidized-bed technology. Three zones would be operated within a single vessel: (1) rapid hydrocarbonization by injecting coal into a draft tube (riser) containing hydrogen and hot recirculating char; (2) rapid separation of char from draft-tube gas by using an internal cyclone coupled directly to the draft tube; and (3) partial combustion of recirculating char to produce process heat. Efficient disengagement is particularly important so that a solid-free oil can be quickly quenched.

Solids loading in a draft tube may be $\geq 1\%$ by volume, but cyclone development has historically focused on loadings of $\leq 0.02\%$. Cyclones at ambient temperature and pressure were tested at loadings of 0.1 to 3% with entrance velocities of 3.7 to 35.5 fps (0.11 to 1.1 m/sec). Actual hydrocarbonization char (approximately -30 +325 mesh) was used, which was removed in 0.875- and 2.125-in.-diam. (2.22- and 5.398-cm) cyclones. Because of its importance to the stability of a recirculation loop, cyclone pressure drop was monitored.

High efficiencies were measured at relatively low entrance velocities, with a 99.8% removal or higher at loadings to 8850 grains ft⁻³ (20,000 g/m³, or 1.9 vol %). It has also been noted¹⁴ that lower entrance velocities may improve cyclone efficiency at increased loading of solids. In addition, pressure drop through the cyclone was observed to decrease when solids were added to the gas stream. Nevertheless, the decrease was experimentally confirmed to be less as

10. D. F. Williams, *J. Inst. Fuel* 48, 182 (1975).

11. R. R. Maddocks and J. Gibson, *Chem. Eng. Prog.* 73(6), 59 (1977).

12. *The Energy Daily* (Washington, D.C.) 5, No. 72 (Apr. 13, 1977).

13. R. A. Graff and J. Yerushalmi, *Improved Techniques for Gasifying Coal*, FE-2340-7 (1977).

entrance velocity was increased. Application of these data to operation of the Lucite reactor model could help to develop a successful reactor concept for rapid hydrocarbonization.

Measurement of physical properties for coal liquids. A continuous-flow, bench-scale system has been designed to investigate the physical properties of the coal liquids at high temperature and high hydrogen pressure. Figure 3.3 is a process flow and instrumentation diagram of the system. Both coal-solvent slurries and solids-free liquids can be handled. The system consists of high-pressure liquid and hydrogen supply systems, separate liquid- and gas-phase preheaters, a catalytic packed-bed reactor, vapor-liquid separators, and the physical property instruments. The preheaters and reactor will be used to simulate processing conditions prior to physical property measurement. Dissolution-type coal liquefaction processes and coal-derived oil hydroprocessing operations such as hydrocracking and hydrotreating can be simulated.

The extreme operating conditions for the preheaters, reactor, high-pressure separator, and physical property instruments are 4500 psig (31.1 MPa) and 1000° F (538° C). The liquid or slurry and gas supply systems are sized to permit liquid hourly space velocities to 5.0 hr and hydrogen treat rates to 10,000 scf, bbl (75.4 kg-moles, m³) in the reactor. This is equivalent to liquid and hydrogen flow rates of 1250 cm³/hr and 100 scfh (120 g-moles/hr) respectively. The liquid-feed preheater is designed to permit variable residence time at constant throughput by varying the length of the flow path. Measurements of viscosity, density, thermal conductivity, and heat capacity of any of the flowing streams can be made. The liquid will be quenched at test conditions and chemically characterized for ultimate correlation of physical properties with chemical composition.

3.2 COAL CONVERSION ENGINEERING STUDIES AND PROGRAM ANALYSIS

Extensive engineering studies concerning coal conversion processes are being conducted for DOE Fossil Energy, Division of Coal Conversion (DCC). These studies include technical and economic evaluations of commercial-scale conversion plants and processes, surveys of industrial equipment capabilities, and surveys of hot-gas cleanup and heat recovery processes. In addition, technical support is being provided to DCC in the development of process modeling techniques.

Process and program analysis studies, which involve most of the coal conversion processes, are being conducted for DOE Fossil Energy, Division of Program Control and Support (DPCS). The objective of the project is to consistently provide 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, and in situ coal gasification.

The Chemical Technology Division is coordinating these efforts for DPCS and is responsible for the in situ gasification and the associated subsystem studies. The direct combustion, advanced power, and low-Btu gas studies are being conducted by other divisions at ORNL. The high-Btu gas and liquefaction studies are being performed under subcontract with industrial firms.

Process Modeling

Process modeling is a joint 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- and energy-balance 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.

Computer programs for acid-gas removal processes. Several computer programs are being developed for the design of acid-gas treating processes of the DEA (diethanolamine), MDEA (methyldiethanolamine), and hot-carbonate types. The programs calculate solvent circulation rates, material and energy balances, equipment duties and sizes, and utilities requirements that are based on user-supplied feed-gas compositions, feed-gas flow rates, and acid-gas removal levels. Thus far, only the MDEA program includes the capability of making a capital cost estimate. It is planned to add this capability to the other programs.

Heat exchanger design and cost estimation. This program, referred to as HDC, was described last

Fig. 3.3. Process flow and instrumentation diagram of the coal fluid-flow system.

year and is undergoing continued development and calibration. The program calculates the mechanical design and cost of a shell-and-tube exchanger based on a user-supplied thermal design. During the past year, improvements were made in the cost estimating portions of the program. A separate routine was written to design flanges by standard ASME procedures; weights of the flanges were then correlated with diameters and pressure ratings. Data on the various alloys in the form of plate, tube, and forgings are being collected for the materials cost section of the program.

A program for the thermal design of a shell-and-tube heat exchanger was completed for the case in which there is no phase change on either side. The flow rates and allowable pressure drops on both sides are specified by the user; the program calculates the heat transfer coefficients and the required surface area and adjusts the baffle spacing, diameter, and tube length to make use of the allowable pressure drop. The logic used is similar to that of the Heat Transfer Research Institute program. The XTD program is being used for calculating heat exchange surface requirements in other DOE-funded work at ORNL.

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; manufacturers were contacted to determine the current and future availability, costs, reliability, and potential problems which may be encountered. The 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.

The equipment subjects included in the surveys were rotating components, valves, hot-gas cleanup, and heat recovery. Reports covering these four subjects are being compared. The results of the survey are discussed below.

Rotating components. Rotating equipment is generally available for most of the clean-stream applications that may be encountered in coal conversion facilities, with the exception of oxygen compressors for pressures greater than 600 psia (4140

kPa). Equipment that is critical to the success of the coal conversion industry and needs to be developed or significantly upgraded includes slurry pumps, high-pressure oxygen compressors, and low-pressure fans and blowers capable of handling dirty streams. The development of expanders is critical to the practicability of several processes. Hydraulic turbines may be desirable for power recovery from slurry streams; however, their unavailability will not seriously affect any processes.

Valves. The survey results show that the valve and valve-actuator industry is capable of manufacturing equipment of the size and for the pressure and temperature range that would be required in the coal conversion industry. However, valve manufacturers do not have product application experience to predict the continuing functional ability of valves used for lock-hopper feeders, slurry feeder, and slag-char beddown service. Developmental and testing efforts to modify existing valve design or to develop new valve concepts for these applications were estimated to range from one to six years. A testing facility to simulate actuation of critical valves under service conditions would be beneficial.

Hot-gas cleanup equipment. The development of a particulate removal system capable of operating at high temperatures and high pressure (HTHP) and able to meet the stringent cleanup requirements needed to ensure acceptable turbine life is a formidable task. Even if existing turbine particulate allowances [0.0002 grain/scf (0.013 mg/m³)] were increased by two orders of magnitude and the particulate carry-over from either a low-Btu gasifier or a pressurized fluidized-bed combustor were held to 5 grains/scf (324 mg/m³), an overall cleanup efficiency of at least 99% would have to be achieved.

In addition to the stringent cleanup demands, the presence of condensable hydrocarbons in a number of gasification processes will require the operation of HTHP filtration equipment at temperatures above 1000° F (538° C). Below this point, HTHP particulate removal may not be a viable option due to problems caused by condensation. In addition, major advances in HTHP filtration technology will apparently be required to make it an economically attractive option.

With regard to the current state of development of various hot-gas particulate cleanup devices, the following observations can be made:

1. Inertial separation devices have most likely achieved their maximum levels of efficiency with existing designs, and research aimed at dramatically

improving their performance appears to be unwarranted.

2. Surface filters of either the Brunsmet metal type or unique high-temperature fabrics have potential use in HTHP gas cleaning applications. This choice is subject to the constraint that sufficiently high throughputs, coupled with acceptable operational life, can be demonstrated.

3. Granular-bed filters, particularly of the more advanced designs (Ducon and Combustion Power Company), are at the stage where on-line operational testing is needed to ascertain their overall filtration characteristics.

4. Major engineering and operational problems need to be resolved before electrostatic precipitators become viable HTHP filtration devices.

A review of the possible concepts for hot-gas removal of hydrogen sulfide suggests that (1) the MERC fixed-bed scrubber, which uses iron oxide-silica sorbent, is the closest to full-scale application; (2) Conoco's fluid-bed system with half-calcined dolomite offers potential advantages over the MERC device but requires further experimental efforts to ascertain technical feasibility; (3) in addition to requiring further research to validate its technical feasibility, Battelle's molten-alkali-salt scrubber presents problems that appear to preclude its use in systems designed to condition fuel gas for turbine operation.

It now appears that commercially available, reliable, and economically competitive hot-gas cleanup systems (hydrogen sulfide and particulate removal) capable of conditioning raw product gas to the levels required for turbine use will not be available for some time.

Heat recovery equipment. Major categories of heat exchangers in this phase of the survey included shell-and-tube, periodic-flow and rotary regenerators, heat pipe arrays, direct phase contactors, and steam and organic Rankine cycles for power generation from waste heat. Primary applications encompassed feed-effluent and other process stream interchangers, combustion air preheaters, and heat recovery steam generators (waste heat boiler-superheaters).

A review of past experience in operating coal conversion plants and of some proposed designs indicates that many flows will probably be in the laminar or transition regimes, and that overall heat transfer coefficients for exchangers involving at least one process stream will be low [$\leq 100 \text{ Btu hr}^{-1} \text{ ft}^{-2} (\text{°F})^{-1}$ ($\leq 568 \text{ W/m}^2\cdot\text{K}$)]. Additional research is needed to obtain more physical property data

(especially viscosities), better heat transfer correlations for multiphase streams (e.g., coal-oil and coal-water slurries), and rates of fouling, corrosion, and erosion.

A questionnaire was sent to 23 companies that specialize in large, severe-service units, requesting their views on the design and fabrication of 12 potentially critical heat exchangers selected from three evaluation design studies of coal conversion plants. It is concluded that the single area providing the greatest potential for extending U.S. industrial heat recovery equipment capabilities as related to coal conversion processes is a research, development, and testing program to acquire more physical property and heat transfer data and more reliable design correlations. Liaison with heat-exchanger vendor and user representatives should be maintained and extended to obtain their ideas on a regular basis regarding program directions.

Technical and Economic Assessments of Processes

Technical and economic assessments are routinely performed for those systems or processes which appear to offer some unique potential but for which development is limited to a preconceptual stage. Data necessary for a true evaluation are generally lacking in these assessments, but experience coupled with a broad base of general coal conversion technology will offer a timely approach to providing preliminary considerations. Examples of current assessments are summarized here.

Hydrogen production by the steam-molten-iron process. A steam-molten-iron concept is compared with the more conventional concepts employed in the Koppers-Totzek and Bi-Gas processes. All three processes are considered as part of an integrated S/C-II system. Process flowsheets, system costs, and product distributions are being prepared for each case, and comparative economics are being developed. A developmental program for bringing the molten-iron process to the state of commercial availability is being considered.

Moving-bed system for cleanup of raw gasifier gas. An assessment was made of two basic hot-gas treatment systems that specifically address sulfur and particulate removal. The reference system incorporates a panel filter for dust removal and fixed-bed adsorber-regenerator units. The project system incorporates a moving-bed filter-adsorber unit, with fluid-bed regeneration of the recycled filter-adsorber media. Both systems produce high-pressure steam

(waste heat boiler) from the regeneration off-gases. The assessment includes simple equipment flowsheets and material balances for both systems.

Flash hydropyrolysis study. This process (FHP) is an emerging technology in which coal is rapidly pyrolyzed in the presence of hydrogen at high temperature and pressure and then quenched to yield (after further processing) products consisting primarily of SNG, an aromatic distillate oil, a fuel oil, sulfur, ammonia, and a usable char. The aromatic distillate oil consists mainly of benzene, toluene, and xylene (BTX). Coal residence time in the reactor is only a few seconds. The process is essentially self-sufficient in hydrogen; hydrogen requirements can be met either by gasifying the spent char from the reactor or by reforming a portion of the SNG produced.

A preliminary technical and economic assessment of two conceptual versions of the FHP process is being conducted by ORNL for DOE. The Cities Service Research and Development Company and the Schoeder-Spencer Chemical Company FHP processes were the two chosen for this assessment. The Schroeder-Spencer process is a catalytic process designed for distillate oil production; the Cities Service process is a noncatalytic process designed primarily to produce SNG, plus a smaller amount of BTX liquid product. The primary objective of the study was to determine whether a more detailed evaluation of the FHP process is justified.

A report¹⁴ has been prepared which presents the results of the study. It was concluded that a more detailed engineering evaluation of the FHP process will be justified after a firm data base for the process has been established.

Synthetic Fuels Process Research Digest. Reviews of current or potential processes relating to coal conversion technologies are provided by the preparation of the *Synthetic Fuels Process Research Digest*. The format and procedures for issuing the periodical have been established, and the first volume has been published.¹⁵

Articles included in the first issue are: (1) Coal Gasification with Chemically Incorporated Catalysts, (2) Flash Hydropyrolysis of Coal, (3) Zinc Chloride Hydrocracking of Coal and Coal Extracts, and (4) Conversion of Methanol to High-Octane Gasoline.

14. S. P. N. Singh, *Scoping Study on Two Flash Hydropyrolysis Processes*, ORNL TM-6265 (in preparation).

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

Topics being considered for the second volume include the SRC-II process, the Consol Synthetic Fuels process, the Fischer-Tropsch process, and the production of low- to intermediate-Btu gas from coal.

Environmental Controls for Low-Btu Gasification

The objective of this program is to evaluate the various environmental control processes that might be used in coal gasification plants. The program includes considerations of economic trade-offs for various levels of environmental controls and for various low-Btu gasification processes. This study is being conducted for DOE-Fossil Energy, Division of Energy Technology.

The project is broadly divided into two phases. Phase I consists of the following five tasks:

1. Development of a detailed work plan for the execution of the project.
2. A survey of the currently available commercial environmental control technologies that may be applicable for producing environmentally clean low-Btu gas from coal, and the selection of 25 of the environmental control technologies for more detailed evaluation.
3. Compilation of information regarding potential gasifiers that may be used for the production of low-Btu gas from coal.
4. Selection of four typical low-Btu gasifiers to be used in example flowsheets showing the application of complete systems of environmental control technologies.
5. Presentation of the results of Phase I to DOE project management.

Phase II consists of the following tasks:

1. Compilation of the costs and energy requirements of the 25 selected environmental control processes over a range of operating conditions, capacities, and levels of contaminant removal.
2. Compilation of information regarding the characteristics and the potential applications of each of the 25 selected environmental control processes.
3. Technical and economic evaluations of complete environmental control systems for conceptual low-Btu coal gasification facilities. Eight cases are proposed to be evaluated to illustrate the trade-offs between economic costs

and environmental benefits associated with various cleanup systems for four different gasifiers. The eight cases will be judiciously selected to cover a range of gas throughputs and levels of pollutant removal.

Phase I of the study has been completed. A list of the 25 environmental control processes selected for a more detailed evaluation is shown in Table 3.2. The four gasifiers tentatively selected for use as examples are the Wellman-Galusha, Lurgi (dry ash), U-gas, and the Babcock and Wilcox entrained-flow gasifier.

Process and Program Analysis

During this report period, process and program analysis studies for DPCS included gas cleanup, coal beneficiation, liquefaction, and the production of high-Btu gas. One additional project, HYGAS modeling, has been undertaken at the request of DPCS. Some of the results are discussed below.

Gas cleanup. This work covered studies of gas cleanup systems used in coal conversion processes. The objective of the program is to provide technical and economic information to permit comparison of competing processes and systems. The following two areas were studied for application to low-Btu gasification systems:

1. *Low-temperature acid-gas removal.* This includes a study of systems of chemical and physical solvents that remove hydrogen sulfide and/or carbon dioxide and related pollutants. At low temperatures, particulate removal poses no problems.

2. *High-temperature acid-gas removal.* This includes a study of solid adsorbents, molten-salt processes, etc., in which the primary goal is removal of hydrogen sulfide. High-temperature particulate removal and prevention of alkali carry-over must also be considered.

A survey was conducted to identify promising applicable processes, concepts, and systems for cleanup of gas streams resulting from conversion of coal. The survey included processes used both in the United States and in other countries. A list of 34 potential processes, concepts, and systems specific to low-Btu gasification cleanup was prepared from the survey. The processes were categorized to permit a general analysis leading to selection of those systems potentially most useful for the treatment of low-Btu gas streams.

Further screening using criteria such as selectivity for hydrogen sulfide, chemical stability, and lack of toxicity reduced the number of processes under consideration to 14. Final evaluation led to the selection of fewer than ten representative processes for low-Btu gas cleanup. Detailed descriptions of these processes, including available cost data, were provided and a report¹⁶ of the project was completed. The report is undergoing review prior to publication.

16. M. S. Edwards, *Selection of Candidate H₂S-Removal Processes Applied to Low-Btu Coal Gas*, ORNL TM-6077 (to be published).

Table 3.2. Proposed environmental control processes for potential application in the production of environmentally clean low-Btu gas from coal

Gas treating processes	By-product recovery processes
1. DEA	1. Chevron WWT
2. MDEA	2. U.S. Steel's Phosam-W
3. Benfield	3. Jones and Laughlin's dephenolization
4. Sulfinol	4. American Lurgi's Phenosolvan
5. Selexol	5. API gravity oil separator
6. Stretford	
7. Claus	
8. Beavon	
9. SCOT	
10. Incineration	
Wastewater treatment processes	Particulate recovery processes
1. Activated sludge	1. Bag filtration
2. Activated carbon, PACT*	2. Cyclones, multiclones
3. Zimpro Wet Air Oxidation	3. Wet scrubbing
4. Sour water stripper	4. Electrostatic precipitation
5. Chemical oxidation	
6. Radox wastewater treatment	

*PACT = powdered activated carbon treatment.

Coal beneficiation study. Coal beneficiation is a generic term used to designate the various cleaning operations performed on the run-of-mine (ROM) coal to prepare it for specific end uses. It encompasses the entire spectrum of operations ranging from the relatively simple physical separation to rather elaborate chemical treatment processes to remove the undesirable impurities such as sulfur and ash from the ROM coal.

The objective of the present study was to identify and analyze various currently used and potential coal beneficiation processes. A draft final report¹⁷ is being prepared which presents the results of the study. As a part of the study, nonproprietary information regarding coal beneficiation processes was obtained from process developers, equipment manufacturers, and open-literature sources. Detailed engineering and economic evaluations were performed on the following four processes: (1) wet mechanical benefi-

ciation (mild cleaning), (2) wet mechanical beneficiation (deep cleaning), (3) Battelle hydrothermal coal process, and (4) TRW-Myers fine-coal process. The first two processes are in commercial use in the coal industry. Processes 3 and 4 are the most developed of the potential coal beneficiation processes.

Three representative U.S. coals were selected for the evaluation because they have high sulfur and ash contents and because they represent major coal-producing regions in the United States.

Capital and annual operating costs were developed for two conceptual beneficiation plants capable of producing 1500 and 15,000 tons (1.36×10^6 and 13.6×10^6 kg) of maf coal per day. Costs were developed for both "grass-roots" and battery-limits types of plants. In the grass-roots facilities, all utilities were assumed to be developed on site; in the battery-limits facilities, all plant utility requirements were assumed to be purchased. Preliminary results of the study are summarized in Tables 3.3 and 3.4 for the grass-roots and the battery-limits type of beneficiation plants respectively.

HYGAS modeling. The objective of this project is to develop a mathematical simulation model of the

17. S. P. N. Singh and G. R. Peterson, *Survey and Evaluation of Current and Potential Coal Beneficiation Processes*, ORNL TM-5953 (in preparation).

Table 3.3. Summary of coal beneficiation processes evaluated for grass-roots facilities

Process description	1500 tons day, maf product						15,000 tons day, maf product					
	Reduction (%)		Recovery (%)		Beneficiation cost ^a		Reduction (%)		Recovery (%)		Beneficiation cost ^a	
	Sulfur	Ash	Material ^b	Thermal ^c	\$ ton ^d	\$ 10 ^e Btu ^f	Sulfur	Ash	Material ^b	Thermal ^c	\$ ton ^d	\$ 10 ^e Btu ^f
Wet beneficiation process												
Mild cleaning												
Pennsylvania coal	26.6	46.6	73.9	86.8	6.03	0.24	26.6	46.6	74.6	87.6	3.93	0.16
W. Kentucky coal	25.5	57.1	80.3	88.6	6.26	0.25	25.5	57.1	81.3	89.6	3.92	0.15
Illinois coal	25.7	37.3	85.4	92.5	5.84	0.25	25.7	37.3	87.5	93.9	3.65	0.16
Deep cleaning												
Pennsylvania coal	43.4	72.8	69.1	88.0	8.06	0.30	43.4	72.8	70.4	89.7	5.43	0.20
W. Kentucky coal	27.8	74.4	76.3	86.5	8.36	0.30	27.8	74.4	77.8	88.1	4.99	0.19
Illinois coal	33.5	57.9	77.4	87.4	7.64	0.31	33.5	57.9	79.1	89.3	5.09	0.21
Battelle hydrothermal process												
Pennsylvania coal	79.3	f	49.5	45.1	59.51	3.12	79.3	f	49.5	45.0	47.19	2.47
W. Kentucky coal	75.7	f	60.4	53.6	50.60	2.46	75.7	f	60.4	53.6	40.09	1.95
Illinois coal	69.6	f	56.1	50.3	50.43	2.76	69.6	f	56.1	50.4	42.18	2.18
TRW-Myers fine coal process												
Pennsylvania coal	78.5	30.0	82.0	88.2	12.43	0.54	78.6	30.0	82.1	88.2	7.30	0.32
W. Kentucky coal	60.8	30.0	86.0	89.5	13.97	0.57	60.8	30.0	86.0	89.6	8.21	0.34
Illinois coal	56.8	30.0	84.0	88.0	13.52	0.59	56.8	30.0	84.0	88.0	7.88	0.34

^aBasis: ROM coal cost = \$20/ton; debt/equity = 70/30; average annual rate of return on equity = 12%; annual interest rate on debt = 9%.

^bBased on moisture-free coal.

^cBased on maf coal.

^dFor moist, cleaned product coal (nominal 5% moisture).

^eBased on heating value of maf cleaned product coal.

^fApparent ash content increased because leachant (NaOH) impregnates the product coal.

Table 3.4. Summary of coal beneficiation processes evaluated for battery-limits facilities

Process description	1500 tons/day, maf product						15,000 tons/day, maf product					
	Reduction (%)		Recovery (%)		Beneficiation cost ^a		Reduction (%)		Recovery (%)		Beneficiation cost ^a	
	Sulfur	Ash	Material ^b	Thermal ^c	\$/ton ^d	\$/10 ³ Btu ^e	Sulfur	Ash	Material ^b	Thermal ^c	\$/ton ^d	\$/10 ³ Btu ^e
Wet beneficiation process												
Mild cleaning												
Pennsylvania coal	26.6	46.6	74.9	88.0	5.06	0.21	26.6	46.6	75.5	88.5	3.97	0.16
W. Kentucky coal	25.5	57.1	81.7	90.1	5.18	0.20	25.5	57.1	81.9	90.3	3.97	0.16
Illinois coal	25.7	37.3	86.9	94.1	4.81	0.21	25.7	37.3	87.5	94.8	3.66	0.14
Deep cleaning												
Pennsylvania coal	43.4	52.8	70.8	90.1	6.87	0.26	43.4	52.8	71.2	90.7	5.56	0.21
W. Kentucky coal	27.8	74.4	78.6	89.1	6.98	0.27	27.8	74.4	78.9	89.4	5.12	0.20
Illinois coal	33.5	57.9	79.7	96.1	6.31	0.26	33.5	57.9	80.1	90.4	5.22	0.21
Battelle hydrothermal process												
Pennsylvania coal	79.3	f	97.2	92.8	7.09	3.25	79.3	f	97.2	92.8	63.37	3.32
W. Kentucky coal	75.7	f	100.0	93.5	55.74	2.71	75.7	f	100.0	93.5	52.23	2.55
Illinois coal	69.6	f	99.1	88.9	56.55	2.92	69.6	f	99.1	88.9	56.46	2.92
TPW-Myers fine coal process												
Pennsylvania coal	78.6	30.0	84.4	90.8	12.06	0.53	78.6	30.0	84.4	90.8	7.99	0.35
W. Kentucky coal	60.8	30.0	88.5	92.1	13.79	0.55	60.8	30.0	88.5	92.2	5.64	0.25
Illinois coal	56.8	30.0	86.4	90.5	13.13	0.57	56.8	30.0	86.5	90.6	8.62	0.38

^aBasis: ROM coal cost = \$20/ton; debt/equity = 70/30; average annual rate of return on equity = 12%; annual interest rate on debt = 9%.

^bBased on moisture-free coal.

^cBased on maf coal.

^dFor moist, cleaned product coal (nominal 5% moisture).

^eBased on heating value of maf cleaned product coal.

^fApparent ash content increased because leachant (NaOH) impregnates the product coal.

HYGAS pilot-plant reactor. This reactor is a multistage fluidized-bed unit consisting of a steam-oxygen gasifier, two hydrogasification stages, and a slurry dryer.¹⁸ In developing the ORNL model, a separate computational module has been constructed for each of the individual beds, and these modules have been linked in such a way that the overall material and energy balance constraints are satisfied. For purposes of analysis, several simplifying assumptions have been made: (1) each stage behaves as a perfectly back-mixed reactor; (2) only physical separation occurs in the slurry dryer; and (3) devolatilization, rapid-rate methane formation, and slow-rate hydrogasification occur independently and sequentially. This last assumption is consistent with the approach of Johnson¹⁹ for modeling hydrogasifi-

cation phenomena. Mathematically, the models chosen to represent each of the independent kinetic steps have been drawn from the available literature.

Devolatilization. In this model,²⁰ it is assumed that devolatilization consists of an infinite set of parallel reactions, each of first-order form:

$$dV_i/dt = k_i(V_i^* - V_i)$$

where

V_i = cumulative yield of volatile product by reaction i ,

t = time,

k_i = rate constant for reaction i ,

V_i^* = ultimate release of volatile product ($t = \infty$).

18. Dravo Corporation, *Handbook of Gasifiers and Gas Treatment Systems*, FE-1772-11 (February 1976).

19. J. I. Johnson, "Kinetics of Bituminous Coal Char Gasification with Gas Containing Steam and Hydrogen," *Adv. Chem. Ser.* 131, 145 (1974).

20. D. B. Anthony, J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization of Pulverized Coal," 15th International Symposium on Combustion, Tokyo (Aug. 25-31, 1974).

Depending on the temperature-time profile of the coal as it is heated and the analytical form of the rate constant, several algebraic solutions are available for computing the total volatile yield. Frequently, the assumption is made that the rate constant is of the Arrhenius form and that the temperature-time profile is linear ($dT/dt = m$). In this case, the amount of volatile release is given by the expression

$$V_i = V_i^* \times [1 - \exp\{(-k_i RT^2/mE_i) \times \exp(-E_i/RT)\}]$$

where

- k_i = preexponential factor for reaction i (sec^{-1}),
 R = universal gas constant (1.987×10^{-3} kcal g-mole $^{-1}$ K $^{-1}$),
 T = final particle temperature (K),
 m = heating rate (K/sec),
 E_i = activation energy for reaction i (kcal/mole).

Currently, kinetic parameters are available for Montana lignite coal, and efforts are under way to obtain similar data for Illinois No. 6 and Pittsburgh seam coal.

Recent progress on the HYGAS project has centered largely on the definition of the various kinetic models to be used in the simulation programs. Future efforts will be devoted to integrating these models into a single-stage algorithm to be followed by a complete analysis of the entire system.

High-Btu gas. This subprogram is being analyzed under subcontract by the Scientific Design Company, Inc. (SD), and is divided into the following two phases:

1. The objective of Phase I is to provide technical and economic evaluations of competing processes, concepts, and systems for the production of high-Btu gas from coal.
2. The objective of Phase II is to monitor and analyze data from the HYGAS pilot plant.

Phase I. The process design and economic evaluation of a 250×10^9 Btu/day (264×10^{12} J/day) pipeline-quality gas plant has been prepared for the Battelle Agglomerating Ash Burner Process.²¹ The process design was based on a preliminary process

flowsheet and material balance provided by Battelle, which was modified by SD as required to achieve an integrated facility. The results indicate that the capital cost for the Battelle process is higher than that of the other processes considered, exceeding the lowest-cost HYGAS (steam-oxygen) and Conoco CO₂ Acceptor by about 50%. The average gas cost (utility financing method), including the cost of coal, is \$5.20/10⁶ Btu (\$4.93/10⁹ J), or ~50% greater than the average of ~\$3.50/10⁶ Btu (\$3.32/10⁹ J) for the other processes. On an "ex-coal" basis, the gas cost is still significantly higher [i.e., \$3.49/10⁶ Btu (\$3.31/10⁹ J)], or ~30% greater than the average of ~\$2.70/10⁶ Btu (\$2.56/10⁹ J) for the other processes. Thus the Battelle process appears economically unattractive on the basis of this comparative evaluation.

Phase II. Engineers from SD continue to monitor the operation of the HYGAS pilot plant in Chicago. Results will be described in a final report.

Liquefaction. The objective of this project is to provide technical and economic evaluation of coal conversion liquefaction processes. The Ralph M. Parsons Company is working under subcontract on this project; major tasks included are a survey of liquefaction processes and a detailed review of high-potential liquefaction processes.

The preliminary draft report summarizing the characteristics of 32 liquefaction processes reviewed during the screening survey has been completed.

As a result of the assessments, Parsons recommended selection of the following processes for more detailed comparison:

1. H-Coal (a catalytic hydroliquefaction process),
2. CSF (a donor solvent process),
3. SRC (a noncatalytic-pseudocatalytic hydroliquefaction process),
4. Fischer-Tropsch using flame-sprayed catalytic heat exchange service (an indirect process), and
5. gasoline via Mobil-M (an indirect liquefaction process followed by catalytic conversion of methanol to gasoline).

The recommended selection of a donor solvent process is based on the availability of information to Parsons to properly evaluate the technology.

A preliminary review was made of the Mobil M-Gasoline process for the conversion of methanol to gasoline, using crude methanol derived from coal.²²

21. Scientific Design Company, Inc., *Evaluation of the Battelle Agglomerating Ash Burner High-Btu Coal Gasification Process*, ORNL Sub-7240-1 (October 1977).

22. Ralph M. Parsons Co., *Coal Liquefaction Process Research Mobil M-Gasoline Process R&D Interim Report No. 1*, ORNL Sub-7240-1 (October 1977).

A plant capable of producing 50,000 bbl (7950 m³) of product gasoline was selected as being representative of present commercial plant sizes. Key process steps included coal gasification to produce synthesis gas, conversion of synthesis gas to crude methanol, and conversion of crude methanol to gasoline.

The projected required gasoline selling price is about \$0.82/gal (\$0.217/liter) based on the use of purchased coal at \$20/ton (\$22/10³ kg), a 12% discounted cash flow rate of return with a 65/35 debt-to-equity ratio, a 9% interest rate, and a fixed capital investment based on mid-1977 dollars. The estimated fixed capital investment is about \$1.6 billion. All economics in this study are based on mid-1977 dollars.

Preliminary engineering was performed as required to obtain the fixed capital investment estimates. About 76% [\$0.624/gal (\$0.165/liter)] of the product cost is attributable to synthesis gas generation, which includes coal costs. The methanol synthesis and methanol conversion to gasoline steps each contribute about 12% to the product cost. The coal cost at \$20/ton (\$22/10³ kg) accounts for ~30% of the required gasoline selling price, which is ~\$0.25 per gal (\$0.066/liter).

In Situ Coal Gasification

The objective of this project is to assist DPCS in performing its program review function by assessing the potential for commercialization of candidate in situ coal gasification processes. To meet this objective, technical and economic evaluations of promising in situ coal gasification processes and systems are being performed. The evaluations will serve as a basis for determining which processes and systems have the best commercial potential.

A report²³ was issued comparing four candidate in situ coal gasification processes (linked vertical well, packed bed, longwall generator, and steeply dipping bed) on the basis of a qualitative assessment of their technical merits and their suitability for application to various resource types and configurations in the continental United States. Three seam thicknesses [≤ 15 ft (4.6 m), 15 to 50 ft (15.2 m), and > 50 ft (15.2 m)] two seam dips ($< 45^\circ$ and $> 45^\circ$), and seam depths to 3000 ft (914 m) were considered. The United States was divided into four regions, and a

predominant or representative coal type was selected within each region for purposes of displaying each candidate process to its best advantage. Russian experience, where it applies to the regional conditions under consideration, is also described.

A draft final report²⁴ covering the second phase of the FY 1977 work was submitted to DPCS for review and approval. This report presents conceptual process designs and cost estimates for three facilities illustrating the following potential applications of underground coal gasification: (1) a 900-MW(e) combined-cycle electric generating plant fueled by low-Btu gas, (2) an SNG plant producing 155×10^6 scfd (4.39×10^6 m³/day) of 954-Btu/scf gas (35.5×10^6 J/m³), and (3) a synthesis gas (syngas) plant producing 388×10^6 scfd (11×10^6 m³/day) of gas suitable for further chemical conversion. Designs were based on experimental data obtained at the Laramie Energy Research Center on the linked vertical well, in situ coal gasification process. In-place coal consumption for the three facilities is 18,073, 22,951, and 22,951 tons/day (16,395, 20,820, and 20,820 metric tons/day), respectively, based on a subbituminous Wyoming coal. Respective capital investments were estimated to be \$395, \$351, and \$312 million in first-quarter 1977 dollars. Product prices were calculated as a function of the debt/equity ratio, the annual earning rates on debt and equity, the cost of coal, and plant factor (on-stream efficiency). Using a debt/equity ratio of 70/30, an interest rate on debt of 9%, an after-tax earning rate on equity of 15%, a coal feed cost of \$5/ton (\$5.51/10³ kg), and a plant factor of 90%, product prices were 19 mills/kWhr for electricity, \$2.89/10⁶ Btu (\$2.74/10⁹ J) for SNG, and \$2.48/10⁶ Btu (\$2.35/10⁹ J) for syngas. Calculated overall thermal efficiencies for the three facilities were 24, 38, and 40%, respectively, based on in-place coal.

In FY 1978, a conceptual design and cost estimate will be prepared for a commercial in situ coal gasification plant, including below- and above-ground facilities, for the production of approximately 15,000 bbl (2385 m³) per day of gasoline via methanol. This evaluation will be based on low-pressure methanol synthesis technology and the Mobil M-Gasoline process.

A preliminary overall block flow diagram for the in situ M-Gasoline facility has been prepared, and to

23. W. C. Ulrich, *Evaluation of In Situ Coal Gasification Processes on a Regional Basis*, ORNL-5279 (December 1977).

24. W. C. Ulrich, M. S. Edwards, and V. Salmon, *Process Designs and Economic Evaluations for the Linked Vertical Well In Situ Coal Gasification Process*, ORNL-5341 (September 1977).

meet energy requirements, a raw-gas split of about 28% to fuel gas and 72% to process feedstock was estimated. Process flowsheets and material balance calculations based on this split were completed for all nonproprietary plant sections of the facility. Inlet and outlet material balances were estimated for proprietary plant sections. After energy requirements for the proprietary plant sections are defined more accu-

ately, a revised energy balance will be determined and the raw-gas split adjusted as necessary.

Equipment sizing calculations were initiated and are continuing. Adaptation of an existing ORNL heat-exchanger design program to help in the design of the large gas-to-gas heat exchangers needed for the facility was completed, and the new program is now in use.

4. Waste Management

4.1 PARTITIONING AND TRANSMUTATION

At the beginning of FY 1977, DOE (then ERDA) asked ORNL to develop a program to establish the technical feasibility and incentives for partitioning (i.e., recovering) long-lived nuclides from radioactive wastes and then transmuting them to shorter-lived nuclides in power reactors. The program developed to accomplish this task is broadly based, consisting of both experimental and computational activities that we believe are required to develop a meaningful and defensible analysis of the partitioning-transmutation (P-T) waste management concept. ORNL is the lead contractor, but several other DOE installations having specialized experience and experimental facilities are also participating in the program. The program duration is expected to be three years.

At the end of the program, it is expected that (1) reprocessing and mixed-oxide fuel refabrication plant partitioning flowsheets will exist which have been at least partly verified by experimental bench-scale work; (2) a meaningful and defensible, but not necessarily sophisticated, cost-risk/benefit analysis will have been completed; and (3) the scope and magnitude of the development program that would be needed to implement the P-T waste management concept will be defined. DOE should then be in a position to judge whether P-T is a waste management alternative that is worthy of development through the demonstration stage.

At the beginning of FY 1978, we were asked to redirect this program by considering only coprocessing flowsheets for partitioning that are consistent with the Administration's nonproliferation objectives. Also, we were asked to consider transmutation in thermal reactors only, although there are significant advantages for transmutation with fast neutrons.

The computational tasks undertaken in FY 1978 as a part of this program include: (1) thermal reactor transmutation studies (Savannah River Laboratory); (2) actinide recycle calculations with ORIGEN

(ORNL); (3) spent fuel reprocessing and refabrication flowsheets that utilize coprocessing concepts (ORNL); and (4) programmatic analysis, coordination, and evaluation (ORNL). During the last quarter of FY 1978 and throughout FY 1979, additional computational tasks will include: (1) risk/benefit analysis of the concept and (2) a detailed economic evaluation of the fuel cycles with and without P-T.

During this report period, experimental work continued at the various sites.^{1,2} In October 1977 this work was consolidated into the following tasks: (1) americium and curium recovery from high-level liquid waste, using the bidentate extractant dihexyl-*N,N*-diethylcarbamylmethylene phosphonate (CMP), Allied Chemical Corporation, Idaho Chemical Programs; (2) americium and curium purification from the rare earths by cation exchange chromatography, ORNL; (3) salt waste treatment by solvent extraction, Argonne National Laboratory; (4) actinide recovery from incinerator ash residues, Rocky Flats Plant; (5) actinide recovery from high-efficiency particulate air (HEPA) filters, ORNL.

The experimental results from the P-T program promise to be useful for reducing uranium and plutonium losses during fuel reprocessing and refabrication, whether or not americium and curium are recovered. The Argonne salt waste treatment system, for example, facilitates the recovery of that uranium and plutonium normally lost to sodium carbonate scrub wastes by extracting the solvent degradation products (primarily a mixture of mono- and dibutyl phosphoric acids) out of the acidified salt

1. D. W. Tedder and J. O. Blomeke (compilers), *Actinide Partitioning and Transmutation Program Progress Report for Period April 1 to June 30, 1977*, ORNL TM-6056 (October 1977).

2. D. W. Tedder and J. O. Blomeke (compilers), *Actinide Partitioning and Transmutation Program Progress Report for Period July 1 to September 30, 1977*, ORNL TM-6174 (February 1978).

wastes. After the degradation products are removed, the acidified salt water containing the actinides (and sodium nitrate) can be recycled to the HA column. The degradation products can then be removed from the solvent, 2-ethylhexanol, simply by a sodium carbonate scrub. The solvent, long used in sol-gel processing, can be recycled directly.

Actinide recovery from HEPA filters and ash residues focuses on the use of hexanitrate ceric acid to dissolve plutonium dioxide. The ceric ion is produced electrolytically and appears to be reasonably effective. A single-leach stage has effected greater than 99% plutonium removals from HEPA waste and has reduced the alpha activity in conventional Rocky Flats Plant incinerator ash to ~600 nCi/g. Plutonium is removed from the electrolytic solutions by tributyl phosphate (TBP) extraction; cerium, americium, and curium are removed by CMP extraction.

4.2 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 and other chemicals (e.g., NH_4^+ , NO_3^-) from aqueous process and effluent streams 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 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 are also being developed that utilize denitrifying bacteria which adhere to particles of anthracite coal or sand. 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

A 10-cm-diam by 5-m-tall fluidized bioreactor has been installed to determine denitrification rates and compare these rate data with those of a smaller, 5-cm-diam by 5-m-tall fluidized bioreactor. These data will be used to design a mobile pilot plant which consists of dual 20-cm-diam by 10-m-tall fluidized bioreactors, as shown in Fig. 4.1. The 5- and 10-cm-diam data for a feed with a nitrate concentration of 235 g m^{-3} are very similar. The denitrification rates are 7.8 and 8.3 kg of N (NO_3^-) per day per m^3 respectively.

When a concentrated nitrate solution is to be processed, the volume of makeup water used for dilution can be significant; therefore, it would be most beneficial to use the very-low-nitrate effluent stream for dilution. A 90% recycle effluent-10% concentrated feed volume test was successfully performed. The resulting mixed feed had a nitrate concentration of 200 g m^{-3} . The denitrification rate was 10 kg of N (NO_3^-) per day per m^3 . It was found that the carbon-to-nitrogen feed ratio must be monitored carefully when operating in a recycle mode. A slight imbalance will increase the amount of nitrate or carbon in the column.

Task III: Isolation of Radioactive Metals, Using Microorganisms

Many operations in DOE and commercial nuclear processing facilities generate aqueous waste streams that contain trace quantities of dissolved heavy metals, including radionuclides. There are a number of physical and or chemical methods for isolating heavy metals from aqueous streams, including chemical precipitation, chemical oxidation or reduction, ion exchange, filtration or ultrafiltration, electrochemical treatment, and evaporative recovery. However, when the initial heavy-metal concentration is in the range of 10 to 100 g m^{-3} and a reduction to <1 g m^{-3} must be achieved, such methods may be ineffective or uneconomical. In these situations the sorption of dissolved metal species by microorganisms offers a means of achieving a reduction in the dissolved metal concentration to <1 g m^{-3} .

Seven monocultures and one mixed culture were tested for their ability to remove uranium from aqueous solution. The cultures were grown to the desired cell concentration, harvested, washed repeatedly with distilled water, and resuspended in solutions containing the desired concentrations of uranium. The rate of uranium sorption and the affinity of the cells for uranium seem quite promising

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Fig. 4.1. Fluidized denitrification bioreactor mobile pilot plant.

for process applicability. Figure 4.2 shows the removal of uranium from solution by washed, resuspended cells of *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa* as a function of time at 40°C. Note that the removal of uranium by *Pseudomonas aeruginosa* was extremely rapid; the uranium concentration was reduced from 83 g m⁻³ to <1 g m⁻³ in 20 min. In this experiment a distribution coefficient of 65,000 was achieved.

Fig. 4.2. Removal of uranium from aqueous solution by washed, resuspended cells of *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa*.

4.3 REMOVAL OF ORGANIC CONTAMINANTS AND TRITIUM FROM FUEL REPROCESSING EFFLUENT STREAMS

This two-task scouting study was begun and completed in FY 1977 in compliance with DOE directives. The study was concerned with the microbial removal of organic contaminants and tritium from aqueous process and effluent streams associated with the nuclear fuel cycle and DOE facilities.

Task I: Biological Removal of Organics

Certain organic compounds must be removed from aqueous process streams to prevent undesirable

interactions with radionuclides or interference with separation operations which would, in turn, reduce process efficiency. The compounds include solvents, extractants, oils, and their degradation products such as carboxylic acids and alcohols. Such dissolved or dispersed contaminants can reach concentrations >10 g m⁻³ in certain aqueous recycle streams. The task undertaken involved screening microbial cultures for utility in removing the organic contaminants and testing various bioreactor concepts with the cultures for process applicability. The cultures tested were Polybac, Phenobac, and Petrobac (obtained from Polybac Corporation, New York, N.Y.). These bacterial preparations were tested with synthetic aqueous wastes containing the organics at different concentrations, individually, and in various combinations. The experiments were conducted in agitated flasks, continuous flow stirred tank reactors (CSTRs), and tapered fluidized-bed bioreactors (TFBBRs). Results of the agitated flask tests are summarized in Table 4.1. The Polybac preparation degraded all of the organics to some degree and the soluble organics almost completely. In the continuous-flow bioreactor studies, the TFBBR achieved carbon degradation rates (on a reactor liquid-volume basis) that were five to ten times

Table 4.1. Organic carbon reduction by three bacterial systems on nuclear fuel cycle organics^a

Component	Carbon reduction (%)	Bacterial system
10% TBP ^b	50	Polybac
	14	Phenobac
	31	Petrobac
30% TBP in dodecane, used ^b	46	Polybac
	12	Phenobac
	42	Petrobac
10% TBP in dodecane, virgin ^b	38	Polybac
	19	Phenobac
	18	Petrobac
HDEHP ^b [di(2-ethylhexyl) phosphoric acid]	88	Polybac
	88	Phenobac
	16.4	Petrobac
0.8 M HDEHP in DHP ^b (diisopropylbenzene)	42	Polybac
	46	Phenobac
	35	Petrobac
DHP ^b	65	Polybac
	46	Phenobac
	50	Petrobac
Kerosene	76	Polybac
	49	Phenobac
	58	Petrobac
Vacuum-pump oil	78	Polybac
	0	Phenobac
	0	Petrobac

^aConditions: 5-day incubation at 30°C, pH 6.8 buffer, 150-rpm shaker, starting concentration of organic = 500 µg/cm³, ~200 µg/cm³, total liquid volume per flask = 100 cm³, bacterial seed, 0.50-cm³ solution made by dissolving 5 g of dry bacterial seed in 50 cm³ of warm water.

^bComponents were obtained from T. A. Kappelmann, Experimental Engineering Section, Chemical Technology Division, Oak Ridge National Laboratory.

greater than those achieved by the CSTR, reaching rates of 10 kg of organic carbon per m³ of reactor volume per day. In some cases, 90% of the organic carbon was removed in a single pass through the TFBBR. Thus the removal of certain organic contaminants, using continuous-flow bioreactors, was shown to be technically feasible.

Task II: Biological Fractionation of Hydrogen Isotopes

Tritium contamination of aqueous streams associated with nuclear reactor operation and fuel reprocessing poses an environmental hazard. Several chemical and physical methods for tritium separation are being studied. The report of a marine bacterium (strain G4A) that effected a hydrogen-deuterium fractionation stimulated interest in the possible use of a microbial process to concentrate and remove tritium. The goal of this task was to examine the relative capabilities of several species of microorganisms for separating hydrogen and tritium and to determine whether additional efforts should be directed toward the development of a separation process based on microbial action.

In addition to strain G4A, other species were chosen for study on the basis of: (1) maximum utilization of environmental water as a source of hydrogen and (2) ability to produce H₂. The microorganisms were grown in medium containing tritiated water under conditions for optimal growth and/or H₂ production. The distribution of tritium between

medium, cells, and H₂ was then determined. The results are summarized in Table 4.2. The distribution coefficient, $[(\text{Ci/g of hydrogen in cells (or hydrogen in gas)}) / (\text{Ci/g of hydrogen in medium})]$, is indicative of the degree of discrimination for, or against, tritium during growth and metabolism. A distribution coefficient less than unity means that the cells discriminate against tritium. In each case studied, discrimination against tritium occurred during growth of microbial cells and during H₂ evolution by *Clostridium pasteurianum*. This observation is consistent with numerous literature reports of discrimination against deuterium and tritium by intact biological systems and isolated enzymes. The nature and degree of this discrimination in the microbial systems studied preclude, at this time, consideration of this phenomenon for tritium removal by a bioprocess scheme.

4.4 FIXATION OF WASTES IN CONCRETES

The purpose of this program is twofold: (1) to determine and characterize the technological feasibility, applicability, economic advantages, and limitations of the use of cementitious materials for isolating high-specific-activity waste, and (2) to develop durable cementitious mixtures with suitable properties for the solidification of specific liquid and solid radioactive wastes.

During the past year, studies were completed on the fixation in concrete of radioactive iodine (¹²⁹I, $t_{1/2} = 1.7 \times 10^7$ years) from concentrated nitric acid

Table 4.2. Distribution coefficients for cellular and gaseous tritium from microorganisms cultured in tritiated water

Organism	Growth conditions	Initial tritium concentration in growth medium (mCi/liter)	Distribution coefficient	
			Cells ^a	H ₂ ^b
Strain G4A(b)	Aerobic, complex organic medium	2	0.12	
<i>Anaerobes</i> <i>flos-aque</i>	Photosynthetic, nitrogen-fixing, mineral salts medium	2	0.28 ^c	e
			0.28 ^d	
		10	0.52 ^c	e
			0.51 ^d	
<i>Thiobacillus ferro-oxidans</i>	Aerobic, mineral salts medium	10	0.002	
<i>Clostridium pasteurianum</i>	Anaerobic, nitrogen-fixing, mineral salts medium, plus glucose	10	0.06	0.07

^aDistribution coefficient = (Ci/g of hydrogen in cells)/(Ci/g of hydrogen in medium).

^bDistribution coefficient = (Ci/g of hydrogen in gas)/(Ci/g of hydrogen in medium).

^cGrowth phase.

^dNitrogen-fixing cells deprived of N₂ by flushing with argon; H₂ evolution phase.

^eInsufficient for analysis.

(the Iodox process) and mercuric nitrate scrubber solutions. The iodine products from these processes are converted to barium iodate and mixed with type I portland cement and water to form a concrete. The Iodox product is converted to barium iodate by the addition of barium hydroxide. In the case of the mercuric nitrate process, a bench-scale demonstration indicated the feasibility of a two-step process:

It was found that the mercuric oxide and sodium hydroxide by-products could be recycled, thus preventing the loss of any iodine in low-level waste effluents to the biosphere.

Leach studies were made to determine the rate of iodine release into various leachants from concretes containing 15 wt % iodine as barium iodate and 5 wt % excess barium hydroxide. The leach rates were diffusion controlled, with effective diffusivities ranging from 1×10^{-10} cm²/sec for distilled water to 4×10^{-15} cm²/sec for water from a local spring. Tap water, seawater, and brine from various locales showed intermediate values.

Studies were initiated to assess the problems associated with the incorporation of high-specific-activity waste in concrete. Preliminary scoping experiments were made to determine the immediate effect of high pressure and temperature on the setting of wet concrete by subjecting mixtures containing type I or type III portland cement to a pressure of 1600 psi and a temperature of 250°C for 24 hr. The resulting specimens were very hard, homogeneous solids with no apparent spallation or surface corrosion. Each of the wet mixtures had the following composition: 44 wt % cement, 10 wt % Kingston fly ash, 10 wt % Indian red clay, 20 wt % water, and a 16 wt % mixture of hydrated oxides of aluminum and lead.

In the coming year a more complete investigation will be made on the effect of temperature and pressure on cement-clay-sludge mixtures. The sludge will simulate the neutralized high-level Purex waste currently stored at the Nuclear Fuel Services plant at West Valley, New York.

4.5 CEMENT GROUTS FOR WASTE SLUDGE DISPOSAL BY HYDROFRACTURE

Plans are in progress for the construction of a new hydrofracture facility for the disposal of all inter-

mediate-level liquid wastes generated at ORNL. In addition, the Gunit tanks currently used for waste storage will be emptied and retired. The ~400,000 gal of sludge contained in these tanks will be slurried with water, mixed to form a cementitious grout, and disposed of by hydraulic fracturing at the new facility. A program was activated in August 1977 to develop the grout mixes that will be used for the disposal of this sludge and to gather data which will assist in the design of the dry-solids blending system.

A Jenike and Johanson Flowfactor tester and consolidation bench was purchased and has been installed. Data from this device will aid in determining the wall angle and the size of the discharge outlet required for the solids storage bins at the new hydrofracture facility. Studies were initiated to determine the effect of the various dry-mix components on the flow behavior of the final mixture.

Work is in progress on the preparation of simulated sludges that will be suitable for use in future hydrofracture grout development studies. Nitrate solutions having metallic components in approximately the same ratio as for some of the actual radioactive sludges were precipitated with sodium hydroxide to a pH of 9.5. Initial results have shown that the rheological properties of grouts made from these simulated sludges are dependent on the amount of soluble components remaining in the sludge. Current studies are examining methods of washing and drying simulated sludge in order to match as closely as possible the chemical and physical values of the actual waste material.

Results from exploratory tests indicated the possibility of the disposal of solid waste via hydrofracture. An acceptable grout was made by mixing 5 lb of the standard dry mix per gallon of slurry (10 wt % shredded solid waste in 0.1 N NaOH). The solid waste was composed of 50 wt % blotter paper, 30 wt % plastic gloves, and 20 wt % cloth shoe scuffs. The materials were ground so that the largest dimension of the resulting particles was less than a few millimeters. As a consequence of this brief investigation, funding was made available for additional studies to be conducted during the coming year.

4.6 CEMENT AND CONCRETE TECHNOLOGY

The Cement and Concrete Technology Program is supported by the Office of Waste Isolation (OWI) Borehole Plugging Program. The objective of this program is to develop the expertise required to assist

OWI in devising and testing cementitious mixtures suitable for plugging holes that may represent a hazard to a repository for radioactive waste. The primary characteristics that these solidified mixtures must demonstrate are high density, low permeability, and long-term durability. Sufficient data must be collected to allow tailored mixtures to be formulated in the event that it is required to match the characteristics of the wall rock. The dominant theme throughout this program is the reliability of the physical and chemical measurements and the quality control that is available or can be exercised on the ingredients and mixing techniques that are used to make the plug material. During the past year, studies emphasized methods and procedures for accurately measuring the permeability, compressive strength, and thermal conductivity of cementitious mixtures as well as natural materials that may be found in the wall rock or incorporated aggregate.

The permeability of borehole plugs to fluid flow is one of the major properties of interest. Measuring the permeability of cementitious materials to water is difficult and extremely time-consuming. In addition, cement continues to hydrate in the presence of water, which causes the permeability to decrease with time. To facilitate more rapid screening of possible plugging mixtures, procedures were investigated for measuring the permeability of solids to gases. Klinkenberg³ has demonstrated that, by measuring the permeability for a gas at several pressures and then extrapolating the results to infinite pressure, a value is obtained that is equivalent to the permeability of the specimen to a fluid.

Studies are in progress using a Hassler cell⁴ and a device developed by Pennsylvania State University to determine the best procedure for measuring the permeability of cementitious mixtures to nitrogen gas. Initial results have shown that specimen preparation and drying are very critical in the procedure. The permeability of specimens cured 28 days in saturated limewater and containing 57 wt % Marquette type I portland cement, 10 wt % Kingston fly ash, and 33 wt % water varied by three orders of magnitude, depending on the drying technique used with the specimen. The permeability values ranged from 8×10^{-11} darcy after simple blot drying to 1.3×10^{-5} darcy after vacuum drying for 24 hr.

Compressive strength is one of the more common measurements made on hardened concrete, since

many of the desirable characteristics of concrete are at least qualitatively related to its strength. Studies were made to determine the most precise method for measuring the compressive strength. The procedure developed uses 2-in. cubes that are cast from the same mix and then coated with a plastic film to prevent any water loss during curing. The procedure yields results with less than a 3% standard deviation.

A laboratory was established to accommodate a program devoted to the development of techniques and methods for measuring the thermophysical properties of cementitious and natural materials. Specimen preparation equipment and a Dynatech TCFCM thermal conductivity instrument (divided bar with guard heater) were installed. Procedures were developed and are being used to measure the thermal conductivities of materials such as the standard rocks supplied by the U.S. Bureau of Mines,⁵ shales, salt, concretes, and saltcretes. The precision of the measurements is dependent primarily on specimen surface preparation. For hard materials such as Pyrex glass, a precision of $\pm 2.5\%$ is easily obtainable at temperatures up to 300°C. However, for natural materials with more friable surfaces, such as shales and salt, the precision is approximately $\pm 10\%$. As all these test procedures are developed, they will be used to measure the characteristics of specimens prepared for parametric studies. These studies will determine the effect of various pozzolans on cement-pozzolan concretes and saltcretes.

4.7 UPDATING OF THE ORIGIN COMPUTER CODE

The effort to update the ORIGIN computer code and its associated data bases, which began during FY 1976, continued during this report period. The principal goal is to place the ORIGIN code and data bases on as firm a theoretical basis as possible. This involves modification of the original ORIGIN code to more accurately reflect the neutronic behavior of the actinides during irradiation; calculation of effective cross sections, using more sophisticated reactor physics codes;^{6,7} and updating the other data libraries.

5. W. W. Krech, F. A. Henderson, and K. E. Hjelmstad, "A Standard Rock Suite for Rapid Excavation Research," U.S. Bur. Mines Rep. Invest. 7865 (1974).

6. N. M. Greene, J. L. Lucius, J. M. Petric, 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).

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

3. L. J. Klinkenberg, "The Permeability of Porous Media to Liquids and Gases," *Amer. Petr. Inst. Drilling Production Practice*, American Petroleum Institute, 1941, pp. 200-213.

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

The multigroup cross-section libraries prepared during the last report period were used during this report period to perform neutron energy spectrum and reactor depletion calculations for both a PWR and a BWR in which the self-generated plutonium is assumed to be recycled. Axial neutron spectrum calculations were performed to determine the degree to which plenum springs and fuel assembly end pieces become activated. These calculations, when coupled with the uranium-enriched PWR and BWR calculations performed during the last report period, complete the reactor physics studies for LWRs operating on the uranium-plutonium fuel cycle (i.e., the U-Pu-cycle LWRs). Literature searches were also conducted to determine: (1) typical calculated discharge compositions for U-Pu-cycle PWRs and BWRs for use as a comparative basis; (2) the structural metal type, mass, and composition (including minor constituents) of the fuel assemblies typical for BWRs and PWRs; and (3) the initial elemental (including minor constituents) and isotopic compositions of UO_2 and mixed-oxide fuel pellets. These results were used to develop a new set of ORIGEN reactor models for U-Pu-cycle LWRs. The new reactor models, as well as the reactor physics calculations and information developed during the literature searches, are being documented and will be published by the end of FY 1978.

Reactor physics studies have also been completed for a PWR fueled by denatured ^{235}U (12 wt % enriched) in thorium. Similar calculations are under way for PWRs fueled by plutonium-enriched thorium fuel and thorium fuel enriched by a mixture of denatured ^{235}U and denatured ^{238}U .

Additional ORIGEN update activities planned for the next report period include: (1) documentation of the updated decay and photon libraries prepared during this report period, (2) documentation of the thorium-based fuel PWR models, (3) generation and documentation of a bremsstrahlung photon library, (4) initiating and completing the calculation of updated LMFBR models for both uranium-plutonium and uranium-thorium fuel cycles, and (5) initiating documentation of the updated ORIGEN computer code itself.

4.8 PROJECTIONS OF RADIOACTIVE WASTES FROM THE NUCLEAR FUEL CYCLE

The primary emphasis during this report period was on updating and documenting the basis used for waste projections. A projection of the spent fuel to be

discharged in the United States was also published for use in the design of the Spent Unreprocessed Fuel Facility (SURFF). The projection was based on the most recent nuclear power forecast by DOE's Office of Assistant Administrator for Planning, Analysis, and Evaluation through the year 2000 and on a forecast by Battelle Pacific Northwest Laboratories thereafter. Present spent fuel inventory and associated characteristics were based on a study made by the Nuclear Assurance Corporation.⁸ Nuclear power growth was 65.8, 194.4, 379.7, 493.7, 552.8, and 543.4 GW(e) of installed capacity in the years 1980, 1990, 2000, 2010, 2020, and 2030 respectively. PWRs predominated over BWRs at a 2:1 ratio with no penetration of advanced reactors. Nuclear power growth after the year 2000 was based on exhausting 3.7 million short tons of U_3O_8 with an enrichment tails assay of 0.1% ^{235}U .

A summary of the U.S. spent fuel projections is given in Table 4.3. In addition, the projections included estimates of the spent fuel inventory at SURFF, assuming that fuel was shipped to SURFF (1) five years after discharge from reactors and (2) ten years after discharge. Accumulations of individual isotopes in the spent fuels were also calculated.

4.9 ASSISTANCE TO OFFICE OF WASTE ISOLATION

In March 1977, OWI authorized the Pilot Plant Section to undertake the Transportation-Logistics Systems Analysis Study as a part of the National Waste Terminal Storage Program. The objective of the transportation-logistics study is to ensure the availability of a viable system for transporting nuclear waste to a federal repository in 1985. Types of waste to be considered are spent fuel, transuranium (TRU) waste, high-level waste, intermediate-level waste, and cladding hulls, with initial emphasis being placed on spent fuel and low-level fuel TRU waste.

To meet the stated objective, a scoping study was conducted to identify problem areas that could, if not recognized and solved, restrict the movement of waste in 1985. The need for rapid development of background information for the study necessitated

8. C. W. Alexander, C. W. Kee, A. G. Croff, and J. O. Blomeke, *Projections of Spent Fuel to Be Discharged by the U.S. Nuclear Power Industry*, ORNL TM-6028 (October 1977).

9. R. M. Fleischman, Battelle Pacific Northwest Laboratories, personal communication to J. O. Blomeke, June 27, 1977.

10. C. B. Woodhull, *U.S. LWR Spent Fuel Inventory and Projection*, Y OWI-SUR-77 42500 (June 1977).

Table 1. Projected accumulation of spent fuel assemblies in the United States

Calendar year	Annual addition						Accumulation through end of year					
	Number of discharged assemblies		Volume (10^3 m^3)	Actinide mass (MT ^a)	Activity (MCi)	Thermal power (MW)	Number of discharged assemblies		Volume (10^3 m^3)	Actinide mass (MT ^a)	Activity (MCi)	Thermal power (MW)
	BWR	PWR					BWR	PWR				
1980	2,830	1,860	0.6	1,340	6,900	30	16,000	8,900	3	6,800	10,960	46
1990	7,550	5,720	1.7	3,890	20,600	89	65,900	46,300	14	32,400	38,500	156
2000	15,300	11,000	3.4	7,620	40,600	177	182,000	131,000	40	90,900	86,400	342
2010	20,500	13,800	4.3	9,800	53,700	233	363,000	259,000	80	180,000	134,000	517
2020	21,700	14,700	4.6	10,400	57,000	247	577,000	406,000	125	284,000	167,000	632
2030	23,500	15,200	4.9	11,000	59,000	256	807,000	560,000	174	393,000	192,000	723
2031	23,600	15,200	4.9	11,000	59,100	257	831,000	575,000	179	404,000	194,000	731
Decay time after 2031 AD (years)												
	100						831,000	575,000	179	404,000	10,400	93
	1,000						831,000	575,000	179	404,000	652	21
	10,000						831,000	575,000	179	404,000	180	5
	100,000						831,000	575,000	179	404,000	21	0
	1,000,000						831,000	575,000	179	404,000	8	0

^aMT = metric ton.

the development of an aggressive plan to organize and utilize the expertise of a group of people already knowledgeable in the field of radioactive materials transport and to extract information through a series of meetings and reports. Four organizations that appeared to best meet the programmatic needs were chosen, and each was awarded a subcontract to supply information based on their particular area of expertise. The subcontractors were Nuclear Assurance Corporation, Rockwell International, Rocky Flats Plant, Battelle Pacific Northwest Laboratories, and Allied-General Nuclear Services. Reports were prepared to document the information developed for OWI.¹¹⁻¹³ The most important problem issues were reviewed and selected based on their relevance to the OWI transportation-logistics study. These problems involve regulatory uncertainties, reluctance of the railroad to transport nuclear materials, risk assessment, cask-facility interface requirements, low-level TRU waste shipping containers, security requirements, cask ownership, and water transport.

ORNL was asked by OWI to develop a comprehensive program plan; update it as required, and coordinate the work performed by outside contractors in support of the plan. The program plan, issued

in March 1978,¹⁴ addresses all important transportation-related action items and how they interact in order to ensure an integrated approach to the problem.

To facilitate this overall approach and to provide for short- and long-term waste management, logistics models have been developed which will enable ORNL to determine shipping schedules, optimize routes, determine the most probable transportation modes, minimize costs, and study personnel exposure. In general, the models^{15,16} are designed to determine the most economic waste shipping policies within the given operational constraints, relative to the operation of shipping and receiving facilities. Such information will permit OWI to specify waste receiving rates at various facilities in order to balance work loads, to evaluate surge capacity requirements, and to estimate projected shipping cask fleet sizes. The programs are tailored to utilize information on the types of waste being received, capacity and location of repositories, location of waste generating facilities, shipping distances, time required to make a shipment, equipment availability, aboveground storage capacities and locations, projected waste throughput rates, and so forth.

11. R. E. Best et al., *Capabilities of U.S. Domestic Transportation Systems for the Shipment of Radioactive Wastes*, Y. OWI SUB-77 22330, Nuclear Assurance Corporation (September 1977).

12. R. J. Merlini et al., *Low-Level Waste Systems Analysis*, RFP-2728, Rockwell International, Atomic International Division, Rocky Flats Plant (in preparation).

13. R. W. Peterson et al., *Current Status and Future Considerations for a Transportation System for Spent Fuel and Radioactive Wastes*, Y. OWI SUB-77 42513, Allied-General Nuclear Services (February 1978).

14. L. B. Shappert, D. S. Joy, and M. M. Heiskell, *Radioactive Waste Transportation Systems Analysis and Program Plan*, ORNL-5362 (March 1978).

15. D. S. Joy and B. D. Holcomb, *Logistics Models for the Transportation of Radioactive Waste and Spent Fuel*, ORNL TM-6192 (in preparation).

16. W. P. Huxtable, *A Complete Program for Estimating Packaging and Costs of Radwaste Transportation (PACRAT): Program Documentation and Users' Manual*, ORNL TM-6119 (in preparation).

5. Basic Science and Technology

5.1 SEPARATIONS SCIENCES

New Separations Agents

Macrocyclic, size-specific coordinating compounds continue to be of interest, particularly when used in combination with other extractants such as organic-phase cation exchangers. A total of 15 new macrocycles have been obtained. These include seven substituted crown ethers, two sulfur-containing crown ethers, and three crown ethers with functional side arms. These compounds are being screened for desirable extraction characteristics. One class of macrocyclic compounds, called porphyrins, has been of special interest. A tetraphenyl-substituted porphyrin was tested as an extractant for several metal ions under a variety of conditions, but no useful extraction has yet been found.

Of the several fluorinated β -diketones examined, the one that is most promising is 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (HFDMOD). This compound is being screened, both in synergistic combination with tri-*n*-octylphosphine oxide (TOPO) and alone, for extraction of a variety of metal ions. Figure 5.1 shows the extraction of some of these ions by 0.10 *M* HFDMOD plus 0.05 *M* TOPO in dodecane as a function of aqueous-phase pH.

Separation and Analysis of Radionuclides from Uranium Ore Processing Streams

Elsewhere in the Laboratory,¹ processes have been developed to recover the uranium that occurs naturally in phosphate rock from the process streams in phosphoric acid production and fertilizer manufacture. These processes are being installed both for economic reasons and to remove the uranium from fertilizer materials.² A need exists for simple and reliable methods for separating natural uranium and its daughters from these phosphatic materials and for obtaining an accurate assay for these radionuclides.

A combination of solvent extraction separation and liquid scintillation alpha counting has been used to give excellent results in uranium and thorium analysis on a variety of phosphatic materials, including phosphate rock (apatite), phosphoric acid solutions of various kinds, and several types of phosphate-containing fertilizers. Samples are placed in solution in nitric and perchloric acids (with hydrofluoric acid added if necessary), saturated with aluminum nitrate to suppress phosphate interference with the extraction, and extracted with TOPO in toluene. The uranium and thorium are then stripped from the TOPO solution, extracted separately into extractive scintillators specific for each element, and determined by liquid scintillation alpha spectrometry.

This procedure allows the recovery of greater than 99% of the uranium and determinations with an overall accuracy of $\pm 2.5\%$ at the 50-ppm level. Reproducibility on the same sample is typically better than $\pm 0.5\%$. Thorium analyses are not quite as consistent, but the reproducibility is $\pm 3\%$ at the same activity level. Lower limits for detection based on a 50-min count and a typical background count rate of 0.01 count/min are 9 parts/ 10^4 for ^{238}U , 5 parts/ 10^7 for ^{232}Th , and 3 parts/ 10^{12} for ^{230}Th . One paper on the analysis of uranium in phosphate fertilizers and other phosphatic materials is in press;³ another, "A Solvent Extraction-Liquid Scintillation Method for Assay of Uranium and Thorium in Phosphate-Containing Material," is in manuscript form.

1. Chemistry Division, ORNL.

2. D. S. Flett, "Solvent Extraction in Hydrometallurgy," *Chem. Ind. (London)* 3, 706 (1977).

3. E. J. Bouwer, J. W. McKivern, and W. J. McDowell, "Uranium Assay of Phosphate Fertilizers and Other Phosphatic Material," *Health Phys.* 34, 345-52 (1978).

Fig. 5.1. Extraction of various ions from a chloride system with the fluorinated β -diketone HFDMD plus TOPO in dodecane.

Separation of Alpha Emitters from Fuel Reprocessing Waste

Attention has been focused on two carbamoyl-methylphosphonates (CMPs), dihexyl[(diethylcarbamoyl)methyl]phosphonate (DHDECMP) and di-(2-ethylhexyl)[(diethylcarbamoyl)methyl]phosphonate (DEHDECMP), in this reporting period. The equilibria associated with their extraction of americium, europium, and lanthanum from nitric acid-sodium nitrate solutions have been studied. Part of this information is reported in Sect. 5.1,

"Distribution Equilibria." Further studies of the optimum aliphatic-aromatic diluent mixture, using mixed dodecane-xylene, indicate that 15 vol % of the aromatic component gives the maximum resistance to third-phase formation with a minimum lowering of extraction coefficient. An important concern in the process application of the CMPs is the extent of extractant degradation produced by heat, acid, and radiation, singly or in combination. Studies indicate that the primary impurity arising from acid hydrolysis is the monoacid alkyl-hydrogen-[(di-alkyl-carbamoyl)methyl]phosphonate.⁴ The degradation products resulting from large doses of gamma radiation from a ⁶⁰Co source are more varied but also include acidic materials. Titration tests indicate either a dibasic acid or two acids of different strengths. A good possibility appears to be a diacid alkyl-dihydrogenphosphonate. All the organic-phase-soluble acid materials prevent effective stripping of the actinides from the organic phase by water; however, the amounts of the acidic degradation products produced by radiation do not appear sufficient to pose a problem in the process. Hydrolysis by nitric acid becomes a point of concern above approximately 3.5 M, and the combination of high acid concentrations (>4 M) and radiation should be examined as a possible threat to the process stability of these reagents.

Waste Stream Processing Studies

The purpose of this program is to provide basic technical information that will be required for the satisfactory treatment of the actinide elements in nuclear fuel reprocessing plants. The efforts are therefore directed toward the study of specific problems involving actinide interactions in order to supply vital information needed for developing feasible process methods. In studies to date, three principal types of interactions have been identified which can promote actinide losses by precipitate formation, promotion of interfacial solids and emulsions during extraction and stripping operations, and the formation of actinide species with undesirable extraction or stripping characteristics. These interactions involve (1) instabilities and solids

4. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5295, pp. 31-32.

5. C. T. Bahner, R. R. Shoun, and W. J. McDowell, *Impurities That Cause Difficulty in Stripping Actinides from Commercial Tetraalkylcarbamoylmethylphosphonates*, ORNL TM-5878 (September 1977).

formation in reactor-fuel reprocessing solutions, (2) metal-ion complexation with tributyl phosphate (TBP) solvent degradation products, and (3) plutonium polymerization.

Continued studies of the formation of precipitates in fuel reprocessing solutions have been primarily concerned with the solubility behavior of molybdenum and the formation of uranium- and thorium-molybdenum compounds. The dissolution of molybdenum in HNO_3 frequently results in the formation of solids (MoO_3 and $\text{MoO}_3 \cdot \text{H}_2\text{O}$) which have lower solubilities than that of the original metal. It was found that at certain conditions, oxide formation is suppressed and metastable solutions of molybdenum can be prepared at four to five times the metal concentration observed for stable solutions. Investigations of solids formation due to uranium-molybdenum compound formation indicate that this will not be a significant problem in fuel reprocessing solutions at most conditions of interest. Compound formation can occur, however, at low-acid conditions (1 M HNO_3), resulting in precipitates that can be tentatively identified as a hydrated form of uranyl molybdate. Initial experiments involving thorium molybdate compound formation indicate that this material will be a significant problem. Precipitates form at temperatures as low as 40°C at low-acid conditions, and the compound precipitates from 7 M HNO_3 at high temperatures and high thorium concentrations.

Acceptable plutonium recoveries are not generally obtained in low-acid uranium-plutonium costripping experiments when loaded solvents are exposed to radiation levels that produce solvent degradation products. It was demonstrated by spectrophotometric analysis of the stripped organic phase that these losses result from plutonium complexation with solvent degradation products, rather than from other loss mechanisms that can occur at low-acid conditions. In conjunction with this study, standard spectra were determined for Pu(IV) and U(VI) complexes of TBP, dibutylphosphoric acid (DBP), and monobutylphosphoric acid (MBP) in 30% TBP-*n*-dodecane (NDD); additionally, mathematical techniques were developed to determine the relative concentrations of the plutonium-MBP complexes in TBP-NDD. Since hot-cell stripping studies demonstrated that plutonium complexation by solvent degradation products can vary significantly with the uranium and zirconium concentrations in the organic phase, studies were initiated to determine the relative complex strengths of plutonium, uranium, thorium, and zirconium for DBP

and MBP as a function of acid concentration. Work to date has shown that high uranium concentrations greatly suppress plutonium complexation with DBP, but significant plutonium complexation with MBP occurs even at uranium saturation of the organic phase. High thorium concentrations have similar effects on plutonium complexations; however, thorium is not as effective as uranium in suppressing plutonium-DBP complex formation. The opposite effect was observed for zirconium-plutonium mixtures; plutonium complexation with DBP is not suppressed with zirconium, while plutonium complexation with MBP is suppressed significantly.

Zirconium and zirconium-plutonium complexes of MBP have limited solubilities in 30% TBP-NDD. Interfacial solids occur at fairly low concentrations (<0.004 M), and such complexes promote severe emulsions at higher concentrations. Spectrophotometric analyses of MBP complexes that contain zirconium indicate that polymerization of the complex species occurs slowly, even at relatively high strip-acid concentrations (0.2 to 0.4 M).

Studies of plutonium polymerization have shown that, when polymer is formed during uranium-plutonium costripping operations, it extracts almost entirely into the organic phase. Following extraction, the plutonium precipitates either partially or completely. Polymer that does not precipitate cannot be stripped out of the organic phase, and polymer that does precipitate promotes severe aqueous-organic emulsions. As little as 0.05 mg of polymer per liter of solution will seriously disrupt stripping operations.

Ash Removal from Solvent-Refined Coal

Partial wetting and scavenging by molten salts continues to be the separation method of choice for removing the micron- and submicron-sized particles remaining in the oil from the slurry-hydrogenation of solvent-refined coal (SRC). It appears desirable (and perhaps necessary) to operate with salts or salt mixtures that melt below the approximately 500°C temperature at which the coal is slurry-hydrogenated. Several salt mixtures that melt below this limit have been identified and will be tested. The lithium-sodium-potassium chloride mixture has already been demonstrated as effective in de-ashing the unfiltered SRC oil but is relatively expensive (because of the lithium content); hence an apparatus has been constructed for conducting tests with very small amounts of the salt mixture and separating the scavenged ash while the mixture is hot.

Physical Separations

The migration of alpha-active material through high-efficiency air filters in series in amounts larger than and in patterns different from those expected from the rated filter efficiency has been observed in three separate air filtration systems in actual use.^{6,7} Evidence has now been obtained which indicates that under some conditions alpha aggregate transport does not occur. Observations were made of a new batch of filters when attempting to recheck some data. Although the filters were supposed to be two batches of the same type of material, one gave rise to alpha transport, while the other did not. Extensive analyses of these two types of filters have shown only one difference. One contains approximately 1 to 4% zinc, while the other contains none. The addition of zinc to a sand lowers the fusion temperature when the sand is used for the production of glass fibers. These data suggest that the presence of zinc in the glass melt used to make HEPA filter media creates a condition in the glass fiber which allows alpha-active material transport, while its absence permits a condition that prevents this transport. Virtually all commercial high-efficiency filters contain 1 to 4% zinc in the glass mix, and our data show that such filters release more alpha activity than that expected from the rated filter efficiency (Fig. 5.2). Our latest findings suggest that it may be possible to manufacture HEPA filters that do not show the aggregate recoil transport mechanism.

Distribution Equilibria

Extraction of weak and unusual acids by basic organic compounds. A program of systematic and fundamental investigation of the extraction of acids other than the common mineral acids (nitric, hydrochloric, and sulfuric) by basic extractants such as amines, alkyl phosphates, and phosphine oxides is under way. Information from this program is expected to be of particular value in separations connected with environmental protection problems of coal conversion. Figure 5.3 shows the distribution of acetic acid between 1.0 M sodium acetate and

Fig. 5.2. Penetration of high-efficiency filters. Dashed lines represent calculated values; solid lines, experimental values.

0.1 M toluene solutions of three long-chain amines: 1-nonyldecyl, didecyl, and trioctyl. The shapes and initial slopes of these curves suggest that the amine acetate in the organic phase is monomeric with the tertiary amine and is associated to approximately a dimer and a tetramer, respectively, with the secondary and primary amines. Examination of these organic phases by vapor-phase osmometry indicates aggregation numbers of 2.4, 1.3, and 1.0 for the primary, secondary, and tertiary amine acetates respectively. Titration data for the same three amines with thiocyanic acid show an apparent different order of base strength for the amines: primary > secondary > tertiary with acetate, and secondary >

6. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5295, p. 34.

7. M. T. Ryan, W. J. McDowell, and G. N. Case, *Observations of the Distribution and Nature of Alpha-Active Particulate Material in a HEPA Filter Used for Plutonium-Containing Dust*, ORNL TM-5765 (February 1977).

Fig. 5.3. Extraction of acetic acid by amines.

primary > tertiary with thiocyanate. Data further indicate that amine thiocyanates exist as trimers in the organic phase with the primary and tertiary amines and as dimers and trimers with the secondary amine.

Crown ethers as size-specific extraction synergists. Investigation continues into the finding reported last year⁸ that the crown ethers may be most useful in solvent extraction as synergists. When mixed with other extractants, these ethers exhibit a synergistic effect specifically for ions that fit the hole in the crown ether. Figure 5.4 shows the extraction of potassium by 0.125 M di(2-ethylhexyl)phosphoric acid (HDEHP), by 0.25 M dicyclohexyl-18-crown-6 (DC18C6), and by a mixture of 0.125 M HDEHP and 0.25 M DC18C6 in benzene. The maximum synergistic factor [$D_K(\text{HDEHP}) + \text{DC18C6} / D_K(\text{HDEHP}) + D_K(\text{DC18C6})$] is about 40, and the separation factor (D_K/D_{Na}) is about 47. Typically, HDEHP extracts sodium more effectively than potassium.

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

9. W. J. McDowell, "Equilibria in the System: Di(2-ethylhexyl) Phosphoric Acid Benzene Water Alkali (Hydroxide, Nitrate)," *J. Inorg. Nucl. Chem.* 33, 1067-79 (1971).

Fig. 5.4. Synergistic extraction of potassium from 0.5 M NaNO₃ by mixed HDEHP and DC18C6 in benzene compared with extraction by each compound singly.

Since the slope of $\log D_K$ vs pH is less than unity and D_K increases at very low pH, it appears that the potassium is being extracted partially as KNO₃, with the HDEHP serving as a means of solvating the nitrate anion in the organic phase. Alcohols and phenols have been previously shown to serve this function.^{8,10}

Bidentate extractants for trivalent actinides. In order to allow meaningful interpretation of the reagent dependence studies previously reported,^{8,11} the loading of 0.5 M DEHDECMP in diethylbenzene (DEB) was studied with europium as a stand-in for americium. The slope of the curve $\log [Eu]_{org}$ vs $\log [Eu]_{aq}$ is 1 in the initial nonloaded portion. The plateau of the loading curve indicates three molecules of DEHDECMP per molecule of Eu(NO₃)₃ extracted. These data are consistent with the previous indications⁸ that approximately three extractant molecules are associated with each

10. W. J. McDowell and R. R. Shoun, "An Evaluation of Crown Compounds in Solvent Extraction of Metals," presented at the International Solvent Extraction Conference 1977, Toronto, Canada, September 1977 (to be published in *Proceedings*).

11. R. R. Shoun, W. J. McDowell, and Boyd Weaver, "Bidentate Organophosphorus Compounds as Extractants from Acidic Waste Solutions: A Comparative and Systematic Study," presented at the International Solvent Extraction Conference 1977, Toronto, Canada, September 1977 (to be published in *Proceedings*).

extracted $\text{Am}(\text{NO}_3)_3$. For the same organic extractant (DEHDECMP 0.5 M in DEB), the dependence of D_{Am} on $[\text{NO}_3^-]$, at constant 0.1 M HNO_3 , but uncorrected for changes in nitric acid activity, varied from about 1.5 power at low nitrate concentrations (between 0.1 and 1.0 M) to third power at higher nitrate concentrations (between 4.0 and 6.9 M). Increasing acid concentration at constant ionic strength ($\text{HNO}_3 + \text{NaNO}_3$) gave a decreasing D_{Am} , which was expected from the competition of the nitric acid for positions on the extractant molecule.

Extraction of alkali and alkaline earths by fluorinated β -diketones and trioctylphosphine oxide mixtures. Experiments are continuing that are designed to provide an understanding of the extraction of the alkali and alkaline-earth elements by HFDMOD (0.05 M) in synergistic combination with TOPO (0.05 M). The pH dependence curves for extraction of the alkali ions from chloride solution into a dodecane solution of the synergistic mixture are first power for lithium and 0.4 to 0.6 power for the other alkalis. We have no explanation for the less-than-unity power dependence of D_i on pH but suspect that the metals are being extracted both as cations and as the neutral MCl species.

Computer-Searchable Separations Systems Data Base

Attempts over the past few years to use standard computer-searchable data bases with conventional indexing have shown that they are poorly designed to retrieve the type of information needed for separations systems. We have therefore begun compilation of a data base designed to contain reference material related to separations systems. This specialized data base will allow the retrieval of information not only by standard author, title, place, and date-of-publication entries, but also by the substances separated (both recovered and rejected), the separations agent used, the matrix from which the separation is effected, and the type of subject matter presented in the reference. An abstract of each entry is included.

Tritium Sorption Studies

Molten lithium appears to be the most promising blanket material for breeding tritium in fusion reactors. One of the techniques being considered for the recovery of tritium from liquid lithium is

sorption on a hydrogen-gettering metal. Tritium sorption from molten lithium and potassium (a potential blanket coolant) has been studied in a batch contactor at temperatures of 250 to 400°C, using metal sorbent samples of yttrium and zirconium. Yttrium has shown significant removal rates from both molten lithium and potassium;^{12,13} however, the sorption rates from potassium appear to be too slow for a practical recovery process. At 400°C, an yttrium sample (weight, 3.55 g; surface area, 13.5 cm²) reduced the concentration of tritium in lithium (7.6 g) by a factor of 2 in 50 min. The controlling mass transfer resistance appeared to be in the liquid lithium phase; consequently, the mass transfer rate should be increased with forced convection.

Twenty-eight batch contactor runs were made with tritiated lithium and a single yttrium metal sample. The first 19 sorption runs were made at 400°C, with contact times ranging from 5 min to 100 hr. An additional nine runs were conducted at temperatures from 250 to 400°C and contact times of 120 to 360 hr to determine equilibrium concentrations. A lithium control sample was removed with each sorption run to confirm the initial concentration of tritium in the lithium.

The results of the first 23 sorption experiments are shown in Fig. 5.5, where the concentration of tritium remaining in the lithium, C , divided by the initial tritium concentration, C_0 , is plotted as a function of the contact time. Runs 1 through 20 were conducted at 400°C, whereas runs 21, 22, and 23 were made at respective temperatures of 350, 300, and 250°C. The sorption rate data are comparable to the data obtained at 300°C;¹⁴ however, the concentration driving force is significantly reduced at the higher temperature. For contact times less than 1 hr (400°C), the tritium

12. S. D. Clinton, P. W. Fisher, F. J. Smith, J. B. Talbot, and J. S. Watson, "Recent Experimental Engineering Studies Related to Controlled Thermonuclear Reactors," *Radiation Effects and Tritium Technology for Fusion Reactors*, CONF-750989, vol. III (March 1976).

13. S. D. Clinton and J. S. Watson, "Tritium Removal from Liquid Metals by Sorption on Yttrium," *Proceedings of the Seventh Symposium on Engineering Problems of Fusion Research*, Oct. 25-28, 1977, IEEE Pub. No. 77CH1267-4-NPS, vol. II (1977).

14. J. S. Watson and S. D. Clinton (compilers), *Advanced Technology Sect. Semiannual Prog. Rep. Sept. 1, 1976, to Mar. 31, 1977. Volume 2: Engineering Science Programs*, ORNL/TM-6012/V2 (in preparation).

Fig. 5.5. Normalized tritium concentration in lithium as a function of contact time for yttrium sorber experiments.

concentration of the lithium decreased as a first-order reaction with a half-life of approximately 50 min (mass transfer coefficient of 2.7×10^{-4} cm/sec). For increasing times greater than 1 hr, the tritium sorption rate decreased slowly and appeared to approach zero for contact times in the order of 100 hr. The slightly lower mass transfer rate observed in run 1 is in agreement with the initial sorption runs using tritiated potassium and tritiated lithium at 300°C.^{14,15} Apparently, the yttrium surface requires a certain amount of time to become activated. The rate decrease observed in runs 19 and 20 can be attributed to a reduced concentration driving force due to tritium accumulation in the yttrium sample. Comparing runs 2 and 20, the bulk tritium concentration in the yttrium increased from 2.4 ppm to 19 ppm.

An additional five runs, 24 to 28, were made at increased contact times, 240 to 360 hr, to establish the tritium solubility in yttrium as a function of

temperature.¹⁶ Smith has measured the solubility of tritium in lithium as a function of temperature (790 to 1000°C) and pressure (0.1 to 760 torr).¹⁷ For tritium mole fractions less than 0.1, the solubility temperature dependence in lithium is given by the following equation:

$$K_s(\text{LiT}) = 42.8e^{10,170/T - 6.7} \quad (1)$$

where

K_s = Sieverts' law constant, ppm to $T^{1/2}$,

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

T = temperature, K.

Extrapolating Eq. (1) to lower temperatures (250 to 400°C) and knowing the tritium concentrations in lithium and yttrium, Sieverts' law constants were calculated for yttrium-tritium as a function of temperature (see Fig. 5.6). The least-squares equation for the yttrium-tritium data is

$$K_s(\text{YT}) = 0.557e^{22,300/RT} \quad (2)$$

Yannopoulos has reported experimental isotherms for the yttrium-hydrogen system at temperatures from 650 to 950°C.¹⁸ For hydrogen mole fractions less than 0.1, a least-squares fit of the data (seven determinations) yields the following temperature dependence for hydrogen solubility in yttrium:

$$K_s(\text{YH}) = 6.80e^{21,300/RT} \quad (3)$$

Compared with Eq. (2), the Sieverts' law constants predicted by Eq. (3) at 250 to 400°C are low by a factor of 3; however, considering the temperature extrapolation and isotopic effect, the argument between the two solubility expressions is excellent.

At the end of run 28, the yttrium sample was analyzed for tritium by dissolving the metal in

15. 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).

16. J. S. Watson and S. D. Clinton (compilers), *Advanced Technology Sect. Semiannu. Prog. Rep. Apr. 1, 1977, to Sept. 30, 1977, Volume 2: Engineering Science Programs*, ORNL TM-6328 V2 (in preparation).

17. F. J. Smith, A. M. La Gamma de Bastistoni, G. M. Begus, and F. J. Land, "The Solubility of Hydrogen Isotopes in Lithium," *Proceedings of the Ninth Symposium on Fusion Technology*, Pergamon, New York, 1976.

18. I. N. Yannopoulos, R. K. Edwards, and P. G. Wahlbeck, "The Thermodynamics of the Yttrium-Hydrogen System," *J. Phys. Chem.* **69**, 2510-15 (1965).

Fig. 5.6. Variation of the Sieverts' law constant with temperature for the yttrium-tritium system.

dilute hydrochloric acid. During the sorption experiments, the estimated accumulation of tritium in the yttrium was 0.93 Ci, and the tritium recovered after dissolution of the yttrium was 1.06 Ci (30.9 ppm).

These data suggest that sorption is a feasible method for recovering tritium from lithium. Studies during the next fiscal year will be focused on the operation of a forced-convection tritium sorption system.

5.2 CHEMICAL ENGINEERING RESEARCH

Three-Phase Fluidized-Bed Reacting System

Three-phase fluidized beds are of particular importance to some coal conversion processes and bioreactors. They contain solid particles that are fluidized by the upward cocurrent flow of gas and liquid. Details of our studies of such systems,

using various packings in 7.62- and 15.2-cm-ID columns, are reported elsewhere.¹⁹⁻²¹

Dimensionless correlations were developed to predict the minimum liquid fluidization velocity and five parameters which can be used to completely describe the gas-, liquid-, and solid-phase holdup profiles in a column. In addition, overall gas- and solid-phase holdups were combined with similar data from the literature to yield dimensional correlations for each of the overall volume fractions.

Residence-time distribution²² and liquid-phase mass transfer measurements were made in the 7.62-cm-ID column, using three sizes of glass beads and one size of Plexiglas beads. Measurements of axial dispersion coefficients in the liquid phase were difficult because of the short response times required to follow the fast-moving tracer pulses. This introduced considerable scatter and uncertainty in the dispersion coefficient results. The gas-to-liquid mass transfer measurements were analyzed only in terms of plug flow and thoroughly mixed (liquid) reactor models, since the uncertainties in dispersion coefficients were considerably large. When better values for dispersion coefficients become available, the results can then be reanalyzed easily using a dispersed-flow reactor model. The overall volumetric mass transfer coefficient increased significantly with both increasing gas and liquid velocities and with increasing particle size and density. This is illustrated in Fig. 5.7, where the mass transfer coefficients calculated using a plug flow model are shown for a constant gas-phase velocity.

Continuous Chromatography

The separation of nickel and cobalt components from a commercial leach liquor has been described

19. J. S. Watson and S. D. Clinton (compilers), *Advanced Technology Sect. Semiannu. Prog. Rep. Apr. 1, 1977, to Sept. 30, 1977. Volume 2: Engineering Science Programs*, ORNL TM-6328 V2 (in preparation)

20. J. M. Begovich and J. S. Watson, "An Electroconductivity Technique for the Measurement of Axial Variation of Holdups in Three-Phase Fluidized Beds," *AIChE J.* 24, 351 (1978).

21. J. M. Begovich and J. S. Watson, "Hydrodynamic Characteristics of Three-Phase Fluidized Beds," in *Fluidization, Proceedings of the Second Engineering Foundation Conference*, Cambridge, England, Apr. 26, 1978, Cambridge University Press (1978), p. 190.

22. R. S. Cherry, A. C. Sharon, and Z. P. Chen, *Parameters Influencing Dispersion in a Three-Phase Fluidized Bed*, ORNL MIT-254 (1977).

Fig. 5.7. Effect of particle size and density on the overall volumetric mass transfer coefficient.

previously.^{19,21,24} Significant improvements in the quality of the separation have been made recently. The use of a porous Teflon support and discrete exit points has greatly reduced mixing at the exit. Separations have been performed with the copper-nickel-cobalt-carbonate-amine system. Copper and nickel are generally present in the carbonate leach liquor obtained in the processing of cobalt ores. The separation of the two cobalt compounds,

nickel, and copper is shown in Fig. 5.8. This chromatogram was obtained using an in-line spectrophotometer connected directly to one of the exit ports on the chromatograph. Separation of copper, nickel, and cobalt-1 is difficult and requires careful control of the eluent pH. This particular experiment resulted in essentially complete separation of all four components.

Since the continuous chromatograph is being developed primarily as a large-scale, preparative device, some investigation of the dilution (bandwidth spreading) experienced was appropriate. Several experiments were conducted in which only the concentration of the feed was varied. The dilution did not change greatly under these conditions (Fig. 5.9). However, when the volumetric feed rate was varied (Fig. 5.10), a significant decrease in the dilution factor was observed. Dilution for the cobalt-2 fraction was reduced from a factor of 15 to a factor of 3 when the feed rate was increased from 1 cc/min to 8.8 cc/min. This reduction may be partly explained by the difficulty in making accurate measurements of the initial bandwidth at low flow rates, but the decreased importance of band spreading at higher flow rates is obvious.

23. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977. ORNL-5295 (October 1977).

24. R. M. Canon and W. G. Sisson, "Operation of an Improved, Continuous Annular Chromatograph," accepted for publication in the *Journal of Liquid Chromatography*, 1978.

ORNL DWG 77-2063

Fig. 5.8. Separation of nickel, copper, Co-1, and Co-2 with 1 M $(\text{NH}_4)_2\text{CO}_3$ at pH 7.8 in a 45.8-cm continuous chromatograph. Eluent velocity, 2.52 cm/min; feed composition, 3.0 g of Ni, 0.75 g of Cu, 0.75 g of Co-1, and 0.75 g of Co-2 per liter; feed rate, 1 cm³/min.

Fig. 5.9. Effect of feed concentration on dilution factor in 1 M $(NH_4)_2CO_3$ at pH 7.8. Eluent velocity, 2.52 cm/min; feed composition, Ni, Cu, Co-1, and Co-2 present at a ratio of 4:1:1:1; feed rate, 2.75 cm³/min.

Fig. 5.10. Effect of volumetric feed rate on dilution factor for 1 M $(NH_4)_2CO_3$ at pH 7.8. Eluent velocity, 2.52 cm/min; feed composition, 3 g of Ni, 0.75 g of Cu, 0.75 g of Co-1, and 0.75 g of Co-2 per liter.

Investigations of a scouting nature were performed on other systems during this period. The separation of praseodymium and neodymium with citric acid was examined for potential use in continuous chromatography. Separation was attempted using Dowex 50W-X8 resin with citric acid concentrations ranging from 0.1 to 10% at various flow rates and column lengths. No acceptable separation was achieved under any conditions, and the large volume changes in the resin caused serious problems in the operation of the continuous chromatograph.

The acid-leach method of resource recovery from fly ash results in a highly acid liquor containing iron, aluminum, and other metals (as nitrates or sulfates, depending on the selected acid). As received, this liquor will not load on a cation exchange resin due to the large amount of free acid present; however, the liquor can be evaporated, essentially to dryness, and then redissolved in weak acid. Investigations using H_2SO_4 as the eluent were successful, but the distribution coefficients were large, and the separation was marginal at reasonable feed rates. Use of $(NH_4)_2SO_4$ adjusted with H_2SO_4 to a pH of 2.2, resulted in faster elution rates and greatly improved separation. The continuous chromatograph was operated using a feed that contained 10 g of iron and 10 g of aluminum per liter and eluting with 0.50 M $(NH_4)_2SO_4$ plus 0.025 M H_2SO_4 (pH = 2.2). Under these conditions, the peak iron concentration in the eluate occurred at 30 min and the peak aluminum concentration at ~109 min. The high dilution factors (19 for iron and 50 for aluminum) result from high feed concentrations and low feed and eluent flow rates. Methods for reducing this dilution significantly while still maintaining adequate separation are available.

A new chromatograph has been fabricated and installed. It is approximately 20% longer and incorporates improvements developed over the past 18 months. Gradient elution is now easily achieved through the use of a differential-pressure transducer to maintain a constant liquid level and eluent velocity. This control scheme replaces the optical device used previously and is not affected by ambient light fluctuations. Gradient elution experiments using a pH gradient in the cobalt-nickel-copper system have been very encouraging. Eluent mixing has been largely avoided with this control method. Further, investigations with the iron-aluminum system are planned, and a reduc-

tion of the dilution factor will be the primary objective. Studies of gradient elution chromatography will continue.

Hydraulic Cyclone Studies

Hydraulic cyclones (hydroclones) have found many uses in the physical removal of solids from liquids or the concentration of solids, indicating a potential use of hydroclones as devices for removing solids from coal liquids. Therefore, experiments for evaluating the performance of a 10-mm hydroclone were continued in order to examine its ability to separate micron-size particles from relatively viscous liquids. Performance criteria are usually defined by the pressure drop, the ratio of underflow to overflow rates, and the hydroclone efficiency, and these criteria are dependent on the physical properties of the solids and liquid medium.

Slurries have been tested with ~5 wt % solids in water-glycerin solutions which simulate coal liquids having viscosities in the range of 1 to 85 cP. Slurry from a stirred tank is recirculated by a pump through a 10-mm Dorr-Oliver hydroclone. The inlet, overflow, and underflow streams are sampled at each pressure drop, and particle size distributions are determined. Samples of the overflow are dried and weighed to determine solids concentrations. Recent experiments were conducted using slurries of kaolin (sp gr = 2.40 g/cc) in water-glycerin solutions with viscosities of 1, 4.2, and 12.4 cP. The kaolin particles are <10 μ in diameter (~70% of the particles by weight are <5 μ in diameter). The data obtained at 1 and 4.2 cP are in good agreement with the literature, which states that the pressure drop is proportional to the square of the feed rate. At 12.4 cP, the ratio of the underflow to overflow rate falls below unity in a series of runs having pressure drops which vary over a wide range, as observed previously at even higher viscosities.

Viscosity of the liquid medium also affects hydroclone efficiency. Gross efficiency, the ratio of the solids discharge rate at the underflow to the total solids feed rate, decreases at higher viscosities. At viscosities >30 cP, the fraction of solids and the fraction of liquid that go to the underflow are essentially equal. Particle size distributions in all streams have been measured for runs with liquid viscosities of 1, 4.2, and 12.4 cP to evaluate the hydroclone efficiency at various particle sizes. Figure 5.11 shows typical size distributions for the slurry feed, overflow, and underflow for a kaolin-glycerol solution with a viscosity of 1 cP. At higher viscosities,

Fig. 5.11. Removal and separation of solids using hydroclones.

the size distribution curves for the overflow stream become less steep; the hydroclone becomes less efficient after the removal of the small-diameter particles. For example, at an average pressure drop of 66 psig for slurry viscosities of 1, 4.2, and 12.4 cP, the particle diameters which correspond to 50% by weight less than that size are 1.39, 2.28, and 2.90 μ respectively. Point efficiencies are to be calculated from the data for the particle size analyses, solids concentration, and flow rates of both the overflow and underflow streams. Suitable correlations are being developed for predicting hydroclone performance over the wide range of physical properties being studied.

Mass Transfer Studies Using Stirred, Nondispersing Water-Mercury Contactors

Mechanically agitated, nondispersing two-phase contactors are useful devices for applications where entrainment must be minimized. An electrochemical technique was used to study aqueous-film mass transfer coefficients in a water-mercury system. An extensive set of data from experiments using this system has been reported previously.^{25,26} The

25. C. D. Scott et al., *Experimental Engineering Sect. Semiannual Prog. Rep. (Excluding Reactor Programs)* Sept. 1, 1975, to Feb. 29, 1976, ORNL TM-5533 (July 1977).

26. J. S. Watson and S. D. Clinton (compilers), *Experimental Engineering Sect. Semiannual Prog. Rep. Mar. 1 to Aug. 31, 1976. Volume 3: Engineering Science Programs*, ORNL TM-5865, V3 (in press).

variables tested in the experiments include the cell size, phase volumes, agitator diameter, agitator speed, and aqueous-phase physical properties (principally viscosity).

The measured mass transfer data were correlated by the equation

$$N_{Sh} = [0.03 \exp(3 \times 10^{-6} N_{ReM})] N_{ReW}^{0.8} N_{Sc}^{0.5} \quad (4)$$

where

N_{Sh} = Sherwood number, kd/D ;

N_{ReM} , N_{ReW} = Reynolds number based on the mercury or water phase,

$$Nd^2/\nu_{(M \text{ or } W)};$$

N_{Sc} = Schmidt number, ν_w/D ;

k = aqueous-film mass transfer coefficient, m/sec;

d = agitator diameter, m;

D = quinone diffusion coefficient, m^2/sec ;

N = agitator speed, rps;

ν_M , ν_W = kinematic viscosity of mercury and water phases, m^2/sec .

A plot of the experimental Sherwood number vs the Sherwood number calculated from Eq. (4) is given in Fig. 5.12. If a perfect correlation existed, all of the data shown in Fig. 5.12 would lie on the 45° line through the origin. The correlation given by Eq. (4) is, however, quite good, since the correlation coefficient is 0.98 and the F statistic is calculated to be 4750. The correlation coefficient and F statistic would be 1.0 and $+\infty$, respectively, for a perfect correlation.

A correlation similar to Eq. (4) is reported in the literature²⁷ for aqueous-organic systems; however, that correlation was based on data measured over a much narrower range of Sherwood numbers (500 to 3000 vs 100 to 100,000). The main dissimilarity between the literature correlation and Eq. (4) is that a different intercept term was found (our intercept term is shown in brackets at the top of Fig. 5.12).

27. J. Bulicka and J. Prochazka, "Mass Transfer between Two Turbulent Liquid Phases," *Chem. Eng. Sci.* 31, 137 (1976).

Fig. 5.12. Experimental Sherwood number plotted vs the calculated Sherwood number for the data measured in the water-mercury system.

Agglomeration Studies

Studies of the mechanisms of solids agglomeration in coal-derived liquids have involved separating the liquids into their principal components and observing agglomeration in the presence of various combinations of the components. The electrical forces from solid char, ash, and precipitated asphaltene particles were also measured.

Liquefied coal from the SRC process was chemically fractionated into four components: (1) solids, (2) carbenes and carboids, (3) asphaltenes, and (4) oils and resins. Use of an optical microscope at a magnification of 450X showed that asphaltenes are necessary for agglomeration to take place in the presence of an antisolvent. This was accomplished by sequentially adding components 1, 2, and 3 to 4, followed by treatment with 20% *n*-decane, a known de-ashing solvent. The solids were collected as a precipitate only when asphaltenes were present in the solution of oils and resins.

To characterize the mechanism of agglomeration, a simple double-charge layer model was assumed, and an electrophoresis apparatus that would function with a nearly opaque liquid was developed and used to verify the existence of charges associated with the particles. Initial results proved the existence of

significant charge associations. The zeta potentials, in order of decreasing magnitude (with charge sign in parentheses), were: asphaltenes (-), carbenes and carboids (+), and solids (+). Zeta potentials of these magnitudes (10 to 30 mV) are considered significant in nonaqueous systems.

Petroleum-derived asphaltenes have been characterized previously as positively charged colloidal systems. The coal asphaltene particles described above were $>1 \mu$ in size and, thus, just outside the colloidal range. They had been separated and recombined with oils and resins, a procedure that may have altered the asphaltene surface. Measurements of the effect of asphaltenes on the viscosity of coal liquids at various temperatures did not fit the Einstein colloid model for round, uncharged spheres. Calculated values from this model were $\sim 50\%$ lower than the measured values.

Future research will include modeling of asphaltenes as charged, anisometric, colloidal particles dispersed in oils and resins. Also, the relationship of the charge to the stability of unconverted coal particles will be determined.

Deep-Bed Filtration

The removal of small particles from process or waste streams is both expensive and difficult. The need for such separations arises frequently in energy-related processes such as coal liquefaction and gasification and nuclear fuel reprocessing. Deep-bed filtration is a promising method for removing small particles from both liquid and gas streams. Deep-bed filters have the advantage of being regenerable and providing high efficiencies and throughputs at low pressure drops. They can also be operated under normally corrosive conditions of high temperature and pressure. Deep-bed filtration has been applied to water and wastewater treatment, but applications to more general systems have not been studied. A more complete understanding of the functioning of deep-bed filters is necessary for reliable extrapolation to novel systems.

A study of the fundamentals of deep-bed filtration has been initiated. Removal efficiencies and hydrodynamics are to be studied and related to their basic properties. Work has been started using liquid-solid systems and will be expanded in scope to include gas-solid separations.

Figure 5.13 shows sample data for the "break-through" of colloidal ferric hydroxide particles in the effluent from a test bed. The bed has an inside diameter of 3 in. and is 10 in. long; the filter medium

Fig. 5.13. The pH and iron concentration breakthrough curve for deep-bed filtration of colloidal ferric hydroxide.

(packing) is 0.25-mm-diam glass spheres. An interesting phenomenon seen here is the behavior of the pH of the effluent. This behavior is very important, since the pH has a strong effect on surface potential, which in turn strongly influences the stability and filtering properties of the suspension.

Other systems that are similar to industrially important separations will be studied in the future. Results obtained for all these systems will be explained in terms of a state-of-the-science computer model of the mechanisms governing deep-bed filtration.

Packed Columns for Cryogenic Sorption Systems

A knitted, stainless steel, wire-mesh Goodloe packing²⁸ has been under consideration for use in cryogenic gas-liquid sorption systems for the treatment of off-gas streams in nuclear fuel processing plants. An experimental study of flooding rates and gas-liquid mass transfer characteristics was continued during this report period.²⁹ Previous results were extended to include liquid-to-gas mass flow ratios up to two orders of magnitude larger than those studied previously.³⁰⁻³²

28. Manufactured by the Packed Column Co., a Division of Metex Corp., Edison, N.J.

29. J. S. Ayala, B. W. Brian, and A. C. Sharon, *Flooding and Mass Transfer in Goodloe-Packed Columns, Part 2*, ORNL, MIT-253 (April 1977).

30. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1975*, ORNL-5050 (October 1975).

31. W. M. Choi, R. C. Michel, and J.-L. P. Varlet, *Flooding Characteristics of Packed Columns with High Efficiency Packings*, ORNL, MIT-223 (February 1976).

32. E. J. Chao, R. J. Bertolami, J.-L. P. Varlet, and G. R. Wilkes, *Flooding and Mass Transfer in Goodloe-Packed Columns*, ORNL, MIT-234 (May 1976).

Flooding data obtained in the 6.35- and 15.2-cm-ID columns are compared with previous results and the packing manufacturer's correlation³³ in Fig. 5.14. The coordinate axes correspond to the generalized flooding correlation for packed beds,³⁴ where

G = superficial gas mass flux, $\text{g cm}^{-2} \text{sec}^{-1}$;

ϕ = ratio of water density to liquid density, dimensionless;

μ_L = liquid viscosity, cP;

g = gravitational constant, 980 cm/sec^2 ;

ρ_L = liquid density, g/cm^3 ;

ρ_G = gas density, g/cm^3 ;

L = superficial liquid mass flux, $\text{g cm}^{-2} \text{sec}^{-1}$.

For high liquid/gas (L/G) ratios (>10), the data appear to fall along an extension of the Goodloe correlation, whereas at lower L/G ratios, the data deviate significantly from the correlation. Since the data shown in Fig. 5.14 have been obtained by several investigators, the use of the dashed curve representing the experimental fit is recommended for this type of packing. For design purposes, a safety factor of $\sim 30\%$ should be allowed for scatter in the data.

Using an air-carbon dioxide-water system, new mass transfer data were combined with previous results to yield the following dimensional correlation for the overall volumetric mass transfer coefficient:

$$K_L a = (0.014 \pm 0.002) \cdot L^{1.006 \pm 0.274} \quad (5)$$

where the coefficients are given with their 95% confidence limits. Equation (5) was based on 27 points, and the mass transfer coefficient was calculated by assuming plug flow in the gas and liquid phases. As can be seen in the correlation, gas velocity or column diameter had no significant effect on the mass transfer coefficient.

No future work is planned in this area. Use of the experimental curve in Fig. 5.14 and Eq. (5) will yield accurate estimates of the flooding rates and mass transfer characteristics, respectively, for Goodloe-packed columns operating under conditions similar to those used in this study.

33. *Packed Column Information Bulletin*, Packed Column Co., a Division of Metex Corp., Edison, N.J.

34. J. S. Eckert, "Selecting the Proper Distillation Column Packing," *Chem. Eng. Prog.* 66(3), 39 (1970).

Fig. 5.14. Comparison of flooding data obtained in Goodloe-packed columns.

5.3 RESOURCE RECOVERY

Process Chemical Development

Increased use of coal as a fuel will impose an increasingly difficult disposal problem for large amounts of ash, which currently exceed 6×10^7 tons per year ($\sim 5.4 \times 10^7$ metric tons).³⁵ Since the ash contains some minerals of value (principally aluminum), is finely divided material, and will require handling for disposal in any case, consideration is being given to the possibility of recovery of the mineral values and/or conversion of the ash to some useful material. We have made laboratory-scale investigations of several methods for the recovery of aluminum and other metal values from Kingston fly ash. These include reported processes such as lime-sinter and lime-soda-sinter (which, in our tests, have been shown to be capable of recovering only 50 to 60% of the aluminum) and the obvious direct leach methods (that recover a maximum of $\sim 65\%$ of the aluminum).

35. J. H. Faber, "U.S. Overview of Ash Production and Utilization," presented at the Fourth International Ash Utilization Symposium, St. Louis, Mo., Mar. 24-25, 1976.

Several new combination sinter-dilute acid leach methods have also been reported,³⁶ and two of these appear to have the highest potential for practical application. In both of these combination procedures, greater than 95% of the aluminum originally present in the fly ash is recovered. The recoveries of iron, titanium, manganese, uranium, and thorium are also high. In the first of these two new methods, fly ash is sintered with an $\text{NaCl-Na}_2\text{CO}_3$ mixture at 1000°C and leached first with water and then with 1 N HNO_3 or H_2SO_4 . In the second method (see proposed flowsheet, Fig. 5.15), fly ash is sintered with a $\text{CaSO}_4\text{-CaCO}_3$ mixture at 1200 to 1400°C ; next the sinter cake is pugged with $36\text{ N H}_2\text{SO}_4$ and then diluted to 4 N for a second leaching period. Both of these proposed sinter-leach methods provide considerable product-option flexibility. Alumina can be recovered as a single product; however, the addition of a solvent extraction cycle not only produces an Al_2O_3 product of higher purity but also provides a means for the separation and recovery of the minor metals mentioned above. Our investigations have shown that an attractive feature of the $\text{CaSO}_4\text{-CaCO}_3$

sinter- H_2SO_4 -leach method is that the sludge solids from a lime scrubbing unit for the removal of sulfur dioxide from stack gases can be used in place of the CaSO_4 . Thus this latter method offers the possibility of utilizing two potentially troublesome waste products to recover useful resource materials and at the same time to reduce the total waste volume.

Engineering Studies

The purpose of this program is to recover resource materials from waste produced by using coal as a fuel. Several processes proposed for use with ash from western coals have been studied, and a new, unique group of processes has been conceived which mixes the ash with inorganic salts, sinters the mixture at temperatures near 1000°C , and leaches aluminum and most metal values with nitric or sulfuric acid. Aluminum, iron, titanium, uranium, and any important trace metals are removed by extraction with a solvent such as Amerlite-LA3 amine.

One particular process in this group, the Calsinter process, has been developed which sinters fly ash with CaSO_4 sludge, a by-product of the sulfur dioxide stack gas scrubbing and the leaches with sulfuric acid. This process, which combines two waste materials to recover useful resource materials and reduces the volume of waste requiring disposal, looks particularly promising. In testing this process, dewatered sludge was mixed in varying proportions of fly ash

36. This work was sponsored by the Exploratory Studies Program Committee at ORNL. For further details, see the following: 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).

Fig. 5.15. Calsinter process flowsheet for the recovery of aluminum and other metal values from fly ash.

and, in some cases, additional CaCO_3 . The mixture was sintered between 1000 and 1400°C and leached with 1 to 8 N H_2SO_4 at reflux conditions. Aluminum recovery improves with increased sintering temperature and can be significantly greater than 85%.

A second process has been developed using the waste ash from the ORNL bench-scale hydrocarbonization test unit. Direct leaching of the ash with 4 N H_2SO_4 under reflux conditions recovered more than 90% aluminum. The ease with which the aluminum is extracted is attributed to the low temperature (571°C) at which the ash is fired in hydrocarbonization. Similar behavior is expected with ash from all low-fired coal conversion processes. The ease of recovery of valuable and hazardous materials from ash may become an important factor in coal utilization processes.

5.4 INTERPHASE TRANSFER KINETICS

The use of fast solvent extraction contactors in reprocessing radioactive fuel is advantageous because they minimize the contact time between the organic solvent and the highly radioactive fuel solution. The shorter contact time reduces both the radiolytic degradation of the solvent and resultant operational problems. This program is dedicated to the determination of the transfer kinetic data for actinides and fission products which is required for the prediction of the separations obtainable in fast, nonequilibrium contactors.

During this year, due to the increased emphasis on thorium-containing fuel, extraction kinetic studies have examined Thorex-type systems. The kinetics of the solvent extraction of uranium, thorium, and important fission products with TBP in dodecane was studied using the drop method, in which aqueous drops fall and organic drops rise through a column of the opposite phase.

The differential equations describing the net mass transfer are

$$\frac{dc}{dt} = -\frac{kac - k'ac'}{v} \quad (\text{organic drops}), \quad (6)$$

$$\frac{dc'}{dt} = \frac{kac - k'ac'}{v'} \quad (\text{aqueous drops}), \quad (7)$$

where k' and k are the rate constants for the aqueous-to-organic and organic-to-aqueous transfer, respectively, c is the concentration, v is the drop volume (assuming spheres), and a is the interfacial

area between the drops and bulk phase. The primed values refer to the aqueous phase; the unprimed values indicate the organic phase.

Integrated equations for the four possible modes of transfer, namely, aqueous-to-organic and organic-to-aqueous transfer in both falling and rising drops, were used to calculate the kinetic constants, k and k' . In tests involving the transfer of uranium and thorium, a simulated aqueous feed containing 0.5 M Th-0.37 M U-0.03 M F-0.065 M Al-2.1 M HNO_3 was used.

Assuming that the transfer mechanism is the same in the bulk and drop phases for a given transfer direction, both falling and rising drop modes should give the same value for the transfer rate constant. This was determined to be true for both transfer directions for uranium. The values of the constants for the two modes in the forward transfer of thorium are approximately the same, even in the case where a third phase forms in the rising drop mode. However, for thorium in the reverse direction (organic to aqueous), extraction rates in the rising drop mode are faster than in the falling drop mode. This apparent difference in extraction mechanisms is receiving further study.

A comparison of forward extraction of both thorium and uranium with and without the presence of fluoride (and aluminum) shows that the extraction rates for both are slower (by factors of 4 to 5) with the fluoride present. Aqueous complexing of both uranium and thorium (as well as aluminum) by fluoride may occur and decrease the extraction rates. In reverse organic-to-aqueous extractions, however, the presence of fluoride in the aqueous phase has little effect on the rate.

Forward extraction rates for uranium and thorium increase with increasing TBP concentrations, reach maxima at about 0.5 M TBP, then decrease (upper two curves of Fig. 5.16). These maxima are possibly the result of the change from chemically controlled kinetics at lower TBP concentrations to predominately diffusion control at higher TBP concentrations. Reverse extraction rates (shown as the two lower curves of Fig. 5.16) are slower than the forward rates, particularly for uranium. In other tests, both forward and reverse extractions were shown to increase with increasing temperature.

A fast contactor system for studying separations of uranium, thorium, and fission products has been successfully operated and will be used to study separations attainable in nonequilibrium conditions. Also, computer models are being developed which

Fig. 5.16. Extraction rates of uranium and thorium as a function of TBP concentration.

will allow the prediction of the performance of fast, nonequilibrium contactors from transfer kinetic constants.

5.5 FUSION ENERGY STUDIES

Cryosorption Vacuum Pumping for Fusion Reactors

The cryosorption vacuum pumping program initiated experiments designed to determine the best combination of adsorbent and operating temperature for near-term neutral-beam injector systems. Vacuum pumps for these systems will have to accommodate only hydrogen at pressures near 10^{-4} torr during beam pulses. Cryocondensation pumps are employed in all present beam lines, but cryosorption pumps have advantages that could make them attractive for use in future systems. These advantages include a higher operating temperature, the ability to take larger heat loads, less sensitivity of pumping speed to small fluctuations in panel temperature, and the easier control of regeneration rates. A new pump has been designed, constructed, and added to the test stand.¹⁴ This pump will facilitate the optimization of the following important variables for cryosorption pumping: type of adsorbent, operating temperature, adsorbent support design, and baffle design.

Figure 5.17 shows a schematic cross section of the pump, which has four basic parts: a variable-

Fig. 5.17. Cross-sectional view of demountable variable-temperature cryosorption pump. LN₂ = liquid nitrogen; LHe = liquid helium.

temperature cryostat, a cryosorption panel, a chevron, and a test chamber (not shown). Temperature control is achieved by metering the flow of liquid helium to the back of the cryosorption panel,

which is heated and controlled at the desired temperature. Several temperature sensors are attached to both the front and back of the panel. Cryosorption sensors are attached to the cryostat through a lead O-ring joint, and any cryosorption panel with a compatible flange can be tested.

Panels have been prepared with molecular sieves (MS) 5A, 13X, and Na-Y on cross-milled and screen substrates. Other panels will be prepared as needed. Each experimental run lasted 5 min, with 10 min allowed between runs. Performing tests at specific leak rates for specific times permits rapid, direct comparisons of results, especially the comparison of the effects of panel temperature and the type of adsorbent.

A total of 82 runs in nine series were made with a cross-milled MS-5A panel at various temperatures, panel heating cycles between runs, and feed rates.¹⁶ The time-averaged surface temperature, speed, and pressure were determined for each 5-min run. The panel temperature could be held essentially constant for most runs; the only exceptions were those made at the highest feed rate (8.5×10^{-2} torr-liter/sec). During all runs, the temperature at the center of the chevron was observed to be between 120 and 140 K, and the temperature at the bottom of the copper radiation shield was about 130 K. Plots of average pump speed vs reciprocal panel temperature and of average pressure vs reciprocal panel

temperature were prepared for each specific feed rate. The maximum pumping speed observed for hydrogen, using the 10-cm-diam MS-5A panel in this pump, was approximately 825 liters/sec. At the lowest feed rate (8.2×10^{-5} torr-liter/sec), the speed approached this value with decreasing temperature. Cross plots of average speed vs average pressure are presented in Fig. 5.18. A comparison of similar curves for various cryosorption panels will allow us to choose the best adsorbent for hydrogen pumping. For the sorbent material (MS-5A) used in these initial tests, it appears that the best pumping speeds are obtained at the lowest temperatures.

A cross-milled MS-Na-Y has been installed in the pump, and some preliminary results are presented in Fig. 5.19. These data show that average speeds in the range of 20 to 25 K are about an order of magnitude higher for the MS-Na-Y panel than they were for the MS-5A panel at the same conditions. These results are encouraging because they indicate that our proposals regarding optimal choice of sieve were correct. It was anticipated that the MS-Na-Y sieve would have a higher pumping speed than that of the MS-5A because it has a more open structure and higher diffusivities. Favorable results for the MS-Na-Y sieve have led to its selection as the adsorbent in a large cryosorption pump under construction in the Fusion Energy Division of ORNL.

Fig. 5.18. Average speed as a function of average pressure for 5-min runs made with an MS-5A cryosorption panel.

Fig. 5.19. Preliminary comparison of results for the MS-Na-Y panel with the MS-5A panel.

TNS Support Studies

During FY 1977, the Chemical Technology Division provided technical support to the Fusion Energy Division's preliminary design of a Tokamak experimental device known as The Next Step (TNS). This is the next device to be tested after the Tokamak Fusion Test Reactor, which is now under construction at Princeton. The TNS will be an ignition device and will incorporate many aspects of fusion reactors not included in any present system. One such aspect, of major importance, is an on-site fuel recycle system. Westinghouse Corporation was the major subcontractor for all engineering design activities, including the fuel recycle system. Chemical Technology followed and supervised the

Westinghouse design of the fuel recycle facility. The preliminary design was completed³⁷ at the close of FY 1977. The TNS program was then reduced considerably in FY 1978 to a more detailed study of a few aspects of the system; hence further work on the fuel system is planned immediately.

Tritium Recovery from Irradiated Lithium-Aluminum and Sintered Aluminum Product Alloys

The tritium release rates from irradiated samples of lithium-containing aluminum (Li-Al) and sintered aluminum product (Li-SAP) were investigated to evaluate the potential application of both materials in fusion reactors. This study differs from current studies³⁸ of solid aluminum alloy blanket materials at other laboratories because of the low (ppm) lithium and tritium contents, the incorporation of oxygen (17.7 wt % Al_2O_3) within the SAP samples, and the use of large samples rather than powders.

To study the tritium release rates, an irradiated sample is heated to a desired temperature between 300 and 500°C. Tritium was produced in the samples by irradiating the lithium-doped alloys at about 55°C in a thermal neutron flux to achieve the desired burnup. Preheated argon flushes the released tritium to a tritium monitor. At this point, the tritium-bearing argon is routed to a trapping system composed of a copper oxide bed (at 600°C), two water bubblers, a molecular-sieve trap, and another tritium monitor to detect the tritium that is ultimately released to the radioactive off-gas stack.

Tritium release rates were measured for eight Li-SAP samples and one sample of Li-Al. The percentage of tritium released from each sample and the total tritium concentration determined for each sample are shown in Table 5.1. The fraction of the tritium released from Li-SAP varied from 1.8 to 62.0%, depending on sample temperature, sample thickness, and run duration. The total concentration of tritium in the Li-SAP samples ranged from 20 to

37. H. J. Garber (Westinghouse) and J. S. Watson, "Tritium Systems Preliminary Design for TNS," *Proceedings of the Seventh Symposium on Engineering Problems of Fusion Research*, Knoxville, Tenn., Oct. 25-28, 1977, TCH12674-NPS, pp. 95-100.

38. R. H. Wiswall and E. Wirsing, "Tritium Recovery from Fusion Blankets Using Solid Lithium Compounds. II. Experiments on Tritium Removal and Absorption," *Radiation Effects and Tritium Technology for Fusion Reactors*, CONF-750989, vol. III, pp. 232-52 (March 1976).

Table 5.1. Tritium release from solid blanket materials

	Li-SAP samples								Li-Al sample
	1	2	3	4	5	6	7	13	11
Temperature of sample, °C	340-420	450	400	475	450	500	26-450	425	450
Weight of sample, g	0.4870	0.1312	0.1690	0.1440	0.2550	0.1928	0.3425	1.0480	0.8695
Thickness of sample, cm	0.1143	0.0508	0.0609	0.0524	0.0609	0.0533	0.0613	0.5689	0.3124
Surface area of sample, cm ²	4.3273	2.7406	3.0012	3.4681	3.7100	3.3520	3.8971	2.8942	4.5182
Length of run, hr	30	30	26.5	25	121	47	32	29	22
Tritium released from sample into sweep gas, mCi	3.042	4.704	0.626	2.236	2.193	17.88	4.561	1.337	91.79
Tritium from sample dissolution, mCi	35.24	11.43	3.358	9.142	5.639	10.94	39.13	71.93	0.326
Percent tritium released from sample	7.95	29.2	15.7	19.7	22.0	62.0	10.5	1.8	99.7
Total amount of tritium in sample, appm ^a	66.51	104.1	19.97	66.25	25.92	126.1	108.3	52.15	94.8

^aDefined as atomic parts per million.

126 atomic parts per million (appm). Near-complete tritium release from the Li-Al sample (99.7%) was observed during the 22-hr run at 450°C. The tritium concentration in this sample was measured as 94.8 appm.

The release rate of tritium was assumed to be diffusion-limited. Diffusion coefficients were determined for each sample by using the solution for transient diffusion in a plane sheet and assuming a uniform initial concentration distribution and equal surface concentrations. The resulting values of the diffusion coefficients for Li-SAP are plotted in Arrhenius form in Fig. 5.20. The dependence of the diffusion coefficient on temperature for Li-SAP from a least-squares analysis was found to be

$$D = 2.275 \times 10^{-4} \exp\left(\frac{-19.58 \text{ kcal/g-mole}}{RT}\right),$$

where

D = diffusion coefficient, cm²/sec,

R = gas constant, 1.987 cal K⁻¹ g-mole⁻¹,

T = temperature of sample, K.

The diffusion coefficients of Li-SAP and Li-Al are 2.988×10^{-10} cm²/sec and 1.462×10^{-9} cm²/sec at 450°C respectively. A possible explanation of the easier release of tritium from aluminum than from Li-SAP is that there is greater trapping of tritium at the internal interfaces between the aluminum and

Al₂O₃ particles in the Li-SAP.³⁹ Hence these effective traps retard the tritium release to the external surface of the SAP sample. These data indicate that continuous extraction of tritium from Li-SAP or Li-Al at appropriate temperatures would maintain acceptably low tritium inventories in fusion reactor blankets of these materials; the inventory, of course, would be lower in the Li-Al blankets.

5.6 ACTINIDE OXIDES, NITRIDES, AND CARBIDES

Thermodynamics of the Actinide-C-O System

Equilibrium thermodynamic calculations were performed to determine actinide segregation and partial pressures in the system (U,Pu)C_{1-x}O_y + (U,Pu)C_{1.5} as a function of temperature and actinide, carbon, and oxygen concentrations. The computations indicated that plutonium significantly segregates to the sesquicarbide in almost all cases. The equilibrium partial pressures calculated indicate that, during the carbothermic reduction of mixed oxide, the plutonium pressure approaches that of CO as y decreases. This is believed to be a major cause of the significant evaporative losses of plutonium which have been observed. The results suggest that the losses can be minimized by performing the reduction

39. F. W. Wiffen, ORNL, personal communication, February 1978.

ORNL DWG 77-1982R2

Fig. 5.20. Diffusion coefficient for tritium in solid Li-SAP.

at high temperature (~2000 K) and/or by allowing substantial amounts of oxygen to remain dissolved in the monocarbide. An apparatus was constructed and is being made operational in an alpha-active facility for measuring CO pressures over various compounds in the U-Pu-Th-C-O system and its subsystems.

Transition Metal-Actinide-C Phase Equilibria

Studies are continuing to determine the thermodynamic conditions for the chemical interaction of Cr-Fe-Ni alloys with the actinide carbides. These are basic studies related to the chemical compatibility of advanced LMFBR fuels with potential clad alloys.

The UNi₃ is the principal intermetallic compound formed in reactions between Cr-Fe-Ni alloys and uranium carbides. We have reassessed the free energy of formation for the compound UNi₃. The following equations were used in this assessment:

We measured the equilibrium nitrogen pressures for the reaction given by Eq. (8). The values obtained were very close to those reported by Imoto and Namba.⁴⁰ To obtain the free energy of formation for UNi₃, we combined the standard free energy change for Eq. (8) with the standard free energy change for Eq. (9). Thermodynamic values for Eq. (9) were obtained from recent values given by Mills et al.⁴¹ This procedure yields

$$\Delta G_f^\circ(\text{UNi}_3) = 97.53T - 2.960 \times 10^5 \text{ J/mole} \quad (10)$$

(1125-1325 K)

Thermodynamic modeling of the fuel-clad interface is a method we have developed for assessing chemical compatibility. In the thermodynamic modeling, we determine the phases present in the interface, or reaction area, between bulk fuel and bulk clad alloy. In terms of a phase diagram, this interface is represented by a line that extends from a point corresponding to the clad alloy composition to a point corresponding to the fuel composition.

We have made thermodynamic calculations of the fuel-clad interface for the thorium carbides with the Cr-Fe-Ni compositions of seven alloys. The alloys we considered are: type 316 stainless steel, type 330 stainless steel, A286, M813, PE-16, Inconel 706, and

40. S. Imoto and S. Namba, "Thermodynamics Applied to Compatibility of UN with Ni, Cr, and Fe," *J. Nucl. Mater.* 51, 106 (1974).

41. K. C. Mills, P. E. Potter, and T. Takahashi, "Chemical Thermodynamics of the Actinide Pnictides," I.A.E.A. (to be published).

Inconel 718. We used the computer program SOLGASMIX-PV⁴² to perform the calculations at 1173 K. The following species were considered as possible reaction products in the interface: $[\text{Cr}_2\text{C}_6]$, $[\text{Cr}_3\text{C}_4]$, $[\text{Cr-C}_3]$, $[\text{Fe-D}_3]$, $[\text{Cr}_3\text{C}_2]$, $[\text{ThC}_x]$ ($x=0.67-0.97$), $[\text{ThC}_{1.92}]$, $[\text{C}]$, $[\text{Cr-Fe-Ni}]$, $[\text{Th}_2\text{Ni}_2]$, $[\text{Th}_2\text{Fe}_2]$, $[\text{ThNi}_2]$, $[\text{ThFe}_2]$, $[\text{Th-Ni}_2]$, $[\text{Th-Fe}_2]$, $[\text{ThNi}_2]$, $[\text{ThFe}_2]$, and $^{\circ}\text{Th}$. Note that the bracketed species denote solid solution. Thermodynamic values used in the calculations were obtained from refs. 43-46.

The solid solutions $[\text{ThNi}_2]$, $[\text{ThFe}_2]$ and $[\text{Cr-C}_3]$, $[\text{Fe-C}_3]$ were found to be the principal reaction products in all of the calculated interfaces. Type 316 stainless steel showed significantly less reaction than any of the other alloys considered. This is due to its relatively higher iron content when compared with the other materials. Nickel forms 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 both intermetallic compounds and carbides; however, the contributions to the free energy of formation by nickel in the intermetallics and by chromium in the carbides are much more significant.

42. T. M. Bessmann, *SOLGASMIX-PV, A Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems*, ORNL TM-5775 (April 1977).

43. J. F. Smith, "Thermodynamic Properties of Binary Thorium Systems," *J. Nucl. Mater.* 51, 136 (1974).

44. A. D. Kulkarni and W. L. Worrell, "High-Temperature Thermodynamic Properties of the Chromium Carbides Determined Using the Torsion-Effusion Technique," *Metall. Trans.* 3, 2363 (1972).

45. R. Lundberg, M. Waldenstrom, and B. Uhrenius, "Isothermal Sections of the Fe-Cr-C System in the Temperature Range of 873-1373 K," *Calphad* 1, 159 (1977).

46. M. H. Rand, "Thermochemical Properties," p. 7 in *Thorium: Physico-Chemical Properties of Its Compounds and Alloys*, Atomic Energy, Review Special Issue, No. 5, I.A.E.A., Vienna, 1975.

6. Biotechnology and Environmental Studies

6.1 BIOENGINEERING TECHNOLOGY

This program is concerned with the development of biochemical engineering technology whereby individual process steps, at least one of which utilizes a biological entity, can be integrated to result in a highly useful overall process. Areas of concern to DOE that will benefit directly from this technology include energy production and conservation, resource recovery, and pollution abatement. Investigations specific to problems in nuclear waste management include the removal of radionuclides and chemical contaminants from aqueous process and effluent streams and are discussed in Sects. 4.2 and 4.3. Additional investigations involving bioengineering research and bioprocess development and demonstration are summarized below.

Bioengineering Research

Bioengineering research activities were focused on three areas during this reporting period: (1) enzyme catalysis, (2) treatment of aqueous effluents from coal conversion processes, and (3) bioreactor scale-up and process modeling studies.

Investigations associated with the enzyme-catalyzed reduction of water to produce hydrogen included studies of ferredoxin reduction by sodium dithionite and oxidation by molecular oxygen. Kinetic parameters, including maximum velocity and the Michaelis constant, as well as reaction stoichiometry were determined for ferredoxin reduction. The rate of reaction of ferredoxin with dissolved oxygen was found to be very rapid, whereas several seconds were required for complete reaction with gaseous oxygen. Complete autooxidation of ferredoxin required several minutes.

Chloroplasts were prepared from spinach, and cell extracts containing hydrogenase and ferredoxin were prepared from *Clostridium pasteurianum* for use in studying the rates of hydrogen production by photooxidation. Results of the oxidation studies

indicated that it will be necessary to remove oxygen chemically or biochemically as it is formed.

Studies on the biological treatment of aqueous effluents from coal conversion processes were continued, with emphasis on the development of an integrated process which addresses a combined physical-chemical-biochemical treatment of hydrocarbonization wastewater. Acidification followed by sedimentation of particulates from the wastewater prior to biological treatment was found to improve bioreactor performance significantly. Reactor performance was studied under both prediluted feed (once-through) and recycle conditions. Studies of biomass inventory control have shown that a biomass yield of 12.5 g (dry wt) per day can be obtained at a phenol degradation rate of 10 g per day per liter, using a synthetic feed. This result indicates that 20% of the bed must be removed and replaced each day in order to maintain a constant biomass inventory in the reactor.

Tapered fluidized-bed bioreactors were the subject of scale-up and process modeling studies. Such studies are necessary for the design of full-scale industrial reactor systems from process data obtained at the pilot or bench scale. The continuity equation for a tapered reactor was derived for a conical coordinate system and expressed in dimensionless form. The equation was then solved for two sets of assumptions:

1. a steady-state, first-order reaction with plug flow,
2. a steady-state, n th-order reaction with plug flow.

The model was then used to analyze experimental data obtained during biological conversion of dissolved nitrates to molecular nitrogen by *Pseudomonas* bacteria. Using a variable first-order reaction rate coefficient, expressed in terms of initial nitrate concentration, the agreement of the experimental effluent concentrations with those calculated from the model based on the first assumption was

excellent. A more complete and presumably more valid mathematical model incorporating void volume changes and particle size distribution is being developed.

Bioprocess Development and Demonstration

The ANFLOW demonstration pilot plant, started up in November 1976 at the Oak Ridge East Wastewater Treatment Plant, has been in essentially continuous operation for 16 months. The pollutant removal efficiencies of the pilot plant have been determined at feed rates of 1000, 1500, 3000, 4000, 5000, and 6000 gal (4, 5.6, 11.3, 15.1, 19, and 22.7 m³) of raw sewage per day. The resulting process data have been obtained under widely varying operating conditions. Seasonal variations have produced feed temperatures ranging from 10.7 to 24.6°C and pH levels ranging from 6.2 to 7.9, with occasional spikes of 1.5 to 11.8. The process has shown strong resistance to both low temperatures and pH spikes. Analyses of raw sewage samples taken during the operational period have shown concentrations of biochemical oxygen demand (BOD), total organic carbon (TOC), and total suspended solids (TSS) ranging from 57 to 182 ppm, 32 to 118 ppm, and 61 to 208 ppm respectively. Typical pollutant removal efficiencies for the pilot plant have been 60% for BOD, 60% for TOC, and 75% for TSS. Monthly average percent removal rates of 82, 81, and 83% for BOD, TOC, and TSS, respectively, were achieved during February 1978.

The ANFLOW effluent quality has consistently met EPA standards for secondary sewage treatment for pH and TSS levels; the process has also met EPA standards for TOC and BOD, but not consistently at the present stage of development. The process has, however, been very successful at converting dissolved carbon to physically removable, suspended carbon. Possible polishing steps for the ANFLOW system are being investigated. Tests with alum settling, membrane filtration, and sand filtration have shown that each of these methods can be used to reduce BOD and TOC levels in the ANFLOW effluent to well below the EPA discharge standards.

Gas production rates have generally increased with increased feed temperatures; these rates have varied from 60 to 110 std liters per day, with methane concentrations ranging from 40 to 70 vol % of the total gas produced. Gas production is typically 90 to

100 std liters per day, with a methane concentration of 60 to 65 vol %.

The feasibility of constructing and operating a large-scale [30,000- to 50,000-gpd (110- to 200-m³)] ANFLOW demonstration system in cooperation with industry is being considered. Agreement, in principle, for implementing such a cooperative project has been reached with the Tennessee Valley Authority. Feasibility evaluations will be partially based on engineering conceptual design reports and an economic analysis being prepared from process data obtained from the demonstration pilot plant.

6.2 BIOANALYTICAL TECHNOLOGY

It is anticipated that biological systems will play a primary role in solving some of the environmental problems associated with new sources of energy. In addition, new point sources of energy will be scrutinized very closely for their potential mutagenic effects on surrounding human populations. Thus, as new energy technology is developed, increasing demands will be placed on analytical methodologies to provide timely, pertinent, and more sensitive data on their potential environmental effects.

Advanced Analytical Techniques

A continuing emphasis on the development of automated methods and instrumentation for the measurement of mutation rates has resulted in the evolution of a new, advanced concept in high-resolution electrophoresis. A conceptual design, achieved via interdisciplinary meetings between engineers, chemists, and geneticists, has been transformed into a prototype system capable of demonstrating all aspects of the new electrophoretic methodology.

Engineering development. Engineering efforts were concentrated on the development and fabrication of a new, automated, prototype electrophoresis system which can electrophorese, stain, and scan many samples in a relatively short time. In addition, a new concept in detection systems for continuously monitoring enzyme activity in the eluent from a chromatographic column has been developed and tested.

Prototype electrophoresis system. Within the past few years, a variety of studies on electrophoretically detected enzyme variation in insects have suggested the occurrence of additional variant classes not normally resolved by standard electrophoretic

techniques.¹⁻⁴ Electrophoretic methods provide direct evidence of some difference between two variants by showing that the mutant proteins migrate to different band positions when electrophoresed under identical conditions. However, it cannot be safely assumed that two variants are identical when their bands are found to be located at the same position on a gel. The validity of such an assumption depends on the amount of variation detected by the technique (changes in the protein may not result in a sufficient difference in the net charge to enable resolution of two bands). To enhance resolution and uncover the so-called "hidden heterogeneity" of variant proteins, Johnson^{4,5} has demonstrated the utility of electrophoretic separations on acrylamide gels of varying pore sizes. The mathematical model for the migration of a protein during polyacrylamide electrophoresis, as expressed by Rodbard and Chrambach,^{6,7} is the theoretical basis for this technique:

$$R_f = M_n U_f \exp(K_f T),$$

where

R_f = mobility of the protein relative to a solvent front,

M_n = free electrophoretic mobility of the protein,

U_f = apparent mobility of a moving boundary in front of the resolving phase (a constant known for most common buffer systems),

K_f = retardation (frictional/hydrodynamic) coefficient, $K_f = K_f / 2.303$,

T = percentage of acrylamide (determines pore size and is inversely proportional to it).

By examining R_f at several values of T , the free electrophoretic mobility (M_n) and the retardation coefficient (K_f) can be estimated for any protein which can be discretely detected in a heterogeneous mixture. In experimental practice, a linear regression of $\log R_f$ on T yields a line with slope K_f and intercept $M_n U_f$. The retardation coefficient is directly related to both the size and shape of the protein.⁸ This provides the foundation for a powerful, comparative electrophoretic technique; the inclusion of internal standard proteins on each gel serves to standardize individual determinations of R_f on different gels for the purpose of providing a measure of experimental error.

Implementation of this technique requires that each sample be electrophoresed on at least four different acrylamide gels, with two internal standards on each gel. The logistics of such measurements requires the use of automated techniques in (1) casting the gels, (2) electrophoresing, (3) staining, and (4) scanning the stained gels for measurement of protein mobilities. The prototype system being fabricated will consist of four modular elements (one for each of the above tasks) in order to maximize sample throughput. This system has been designed to perform the first three operations on a large number of gels, whereas the final scanning will be performed on 12 individual gel columns in ~1 min with a resolution of 100 points per inch.

High-resolution chromatography of macromolecules. As a part of the continuing development of rapid macromolecular separations coupled with continuous monitoring of enzyme activity, an innovative concept in detector systems has been developed and tested. The separation and continuous fluorimetric monitoring of the three isoenzymes of creatine phosphokinase (CPK) were previously described.⁹ This detection system utilized a coupled sequence of enzymatic reactions that ultimately yielded nicotine adenine dinucleotide phosphate as the monitored product, which was proportional to the CPK activity. The reaction mixture included the enzymes hexokinase (HK) and glucose-6-phosphate dehydrogenase (GPDH) and was extremely expensive to use in a continuously flowing system. In addition, monitoring of actual human serum samples revealed the presence of fluorescent impurities which

1. S. Bernstein, L. Throckmorton, and J. Hubby, "Still More Genetic Variability in Natural Populations," *Proc. Natl. Acad. Sci. U.S.A.* **70**, 3928 (1973).

2. R. Singh, J. Hubby, and R. Lewontin, "Molecular Heterosis for Heat Sensitive Enzyme Alleles," *Proc. Natl. Acad. Sci. U.S.A.* **71**, 1808 (1974).

3. R. Singh, J. Hubby, and L. Throckmorton, "A Study of Genetic Variation by Electrophoretic and Heat Denaturation Techniques at the OdH Locus in Members of the *Drosophila virilis* Group," *Genetics* **80**, 637 (1975).

4. G. Johnson, "Hidden Alleles at the α -Glycerophosphate Dehydrogenase Locus in *Colias* Butterflies," *Genetics* **83**, 149 (1976).

5. G. B. Johnson, "Assessing Electrophoretic Similarity: The Problem of Hidden Heterogeneity," *Annu. Rev. Ecol. Syst.* **8**, 309 (1977).

6. D. Rodbard and A. Chrambach, "Unified Theory for Gel Electrophoresis and Gel Filtration," *Proc. Natl. Acad. Sci. U.S.A.* **65**, 970 (1970).

7. D. Rodbard and A. Chrambach, "Estimation of Molecular Radius, Free Mobility, and Valency Using Polyacrylamide Gel Electrophoresis," *Anal. Biochem.* **40**, 95 (1971).

8. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31 1977, ORNL-5295, p. 36.

coeluted with the three isoenzymes of CPK, making quantitation impossible. To overcome these difficult problems, a detection system was designed that utilized a tiny (2- by 17-mm) reactor containing HK and GPDH immobilized on agarose. By employing stream splitting, half of the effluent flow from the separation column (Sephacel, a beaded cellulose) was directed through the microreactor and then through the sample side of a dual-beam uv monitor, while the other half was directed through the reference side of the monitor. This enabled continuous self-blanking of the sample for its endogenous uv-absorbing (340-nm) constituents, with only the enzymatic activity due to CPK isoenzymes being detected. Separations were accomplished in ~30 min, and detection of CPK activity in normal sera was demonstrated.

Development of the Centrifugal Fast Analyzer

Development efforts on the portable Centrifugal Fast Analyzer (CFA) were rewarded by the granting of an I-R-100 award to this new instrument by the magazine *Industrial Research* in 1977. Additional development resulted in improved temperature control and diminished electronic noise in the analog signal.

Engineering development. A modified version of the portable CFA was fabricated and delivered to the National Institute of Environmental Health Sciences. This instrument was designed to be coupled to an external microcomputer with vast data storage, a cathode-ray tube (CRT) for graphical presentation of absorbance-vs-time data, and a hard-copy unit. The external computer utilized for this system was the DEC 11V03 with 20K words of core memory and dual discette drives having 65K words of storage on each discette. Software was developed for this system in FOCAL language and included several CRT graphics programs, linear regression, and other useful rate and equilibrium analysis programs. A quadratic interpolation program was developed to compute the precise time that each individual cuvette was monitored, and this unique time measurement was used in linear regression to obtain rate data for fast chemical reactions (measurements obtained for each revolution starting with the first).

An inertial-impedance rotor was tested for its ability to transfer fluids rapidly and mix binary solutions efficiently using only acceleration forces. This rotor, employing a slight modification to the normal sequential rotor, caused the fluid in the innermost cavity (usually a reagent) to change direction en route to the measuring cuvette and

appeared to mix binary solutions as efficiently as did the parallel-channel rotor. The principal advantage of the inertial-impedance rotor over the parallel-channel rotor is that it can be loaded on the automated rotor loading station, whereas the parallel-channel rotor cannot.

6.3 ENVIRONMENTAL STUDIES

During this report period, our efforts relative to the development of environmental monitors, the determination of antifoulant effects on organic constituents in once-through and recirculating cooling waters, and the determination of disinfectant effects on wastewaters were continued. In addition, ORNL jointly sponsored the Second Conference on Water Chlorination: Environmental Impact and Health Effects with DOE and the U.S. Environmental Protection Agency.

Environmental Monitoring

Comprehensive monitoring of the toxic products and wastes of energy production technologies is an important component of the development and deployment of these technologies. This program, therefore, is concerned with developing new instrumentation for various in-plant monitoring applications. Two such instruments are being developed: (1) a portable, fluorescence-based spotter for polycyclic aromatic hydrocarbon (PAH) contamination on work area surfaces, and (2) a multisegment scintillation flow cell for use as a detector in chromatographic radionuclide separations systems to monitor waste streams from nuclear facilities.

A prototype of the portable fluorescence spotter, shown schematically in Fig. 6.1, has been constructed and was tested successfully using 15- μ g spills of perylene, fluoranthene, and POPOP [1,4-bis-2(5-phenyloxazolyl) benzene]. The device uses beam modulation with synchronous detection of fluorescence to extract the fluorescent signal from more intense background illumination. This instrument can also distinguish between the fluorescence of organic compounds and the luminescence of some inorganic materials, such as uranium compounds, whose excited-state lifetimes are comparable to the beam modulation period. Construction of a portable electronics package to complement this unit and field testing of an advanced version in DOE coal research facilities are being pursued.

The need for a chromatographic scintillation detector that provides both good peak resolution and the desired peak enhancement, achieved via long data

Fig. 6.1. Phototype spotter head.

accumulation periods, can be met by the multicellular flow scintillation counter (MCSC) under development. The MCSC is conceptually based on the position-sensitive scintillation detector (PSSD), which has been assembled and tested.⁹ The PSSD, which consists of a rod of scintillation plastic coupled to photomultipliers at both ends, encodes the position of a radioactive sample from the amplitudes of coincident scintillation pulse pairs detected in the photomultipliers. Using this position-encoding method, the MCSC will track multiple fluid segments and simultaneously accumulate the total counts from each.

Environmental Effects of Antifoulants

Chlorine is the principal biocide used for anti-foulant treatment of cooling systems in electric power generating plants.^{10,11} Nonvolatile chloroorganics are formed during the chlorination of process effluents and once-through cooling-water systems;¹¹ however, relatively little information exists concerning the formation of volatile chloroorganic compounds during the chlorination of once-through and recirculating (cooling-tower) cooling-water systems. In this study,^{12,13} three cooling systems were

investigated, namely, the cooling-tower systems at the Oak Ridge Gaseous Diffusion Plant and the High Flux Isotope Reactor, and the once-through cooling system of the Kingston Steam Plant, Kingston, Tennessee, including the adjacent rivers.

9. W. W. Pitt, Jr., and J. E. Mrochek, *Experimental Engineering Section Semiannual Progress Report for the Period Oct. 1, 1977, to Mar. 31, 1978*, Sect. 3.32, ORNL TM-6377-VI (in preparation).

10. R. M. Block and G. R. Helz, "Proceedings of the Chlorination Workshop," *Chesapeake Sci.* 19, 97-160 (1977).

11. R. L. Jolley, ed., *Water Chlorination: Environmental Impact and Health Effects*, vol. 1, p. 439, Ann Arbor Science Publishers, Ann Arbor, Mich., 1978.

12. R. L. Jolley, R. B. Cumming, W. W. Pitt, F. G. Taylor, J. E. Thompson, and S. J. Hartmann, "Ecological Impact of Chloroorganics Produced by Chlorination of Cooling Tower Waters," in *the Proceedings of the Symposium on Microbiology of Power Plant Effluents*, ed. R. M. Gerhold and H. F. Bernhard, University of Iowa Press, Iowa City, Iowa (in press).

13. R. L. Jolley, W. W. Pitt, F. G. Taylor, S. J. Hartmann, G. Jones, and J. E. Thompson, "An Experimental Assessment of Halogenated Organics in Waters from Cooling Towers and Once-through Systems," in *Water Chlorination: Environmental Impact and Health Effects*, vol. 2, ed. R. L. Jolley, H. Gorchov, and D. H. Hamilton, Jr., Ann Arbor Science Publishers, Ann Arbor, Mich. (in press), pp. 695-705.

The volatile trihalomethanes, chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), and chlorodibromomethane (CHBr_2Cl), are formed during the chlorination of cooling waters, in both closed-cycle and once-through systems. Analytical data and trihalomethane production estimates are presented in Table 6.1 for the cooling-tower systems. The feedwater for the ORGDP and HFIR cooling towers contained 86 to 137 ppb chloroform, the major portion of which was apparently lost to the atmosphere during cycling. The chloroform content of the HFIR tower basin water is ~ 1 ppb, except for one day each week when sufficient chlorine is added to increase the chlorine residual to a calculated 2 ppm. The chloroform concentration in the samples collected from the HFIR tower basin immediately after chlorine addition measured 37 to 38 ppb; however, analyses of samples collected 2 hr later showed only 6.2 ppb. Thus the major portion of the chloroform is lost rapidly to the atmosphere. Presumably the other trihalomethanes were also volatilized, since they were either undetected or present in much lower concentrations in the basin water than in the feedwater. As indicated in Table 6.1.

Table 6.1. Production and loss of trihalomethane concentrations from chlorinated cooling waters in HFIR and ORGDP

	HFIR	ORGDP
Cooling capacity, MW(e)	121	2060
Cooling water		
Flow rate, gpd	37×10^6	324×10^6
Makeup, gpd	1.0×10^6	9.0×10^6
Chlorine (feed), ppm	0.5	1.0
Chlorine (continuous), ppm		0.3-0.5
Chlorine (weekly), ppm	2	
Feed or makeup water		
Chloroform, ppb	120-137	86
Bromodichloromethane, ppb	5-15	7
Chlorodibromomethane, ppb	0.2-0.4	1
Bromoform, ppb	0.1	ND ^a
Tower basin water		
Chloroform, ppb	1-38 ^b	12-31 ^c
Bromodichloromethane, ppb	0.2-1.6	0.9-3
Chlorodibromomethane, ppb	ND ^a	1
Bromoform, ppb	ND ^a	ND ^a
Chloroform production, lb/day	~ 1.1	~ 6.5
Chloroform loss, lb/day	~ 0.5	~ 4.9
Bromodichloromethane production	Trace	Trace
Chlorodibromomethane production	Trace	Trace

^aNot detected.

^bChlorinated weekly to 2-ppm calculated chlorine dose.

^cChlorinated continuously to 0.5-ppm chlorine residual.

the calculated annual production and loss of chloroform from the two cooling-tower systems amount to >1 ton.

Table 6.2 indicates the sampling sites and trihalomethane concentrations determined for the Kingston Steam Plant and its adjacent waterways.

Table 6.2. Analysis of water samples taken at designated sites for the Kingston Steam Plant and its adjacent waterways

No.	Site Description	Concentration (ppb)			
		CHCl_3	CHBrCl_2	CHBr_2Cl	CHBr_3
1	Skinner Dam (Emory River)	1.0	ND ^a	ND ^a	ND ^a
2	Pump station	1.6	ND ^a	ND ^a	ND ^a
3	Condenser No. 2	20.5	1.3	0.4	ND ^a
4	Discharge (50 m)	5.2	0.2	ND ^a	ND ^a
5	Discharge channel	0.6	0.2	ND ^a	ND ^a
6	Discharge embayment	5.0	0.3	ND ^a	ND ^a
7	Clinch River (1.5 km below site No. 6)	2.5	0.2	ND ^a	ND ^a
8	Confluence Clinch and Tennessee Rivers (3 km below site No. 7)	1.1	0.2	ND ^a	ND ^a

^aNot detected.

Chlorination with even the low concentrations of chlorine used in this once-through cooling system (0.2 ppm free chlorine and 0.5 ppm total chlorine residual) produced significant concentrations of chloroform. The Kingston Steam Plant, rated at 1723 MW(e),¹⁴ is a coal-fired electric power generating plant that uses 100,000 to 125,000 gal of cooling water per minute for each of its nine condensers. Each condenser is chlorinated 30 min daily. The condenser tubes are chlorinated individually, in a sequential manner, so that the discharged chlorinated coolant is diluted with unchlorinated water in the discharge canal.¹⁵ The chloroform production for this plant was calculated to be ~ 4.5 to 5.4 lb per day, or nearly 1 ton per year. This occurs despite the high-quality water used in the cooling system and the minimal use of chlorine for antifoulant treatment. The low value for site 5 cannot be explained at this time, although it may be an

14. C. H. Weaver, Tennessee Valley Authority, personal communication to R. L. Jolley, 1977.

15. A. Ridings, Tennessee Valley Authority, personal communication to R. L. Jolley, 1977.

analytical error due to a bubble in the headspace. The values downstream are real and apparently due, at least partially, to the cooling waters. These values are higher than expected, considering the dilution of the cooling waters by the river waters. Samples taken from the relatively pristine Walker Branch on the DOE reservation and from the Clinch River at Melton Dam, ~20 miles upstream, contained 0.06 ppb chloroform.

National chlorination conference. Approximately 370 scientists attended the Second Conference on Water Chlorination: Environmental Impact and Health Effects, which was held in Gatlinburg, Tennessee, on Oct. 31–Nov. 4, 1977. Sixty-seven technical papers were presented at the conference, which was jointly sponsored by DOE, EPA, and ORNL. The conference was conducted and coordinated by the Environmental Research Group, and the *Proceedings* were edited by personnel from each of the sponsoring agencies.¹⁶

Chemical Effects of Disinfectants

The objective of this program, funded by the EPA, is to characterize the nonvolatile organics in

wastewater effluents which have been disinfected with either chlorine, ozone, or ultraviolet light. The organics will be characterized chemically; that is, they will be identified and quantified where possible and screened for mutagenic activity.

A chromatographic comparison of the chemical effects of chlorination, ozonation, and uv irradiation on the uv-absorbing constituents in the primary effluent revealed significant chemical differences between the several disinfectants (Figs. 6.2–6.4). In these figures, the chromatograms for the uv-absorbing constituents in the control sample are shown with the chromatograms of the disinfected samples for comparison purposes. In Fig. 6.2 the undisinfected control sample (185,000 coliform per ml) is compared with a primary sample chlorinated at the Oak Ridge West Wastewater Treatment Plant to a chlorine residual of 0.9 ppm (0 coliform per ml). Some chromatographic peaks are apparently destroyed by chlorination, and some are formed during disinfection with chlorine. As previously reported, some of these constituents formed during chlorination are chloroorganics.¹⁷ In Fig. 6.3 the undisinfected control sample is compared with the primary

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

17. R. L. Jolley, "Chlorine-Containing Organic Constituents in Chlorinated Effluents," *J. Water Pollut. Control Fed.* 47, 601–18 (1975).

Fig. 6.2. Chromatograms of uv-absorbing constituents in chlorinated primary effluent (chlorine residual, 0.9 ppm) compared with undisinfected control primary effluent. Chlorinated sample, 0.77 ml of 800-fold concentrate; unchlorinated sample, 0.77 ml of 700-fold concentrate.

Fig. 6.3. Chromatograms of uv-absorbing constituents in ozonated primary effluent (ozone dosage, 6.9 mg/ml) compared with undisinfected control primary effluent. Ozonated sample, 0.77 ml of 790-fold concentrate; unozonated sample, 0.77 ml of 700-fold concentrate.

Fig. 6.4. Chromatograms of uv-absorbing constituents in uv-irradiated primary effluent (27.5 mJ/cm²) compared with undisinfected control primary effluent. UV-irradiated sample, 0.77 ml of 660-fold concentrate; unirradiated sample, 0.77 ml of 700-fold concentrate.

sample after ozonation in the laboratory with 6.9 mg of ozone per liter of effluent (15 coliform per ml). The high oxidation potential of ozone is clearly evident by the destruction of most of the chromatographic peaks. Because the effluent chlorination was conducted at the waste treatment plant, the exact stoichiometry of the disinfection by chlorination

cannot be compared with that by ozonation. However, it is estimated that the ozone dosage was ~50% greater than the chlorine dosage on a molar basis. In Fig. 6.4 the undisinfected control sample is compared with the primary sample after disinfection with 27.5 mJ/cm² of uv irradiation (0 coliform per ml). The apparent absence of chemical effect on the

absorbing constituents is clearly evident from the close agreement between the two chromatograms. This lack of chemical effect by uv irradiation at levels which disinfect the wastewater may be highly significant and is being investigated further. All samples are being tested for mutagenic activity. Details of the experimental methodology and data for this series of disinfections and chromatographic runs are presented elsewhere.^{18,19}

Characterization of Aqueous Effluents

Sampling of aqueous streams related to various coal conversion technologies is under way. Such streams include those of two external, full-scale operations, as well as two in-house, bench-scale processes. The latter streams are those of the Chemical Technology Division Bench-Scale Hydrocarbonization Experiment (BSHE) and the tapered fluidized-bed bioreactor (TFBBR), which uses the aqueous scrubber product of the BSHE as feed. The external streams include those of the waste treatment plants and/or downstream river samples of a coal chemical manufacturing plant and a coking facility.

Sampling of the BSHE serves a twofold purpose: (1) to provide process development feedback and (2) to determine the specific products resulting from the use of various types of coal. The latter involves the identification of products resulting from the utilization of bituminous and subbituminous coals, as well as treated and untreated coals.

The aqueous scrubber product from a particular BSHE run (HC-25; Wyodak, untreated, subbituminous coal) was subjected to a process water cleanup operation utilizing the TFBBR. This biodigester-centered system is being studied for its efficiency in removing organic contaminants or at least converting them to less noxious products. Efforts have also been made to identify those products which are refractory to sorption-type removal processes and to identify those new products formed by other cleanup steps such as ozonation or microbiological processes. Samples here include (1) raw, untreated HC-25 scrubber water; (2) acidified, filtered, ammonia-

stripped, diluted, and pH-adjusted water; and (3) postbioreactor effluent.

Several samples have been examined from the waste treatment facility of a coal chemical plant. These profile samples include: (1) feedwater to the extractor (ethylbenzene extraction), (2) biodigester tank feed, and (3) clarifier effluent. The purpose of such "before-and-after" sampling is to determine the PAH removal efficiency in the subject wastewater process train, as well as the PAH and phenolic-type refractory organics resulting in this highly specialized biosystem. High-pressure liquid chromatography utilizing three detector systems (uv, 254 and 280 nm; cerate oxidimetry; and native fluorescence) indicates significant organic removal at each step, as well as several refractory peaks of interest.

Finally, sampling is being carried out at a coking plant biotreatment facility, including nearby river and stream profiling. Here, rather than transporting large (22-liter) aqueous samples back to the laboratory, the utility of portable (1 x 6 in. and 1 x 12 in.), open-pore polyurethane, foamed cartridges for field preconcentration is being examined. The voluminous samples are passed through these columns, which facilitate low back-pressure gravity flow, and are then sealed and refrigerated until subsequent elution and identification of trapped components in the laboratory.

6.4 ENVIRONMENTAL CONTROL TECHNOLOGY FOR COAL CONVERSION PROCESSES

As a companion program to our continuing efforts in the development of a variety of coal conversion processes, we have a number of ongoing projects to study the control of the effluents from these processes. During this report period, our effort was concentrated in the areas of environmental control technology assessment, screening tests of aqueous waste treatment methods, and the development of a field monitoring and assessment program.

Assessment of Environmental Control Technology for Aqueous Wastes

Work continued on defining the wastewater problem for coal conversion processes. The wastewater streams were identified, a literature survey was conducted, and pertinent research and development personnel were contacted in order to estimate the sources, quantities, and compositions of the aqueous effluents. Although no federal guidelines exist for coal conversion plants, the effluent guidelines of

18. R. L. Jolley, *Characterization of Nonvolatile Organics in Disinfected Wastewater Effluents, Progress Report for Period Dec. 1 31, 1977*, prepared for the U.S. Environmental Protection Agency.

19. R. L. Jolley, *Characterization of Nonvolatile Organics in Disinfected Wastewater Effluents, Progress Report for Period Jan. 1 31, 1978*, prepared for the U.S. Environmental Protection Agency.

related industries were studied in order to anticipate future effluent standards for coal conversion plants and the impact they may have.

A number of wastewater treatment methods have been assessed for their applicability to the cleanup of wastewater from coal hydrocarbonization. Especially of interest is the impact of these methods on the areas of concern which were identified earlier, namely, trace elements, PAHs, and phenolics.

Biological oxidation shows a very high potential for application to hydrocarbonization wastewater. Numerous experimenters have shown that the level of phenolics, the main contaminant in hydrocarbonization wastewater, can be reduced by as much as 99.9%, to as low as 20 ppb.^{20,21} This method appears to be capable of economically removing large quantities of phenolics from hydrocarbonization wastewater; however, it can remove only marginal quantities of trace metals and PAHs. Costs should approximate \$0.33 to \$0.44 per kg of phenol (\$0.15 to \$0.20 per lb of phenol), or \$1600 to \$2600 per 10⁶ liters of effluent (\$6000 to \$10,000 per 10⁶ gallons of effluent).²²

Sorption on activated carbon is generally more expensive, with costs estimated from \$1.10 to \$2.20 per kg of phenol removed (\$0.50 to \$1.00 per lb of phenol removed).²² Sorption appears to have two possible uses: (1) treatment and recovery of concentrated wastes and (2) "polishing" of more dilute wastes for reuse or discharge. The first application appears to suffer from problems associated with moving and regenerating large quantities of activated carbon; the second application presents fewer complications. In addition, coal conversion process char shows a potential²³ for sorbing wastes, and spent char could be burned or gasified, thereby saving the cost of regeneration and recovering the fuel value of the dissolved wastes. The fate of many of the trace metals and large-molecular-weight organics is still somewhat uncertain.

Ozonation is an even more costly way of removing large amounts of phenol. Present indications are that the complete oxidation of hydrocarbonization wastewater cannot be achieved economically with ozone.²⁴ Ozonation may, however, have some advantage if a very small amount of hydrocarbons needs to be treated, as in a final polishing step, or if only a small amount of degradation is needed, as would be the case when only the aromatic ring structure is to be cleaved and not completely oxidized to carbon dioxide and water. The cost of a single treatment would be \$1.40 per kg of phenol (\$0.65 per lb of phenol), assuming 2.6 g of ozone is required per gram of phenol (2.6 lb of ozone per lb of phenol) at a cost of \$0.55 per kg of ozone (\$0.25 per lb of ozone).

Some investigators have shown that as much as 80% of the chemical oxygen demand of some wastewater streams may be contained in particles, colloidal or larger in size, and that up to 50% of the TOC in the effluent of biological treatment plants may be colloidal.²⁵ The coagulation and flocculation of these particles can lower dramatically the demand on downstream treatment steps. Costs for coagulation and flocculation vary tremendously, depending on the wastewater to be treated, but assuming a representative dose of 0.33 kg per 10³ liters of effluent (3.3 lb per 10³ gal of effluent) and a price of \$50 per metric ton of lime (including capital equipment costs), a cost of \$18 per 10⁶ liters of effluent (\$83 per 10⁶ gal of effluent) is obtained.²⁶

Solvent extraction has attracted the attention of investigators for many years. A variety of solvents for phenol removal in both typical solvent extraction systems and dual solvent processes (polar solvent-volatile solvent) have been investigated. Although high distribution coefficients have been reported for many of these systems, Lurgi's Phenolsolvan process appears to be the only one that is commercially available. Solvent extraction seems to offer an advantage only in cases where a moderate amount of reduction in the phenol content is needed in order to allow an additional waste treatment to operate or when a salable crude phenol can be produced. One study indicated that if the value of the recovered

20. J. Barker and R. Thompson, *Biological Removal of Carbon and Nitrogen Compounds for Coke Plant Wastes*, EPA-R2-73-167, Washington, D. C. (1973).

21. G. J. Capestrany et al., "The Influence of Sulfate on Biological Treatment of Phenol-Benzaldehyde Waste," *J. Water Pollut. Control Fed.* 49(2), 257 (February 1977).

22. R. E. Rosford et al., "Phenols, a Water Pollution Control Assessment," *Water & Sewage Works* 123(3), 96-99 (March 1976).

23. A. J. Forney et al., *Internal Quarterly Technical Progress Report* April-June 1975, PERC/QTR-75/2; July-September 1975, PERC/QTR-75/3; October-December 1975, PERC/QTR-75/4; January-March 1976, PERC/QTR-76/1; April-June 1976, PERC/QTR-76/2; and July-September 1976, PERC/QTR-76/3.

24. H. R. Eisenhauer, "Dephenolization by Ozonolysis," *Water Res.* 5(7), 467 (July 1971).

25. D. F. Bishop et al., "Studies on Activated Carbon Treatment," *J. Water Pollut. Control Fed.* 39, 188 (1967).

26. R. L. Culp and G. L. Culp, *Advanced Wastewater Treatment*, Van Nostrand, New York, 1974.

phenol is $>\$660$ per 10^6 liters of wastewater ($\$3000$ per 10^6 gal of wastewater), then recovery is promising.²⁷ This is equivalent to $\$0.15$ per kg of phenol ($\$0.07$ per lb of phenol) compared with bulk prices of $\$0.57$ per kg of phenol ($\$0.26$ per lb of phenol). Upgrading crude phenol may, however, prove to be quite expensive.

Another area of interest includes membrane processes such as reverse osmosis, ultrafiltration, and electrodialysis. These membrane processes, although considered expensive, may be useful in upgrading wastewater for in-plant reuse. Ultrafiltration and reverse osmosis have shown phenol reductions in the range of 50 to 95%;²⁸ however, these values will still leave phenol concentrations which exceed the anticipated regulations. In addition, a concentrated stream will be produced, and its disposal will need to be handled. It is difficult to estimate the economics involved in membrane processes. Various reverse-osmosis vendors have optimistically discussed numbers in the $\$440$ to $\$1320/10^6$ -liter range ($\$2000$ to $\$6000/10^6$ -gal range). However, these processes produce a concentrated, mixed phenol-water stream that requires additional processing and a dilute aqueous stream that may still contain unacceptable levels of organics.

27. J. P. Earhart et al., "Recovery of Organic Pollutants via Solvent Extraction," *Chem. Eng. Prog.* 73(5), 67-73 (May 1977).

28. S. L. Klemetson, "Treatment of Phenolic Wastes," presented at Environmental Aspects of Fuel Conversion Technology III, Hollywood, Fla., Sept. 13-16, 1977.

A summary of the wastewater treatment methods discussed in this section is presented in Table 6.3.

Aqueous Waste Treatment Studies

One activated charcoal and four ion exchange resins were screened according to their ability to remove PAHs from aqueous solutions. Tests were run with 40 ml of PAH solution and 1 ml of carbon, 0.1 g of resin, or 1.0 g of resin and agitated for either 4 or 16 hr. Concentrations of the PAHs tested varied from 0.002 ppm for benzantracene to 3.0 ppm for naphthalene. These concentrations used were roughly determined by their respective solubility in water, and the results are summarized in Table 6.4. The sulfonated polystyrene resin, Amberlite IR-120, appears to absorb only phenanthrene and no other PAHs. The two trimethylammonium chloride resins, Amberlite IRA-400 and Dowex AG-MP-50, removed most of the PAHs, except when only 0.1 g of IRA-400 was used. Dowex AG-MP-50 is a macroporous version of Amberlite IRA-400. Although adsorption levels may indicate an interest in some of these resins, the 4-hr results were not listed due to significant adsorption.

Several samples of char produced from the hydrocarbonization of Wyodak subbituminous coal at a temperature of 560°C and a pressure in the range of 1800 to 2070 kPa (260 to 300 psig) for 30 min have been tested for their ability to remove phenolics from aqueous streams. This char is $\sim 80\%$ carbon and 12% ash. In a 50-ml column with flow rates of 6 ml/min containing 200 ppm phenol, breakthrough times for the phenol occurred in <10 min, as compared with 50 hr observed when activated charcoal was used.

Table 6.3. Summary of environmental control technology for aqueous wastes

	Biological oxidation	Adsorption	Ozonation	Congulation-flocculation	Solvent extraction	Membrane processes
Potential applicability	High	High	Moderate	High	Moderate	Low
Economics	$\$0.33 - \$0.44/\text{kg phenol}$ ($\$0.15 - \$0.20/\text{lb}$) $\$1600 - \$2600/10^6$ liters ($\$6000 - \$10,000/10^6$ gal)	$\$1.10 - \$2.20/\text{kg phenol}$ ($\$0.50 - \$1/\text{lb}$)	$\$1.40/\text{kg phenol}$ ($\$0.65/\text{lb}$)	$\$18/10^6$ liters ($\$83/10^6$ gal)	$\$0.15/\text{kg phenol}$ ($\$0.07/\text{lb}$) $\$460/10^6$ liters ($\$3000/10^6$ gal)	
Raw materials	None to little	Charcoal or other sorbers	None	Lime or other agents	Solvent	Membrane material
Process compatibility	Moderate to high	High	High	High	Moderate	Low to moderate
Operating conditions	Moderate temperature	Moderate, except for regeneration	Little known	Moderate	Moderate	Moderate
State of development	High	Moderate to high	Fair	High	Moderate to high	Moderate
Additional environmental problems	Disposal of sludges	Disposal of spent sorber	No trace element removal	Disposal of sludges - heavy metal sludges	Little to none if product soluble	Concentrated aqueous waste stream
Energy requirements	Low	Low (except for regeneration)	High	Low to moderate	Moderate to high	Moderate to high
Process availability	High	High	Moderate	High	Moderate to high	Moderate to high

*An aqueous stream having a contaminant level that exceeds the regulation will require additional treatment; a product stream will need to be disposed of if not salable.

Table 6.4. Fraction of polycyclic aromatic hydrocarbon removed

Concentration (ppm)	Activated carbon (1 mg)		Resins (16 hr)				
	4 hr	16 hr	Chelex 100 (0.1 g)	IR-120 (1 g)	IRA-400 (1 g)	IRA-400 (0.1 g)	AG-MP-50 (1 g)
Naphthalene:							
0.3	0.79	0.88	0.69		0.83	0.40	
3.0	0.78	0.96	0.22	0.58	0.92	0.41	
Anthracene:							
0.0375	0.73	0.87				1.00	0.80
0.075	0.50	0.90				0.97	0.75
Benanthracene:							
0.002	0.88	0.94				1.00	
0.01	0.90	0.95				0.90	
Phenanthrene:							
0.232	0.91	0.90		0.78	1.00	0.97	1.00
1.16	0.43	0.77		0.93	1.00	0.84	0.92

Other types of coal conversion char or treated char might show improved adsorption characteristics.

Screening tests were conducted on the ability of several lignitic coals to remove PAHs. With flow rates of 1.2 ml/min of 1.16-ppm phenanthrene solution and 6 ml/min of 3-ppm naphthalene solution passing through a 1-cm-diam column containing 50 ml of lignite, the breakthrough times were 170 and 48 hr respectively. These loadings are ~0.5 to 2.0 mg per gram, and although activated charcoal has a capacity that is 30 to 50 times higher, the cost of lignite and the ability to burn or recycle the coal to a coal conversion facility may make the coal sorbent an attractive alternative.

Work has continued on that treatment of phenolic wastewater from the ORNL hydrocarbonization experiment using the TFBBR. Operating with a feed having a phenol concentration ranging from 30 to 60 ppm (achieved through the dilute feed mode or effluent-recycle mode of operation) and feed rates of from 400 to 700 ml/min, the TFBBR has achieved phenol reductions of ~99.9%. This corresponds to phenol degradation rates of 7 to 10 kg of phenol per day per m³ of reactor volume. During these tests, some buildup of biomass did occur, so that ~16 to 20% of the bed needed to be removed and replaced each day. Screening tests with refractory xylenols known to be present in coal conversion wastewaters indicate that biological degradation occurs at a reduced rate compared with phenol degradation, which explains the residual contaminant levels.

Ozonation was used to degrade both residual phenols and PAHs from wastewaters obtained from the ORNL hydrocarbonization experiment and from

a coal tar chemical plant. Both of these waters had previously undergone biological treatment. Approximately 99% of the residual phenol and 22 to 97% of the remaining PAHs were degraded. Ozone dosages of 0.01 to 0.14 kg of ozone per 10³ liters (0.08 to 1.40 lb of ozone per 10³ gal) were used, although only some 10% of the ozone was dissolved and thus available for reaction.

Field Monitoring and Assessment

Oak Ridge National Laboratory was requested by DOE to develop for consideration an integrated, comprehensive environmental and health plan for the Gasifiers in Industry Program. During a workshop held by DOE, three gasifiers were selected for consideration and plan development; initial emphasis has been placed on the University of Minnesota-Duluth Project (UMD) because of its present state of construction. Work has also begun on the Pike County Project at Pikeville, Kentucky.

Progress over the past year on process sampling and monitoring work relating to both the UMD and the Pike County projects is reported in this section. Sampling and monitoring of the process must provide for characterization of feed, intermediate, recycle, product, and waste streams and must also be adequate for evaluating the efficiency of environmental control systems and for characterizing the process.

Sample port locations were designated and incorporated into the design and construction phases of the UMD plant. A flow schematic of the UMD plant is given in Fig. 6.5. Included on the schematic

Fig. 6.5. Flow schematic and sampling points for the University of Minnesota-Duluth heating plant.

are all of the specified sampling points. On-line gas analysis will be performed by gas chromatographs (GCs) and dedicated SO_2 and NO_x analyzers. The GCs will monitor sampling points 13, 17, 18, and 20. The SO_2 and NO_x analyzers will monitor the main stack at sample point 18. Specifications for the gas analysis equipment were written and are out for competitive bids. A minicomputer is being purchased for installation at UMD which will log data from the gas analysis equipment as well as process information such as temperatures, pressures, flow rates, and levels. The process data will be recorded on magnetic tape for transmittal to UM-Twin Cities and ORNL. Specifications were also written for the minicomputer, and competitive bids have been received from several vendors. Bid evaluation is being conducted, prior to final awarding of the contract.

Preliminary work on process sampling and monitoring has begun on the Pike County gasifier; a flow diagram of the gasifier is given in Fig. 6.6. Included in this figure are the tentative locations for the sampling ports.

Control of Hydrocarbon and Carbon Monoxide Emissions in the Tail Gases from Coal Gasification Facilities

A study was made of the economics of various alternative methods for controlling emissions of

carbon monoxide and nonmethane hydrocarbons in the tail gases from a Lurgi substitute natural gas (SNG) plant. Control of sulfur emissions was excluded from the scope of this study. Processes examined for decontaminating the tail gases included recovery and recycle methods, as well as those which convert the contaminants to harmless products. The most recently proposed EPA emission standards for carbon monoxide and nonmethane hydrocarbons were used as upper limits for the residual contaminants in the treated effluent. Limited assessments were made of the technical and economic feasibility of the ten processes given in Table 6.5. Of these processes, 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. Total capital and operating costs on a 20-year discounted cash flow basis with 100% equity financing and 12% annual after-tax return on investment were estimated to be 4¢ per 10^6 Btu of SNG for the coal-fired boiler and 5¢ per 10^6 Btu for the catalytic case. However, the uncertainties in the costs are greater than the indicated cost differentials. Incineration in a gas-fired boiler using medium-Btu gas was estimated to be 11¢ per 10^6 of SNG.

Fig. 6.6. Flow schematic and sampling points for Pike County gasifier (Pikeville, Ky.).

Table 6.5. Approximate cost of hydrocarbon and carbon monoxide emissions control for a Lurgi-type SNG plant^a

Process No.	Description	Approximate cost (\$/10 ⁶ Btu of SNG) ^b	Technical feasibility for this application
1	Incineration in a coal-fired boiler	4	Good
2	Incineration in a boiler using desulfurized medium-Btu gas	11	Good
3	Catalytic oxidation	5	Unproved
4	Aqua Claus process	c	Unproved
5	Hot carbonate scrubbing	42	Doubtful
6	Cold water scrubbing	56	Doubtful
7	Cuprous ammonium solution absorption	16	Doubtful ^d
8	Adsorption	c	No practical adsorbent known
9	Cryogenic separation	64	Technically feasible
10	Porous membrane separation	c	Doubtful

^aMost of the processes listed here have not been demonstrated in this type of application and cannot be considered available for commercial use.

^bCost includes both capital and operating charges.

^cInsufficient data to permit cost estimation in this application.

^dThis process removes only carbon monoxide.

7. Special Isotope Production and Separations

7.1 TRANSURANIUM-ELEMENT PROCESSING

The Transuranium Processing Plant (TRU) and the High Flux Isotope Reactor (HFIR) were built at ORNL to provide transuranium elements for research. At TRU, target rods irradiated in the HFIR are processed for the separation, recovery, and purification of the heavy actinide elements, which, in turn, are distributed to laboratories throughout the country for their research work with these elements. TRU is the production, storage, and distribution center for the heavy-element research program in the United States. 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. All transuranium-element target materials to be irradiated in the HFIR are prepared in TRU. Such materials include recycled americium and curium in HFIR targets and heavy isotopes in many special forms, including "rabbits" for short-term irradiation.

TRU Operations

The functions of TRU are to recover the transuranium elements and to distribute them to researchers. Since it began operation in 1966, TRU has been the only source of significant quantities of berkelium, californium, einsteinium, and fermium in the United States.

The purposes of this section are to report the production 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 semiannual reports on production, status, and plans.^{1,2}

Status. The primary role of TRU as a supplier of research materials is expected to remain at the present level. During a typical year, 20 HFIR targets containing 200 g of curium are fabricated and irradiated, and two chemical processing campaigns are made to recover transuranium elements from

irradiated targets; 60 mg of ^{249}Bk , 600 mg of ^{252}Cf , 3 mg of ^{253}Es , and 1 μg of ^{257}Fm are produced, and 50 product shipments are made. The present supply of curium feed material, all of which is contained in 34 HFIR targets, is sufficient to sustain operation at the present level for two or three years. Additional feed material (either curium or ^{243}Am) is being procured from other programs at ORNL and the Savannah River Plant (SRP).

Production, shipment and fabrication. During this report period. Campaigns 53 and 54 were made to process a total of 26 HFIR targets. Table 7.1 provides a comparison of the amounts of key isotopes in the products from these campaigns with the total amounts produced at TRU in 11 years of previous operation.

During product finishing operations this year, we recovered and purified 181 μg of ^{253}Es and 75 mg of ^{244}Cm ; these are the daughter products of ^{253}Cf and ^{252}Cf . Forty-one product shipments were made to researchers throughout the country. Thirteen targets were fabricated to recycle curium to the HFIR.

Processes and equipment. Cooling periods for irradiated HFIR targets processed at TRU are kept short to enhance the yields of ^{253}Es (half-life = 20.5 days). Because of this short cooling time, the group of targets processed during a TRU campaign typically contains several hundred curies of ^{131}I when the targets are processed. Several methods for removing radioiodine from the off-gas have been tested and used at TRU. For the past six years, a Hopcalite—charcoal system has been used in the vessel off-gas system (~450 cfm). (Hopcalite is an $\text{MnO}_2\text{-CuO}$

1. I. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June 30, 1977*, ORNL-5358 (December 1977).

2. I. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1977*, ORNL-5415 (in press).

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

Time period	April 1977 to March 1978	August 1966 to March 1977
Number of years	1	11
Number of target campaigns	2	36
Number of targets processed	26	409 ^a
Amounts of key isotopes recovered		
²⁴² Pu	0	141 g
²⁴³ Am	0	248 g
²⁴⁴ Cm	48 g	1783 g
²⁴⁹ Bk	68 mg	357 mg
²⁵² Cf	674 mg	3177 mg
²⁵³ Es	3.5 mg	12.9 mg
²⁵⁷ Fm	1.2 μ g	7.6 μ g

^aNumber of targets includes 212 HFIR targets, 176 SRP slugs and targets, and 21 SRP Pu-Al tubes.

mixture used to catalyze the oxidation of organic materials to compounds that are either not sorbed on charcoal or are less strongly sorbed than iodine.) Although this system has worked well and releases of ¹³¹I have been low, about 5 to 25 Ci of ¹³¹I was sorbed in the system during each campaign; this constituted a potential for accidental release. A scrubber system was installed in the dissolver off-gas system (~0.25 cfm) to remove the bulk of the ¹³¹I and reduce the amount sorbed in the Hopcalite-charcoal system.

During TRU Campaigns 53 and 54, the dissolver off-gas was scrubbed with hyperazeotropic nitric acid (the Iodex process). Equipment performance was satisfactory, and the amount of ¹³¹I sorbed in the Hopcalite-charcoal system was significantly less than in previous campaigns. More than 99% of the ¹³¹I in the nitric acid dissolver solution was volatilized and then sorbed into either 21 or 23 M HNO₃ in a six-stage bubble-cap column. Iodine decontamination factors achieved in the column ranged from 1×10^4 to 8×10^4 , or about 5 to 7 per stage. These were the first tests made of the Iodex process at high-activity levels, and the results were consistent with the results of tracer-level tests.

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 ²⁵²Cf.

Fabrication of neutron sources from ²⁵²Cf. Some of the californium recovered at TRU is incorporated

into neutron sources, which are loaned to researchers. Eight sources containing from 0.72 to 16.5 mg of ²⁵²Cf were fabricated this year; seven of these were doubly encapsulated in type 304L stainless steel in a standard TRU configuration (NSD).³ One source was prepared for the Hanford Engineering Development Laboratory in a doubly encapsulated configuration of their design.

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 ²⁵²Cf. These sources are available for reassignment until the appropriate time for reprocessing to recover the ²⁴⁹Cm daughter. During the report period, eight sources were returned and three were reassigned. Eighty-eight sources are now on loan, and six sources containing from 22 μ g to 5.9 mg of ²⁵²Cf are available for reassignment.

Processing of irradiated ²⁴⁴Pu. The chemical processing of a special ²⁴⁴Pu target that was irradiated for two cycles in the HFIR was begun. The purpose of this special project was to enrich a quantity of ²⁴⁴Pu by "burning out" the lighter isotopes of plutonium by irradiation. The chemical processing included a caustic dissolution of the aluminum target rod sections containing the four plutonium pellets, an HNO₃-HF dissolution of the plutonium oxide microspheres, and an anion exchange purification

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

run. Residual solids from the plutonium procedure were given a second treatment with $\text{HNO}_3\text{-HF}$, and the resulting plutonium solution was also purified by anion exchange. The two plutonium product solutions contained 60 and 10 mg of ^{244}Pu , respectively, and rework solutions contained ~ 6 mg of ^{244}Pu . The specific activity of the irradiated plutonium was reduced to $\sim 6.2 \times 10^4$ alpha counts $\text{min}^{-1} \text{mg}^{-1}$ of ^{244}Pu ; this activity is about three times the specific activity of pure ^{244}Pu and about 17 times lower than that of the feed (unirradiated) plutonium. The isotopic analyses of the feed plutonium and the irradiated plutonium are shown in Table 7.2.

Table 7.2. Isotopic analyses of feed and irradiated plutonium

Nuclide	Feed plutonium (at. %)	Irradiated plutonium (at. %)
^{238}Pu	0.001	0.00004 ^a
^{239}Pu	0.003	0.0076 ^b
^{240}Pu	0.305	0.0016
^{241}Pu	0.074	0.0013
^{242}Pu	1.050	0.572
^{244}Pu	98.57	99.41
^{246}Pu		0.0098

^aDetermined by alpha counting.

^bThis is unexpectedly high, possibly due to sample contamination.

Final purification from residual actinides and fission products will be performed after the ^{244}Pu (half-life = 10.85 days) has been allowed to decay.

Purification of ^{243}Am . Many requests have been received through the years for highly purified ^{243}Am ; however, it was not until a new cave liner was installed in junior cave A that suitable facilities became available for this work. Normal production activities in cave A have been delayed to permit production of the highly purified ^{243}Am . A quantity of excellent feedstock that contained 120 ppm ^{241}Am and 0.4% ^{244}Cm (by weight) was available at the SRP from earlier programs; we were asked to remove the curium to less than 5 ppm. The corresponding ^{252}Cf content that will yield a comparable neutron emission rate is 25 parts per trillion parts of americium. Products of this purity can be achieved only in pristine facilities such as the newly relined cave A.

To date, about 10 g of ^{243}Am averaging less than 1 ppm ^{244}Cm has been prepared using ion exchange techniques. This is sufficient to meet current requests. It is anticipated that a similar amount will be

prepared for future needs before the equipment is used for any other purpose. This ultrahigh-quality ^{243}Am is used for neutron cross-section studies, for capture gamma studies, and as an analytical standard.

7.2 ISOTOPIC SEPARATIONS

Stable Isotope Operations

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 commercial and applications research such as analytical instrumentation, atomic clocks, lasers, and nuclear medicine. Seventy new loans, amounting to approximately 2.6 kg of enriched electromagnetically separated isotopes, were made from the RMC during the past fiscal year. During the same period, 2103 sales were made, which accounted for more than 1.2 kg of separated material whose value was more than \$1.3 million. As in past years, more than half of the shipments were made to foreign customers.

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

Isotopic separations of four elements were either completed or in process at the end of the reporting period. Throughout this period, only one segment of separators (eight beta-type units or six 255° separators) was utilized at any given time for production separation. These units were operated on a 5-day, 24-hr basis. Table 7.3 lists these elements along with the approximate percentage of effort expended for each separation, the isotope of primary interest, the estimated quantity collected (based on monitored ion

Table 7.3. Summary of stable isotope production

Element	Annual effort (%)	Major isotope	Quantity (mg)	Assay (%)
Calcium	24.8	46	27	33
Tellurium	40.7	122	48,000	a
Mercury	17.2	196	325	a
Thallium	17.2	203	370,000	a

^aSeparation incomplete.

current), and the isotopic purity of the isotope of major interest. Each of the nuclides listed is used as a precursor for the production of a radioisotope being utilized in nuclear medicine, namely, ^{47}Ca , ^{123}I , ^{197}Hg , and ^{201}Tl . The other isotopes that either were or are being collected concurrently will be available for potential sales or RMC inventories. In addition to the production separations, a special second-pass effort was made to obtain a $\geq 90\%$ assay of ^{70}Zn to satisfy a long-standing RMC requirement. The separation yielded 1645 mg of 99.72% ^{70}Zn .

The continuing efforts to improve operating techniques have been successful for some specific elements. For example, following a research and development study on tellurium, most of the production samples of ^{122}Te showed a higher ^{122}Te : ^{123}Te ratio than in any previous separation. This ratio is very important in determining the quality of the radiopharmaceutical produced when ^{122}Te is used as a target in the production of ^{123}I . In-process modifications with mercury and thallium have led to higher isotopic purities of ^{196}Hg and ^{201}Tl and to higher ion outputs for both elements. New remote-control systems, which allow the calutron supervisor to make all mechanical adjustments from the control room and at the same time provide a readout indicating the position of the receiver, have been installed on the six 255° separators. These systems provide greater optimization of separator run conditions and help maintain these conditions more precisely than can be done by manual operation. The new hardware is expected to reduce start-up time and provide higher-purity isotopes. Similar systems are planned for the remaining separators.

During the year, four new lots of iron isotopes were added to the inventory to fill sales and/or loan requirements. In addition, 33 new lots of five other elements are awaiting release to inventory pending pricing approval by DOE. Seventy-three samples, which had been on loan from the RMC, were reprocessed and returned to the loan pool.

The 180° sector separator was used in preparing ^{16}O targets for research by implantation of the enriched isotope into 20- $\mu\text{g}/\text{cm}^2$ polycrystalline aluminum substrates. To ensure saturation, the implantations were started at a beam energy of 5 keV. The beam energy was then reduced to 2.5 keV, and the substrates were subjected to ~ 1.5 times the calculated ions needed for saturation at each energy.

Separator Research and Development

The thrust of our effort this year has involved the attainment of higher-purity samples of ^{122}Te , ^{201}Tl ,

^{107}Ag and ^{109}Ag , and ^{70}Zn (the latter by a second-pass separation); improvement in both production rate and purity for ^{196}Hg ; and further investigation of changes in existing high-temperature source designs.

A program started last year to improve on past separations of ^{122}Te was continued. Efforts were directed toward problems in three areas: source, vacuum, and collector. Demonstration runs yielded ^{122}Te with an assay of $\geq 97\%$ and $\leq 0.3\%$ ^{123}Te . Initial production runs essentially duplicated these values, but as equipment became dirty, flakes of tellurium fell into collector pockets and contaminated the isotopic sample. To minimize contamination from such flakes, the ^{122}Te ions were collected in a special two-part pocket positioned and shaped so that the front part was a "flake catcher" and the back part was the "ion catcher." A total of 42 samples was recovered from each position; only five "flake catcher" portions yielded $\geq 95\%$ ^{122}Te . By comparison, 25 "ion catcher" portions exceeded 95% ^{122}Te . The total separation yielded a 10-g quantity of the highest-assay ^{122}Te ever available from ORNL.

Prior purities of ^{201}Tl have been limited to $\leq 95\%$, due principally to source sparking and poor vacuum. Substitutions of Tl_2S for thallium metal as a feed and the application of calcium pumping to offset the additional sulfur produced marked improvement in operations. Introduction of these concepts into a production series resulted in a 50% increase in ion throughput and ^{201}Tl samples having purities of 96 to 97%.

The preparation of ultrapure ($\geq 99.9\%$ isotopic assay) ^{107}Ag and ^{109}Ag was achieved by using equipment designed to maximize the process efficiency and minimize the operating gas load. To further reduce isotopic contamination, the ^{107}Ag was collected in a position ~ 18 in. behind the beam focal point. The system was also operated to achieve the maximum possible peak-to-valley ratio. The contaminants in these samples were a factor of 10 lower than the best material previously available.

Two second-pass separations yielded a sample of ^{70}Zn with an isotopic purity of 99.7%. The feed for these runs was 10 g of charge pre-enriched to $\sim 75\%$ ^{70}Zn . The operation was adjusted to achieve a high process efficiency and thus to acquire the maximum possible sample weight from the available feed. Success is evidenced by the attainment of a process efficiency of 14.8% as compared with 9.6% from prior efforts.

The development of an ion source to process high-temperature feeds is continuing. In the present design, structural components such as silver, copper,

and type 304 stainless steel are either melted and vaporized in the charge oven or lose their mechanically desirable properties; therefore, graphite has been utilized whenever possible. In operation, the initial ion input gradually decreases as vapors condense on the colder surfaces forming the ion exit slit. This output is reduced by as much as an order of magnitude or more before 20 g of charge can be vaporized. Considerations of space and geometry have precluded design changes which could eliminate

the cold spots in the arc chamber assembly. The source has operated at an oven temperature of $\sim 1500^{\circ}\text{C}$, using Dy_2O_3 chlorinated with a controlled flow of CCl_4 as a charge material. Arc chamber geometry, ion exit size, and accelerating electrode configuration have been varied to determine their effect on the process efficiency. The attainment of a high-temperature ($\sim 1500^{\circ}\text{C}$) chlorination region apparently has more effect on efficiency than does any other parameter studied.

8. Nuclear Regulatory Commission Programs

8.1 REACTOR SAFETY RESEARCH

Fission Product Release from LWR Fuel

The objectives of this experimental program are to determine the quantities and characteristics of radiologically significant fission products released from light-water reactor (LWR) fuel rods under typical accident conditions. The experiments are not intended to simulate specific hypothetical accidents but rather to duplicate the general conditions of a spent-fuel transportation accident (SFTA) and a controlled loss-of-coolant accident (LOCA). The observed results have been used to develop preliminary models for cesium and iodine release; subsequent computer modeling efforts at Battelle Columbus Laboratories will relate these results to specific accident behavior.

Following a series of experiments in which simulated fission products were implanted into unirradiated fuel rods,¹ release tests with irradiated rods were begun.² Nine release tests with highly irradiated fuel specimens from the H. B. Robinson reactor were conducted during this report period. Two tests were conducted in air (applicable to some SFTA conditions), and the remainder were carried out in steam; all of the tests were performed in the temperature range 500 to 1200°C. Experimental conditions and results have been reported in detail previously.^{3,4} Different experimental techniques were employed to investigate the two modes of release. Some rods were ruptured by internal pressure at 900°C to measure the "burst release" (that which is carried out immediately during rod depressurization); other rods were predrilled before heating to determine the "diffusion release" (that which diffuses from the gap space as a function of time at constant pressure).

The principal radioactive species released in these tests were cesium, iodine, and krypton, with antimony and ruthenium being detected in some

cases. In addition, small amounts (~0.02%) of the UO₂ fuel were ejected as dust in the burst tests. The quantities of these released species were compared with the total inventories in the fuel, as calculated from irradiation data, and with the gap inventories (the fractions released to the fuel-cladding gap during irradiation), which were based on measurements of the inert-gas release. The values for cesium release in steam are illustrated in Fig. 8.1, which shows the temperature dependence of diffusive release and the dominance of rupture release below about 1100°C. Fractional release of iodine was approximately equal to that of cesium for tests at 900°C or higher. Measurable release of ruthenium was detected only in air; release of antimony was noted only in steam at 900°C or higher.

Using the above results, preliminary empirical models for the release of cesium and iodine in steam were formulated. The models assume that the release is the sum of two components, burst release and diffusive release. The mass of each element vented in the burst release is a function of the gap inventory,

1. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, and S. R. Manning, "Fission Product Release from Simulated LWR Fuel," *Proceedings of the Specialist Meeting on the Behaviour of Water Reactor Fuel Elements under Accident Conditions*, Spåning, Nord-Torpa, Norway, Sept. 13-16, 1976, Session I, Paper No. 13, CSNI Report No. 13 (March 1977).

2. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5295, pp. 67-68.

3. A. P. Malinauskas et al., *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period January-March 1977*, ORNL NUREG TM-122 (June 1977).

4. A. P. Malinauskas et al., *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period April-June 1977*, ORNL NUREG TM-139 (September 1977).

5. A. P. Malinauskas et al., *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period July-September 1977*, ORNL NUREG TM-170 (January 1978).

6. A. P. Malinauskas et al., *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period October-December 1977*, ORNL NUREG TM-186 (March 1978).

Fig. 8.1. High-temperature release of cesium in steam from low-heat-rated LWR fuel rods, comparing burst release and diffusive release.

the absolute temperature, and the volume of gas vented. The diffusive release for each element was found to be a function of the initial gap inventory, the width of the fuel-cladding gap, the total pressure of the system, the absolute temperature, and time. Comparison of the results of model calculations with experimental data provided good agreement. A comparison of the results with the release values quoted in the Reactor Safety Study⁷ indicated that these results yield lower estimate values for cesium and iodine release by factors of 200 and 60 respectively.

Fission Product Transport Tests

A conceptual design and cost estimate of a facility for determining transport characteristics of selected fission products in the primary circuit of a pressurized water reactor (PWR) following a controlled LOCA event were completed and submitted to the U.S. Nuclear Regulatory Commission (NRC). The rig was designed as a 1/200 model (based on flow

area) of components of the PWR primary circuit, including the hot- and cold-leg piping, the heat exchanger, and the pump. Additionally, the facility would include a steam supply source, a means for injecting fission products, a steam condenser, and a cleanup system. Fission product deposits would be analyzed using removable inserts situated on the various components. Cost estimates were performed on assumed facility locations in the vicinity of the West Coast, the Southeast, and specifically for a site in Building 9201-3 at the Y-12 Plant in Oak Ridge.

Subsequently, an NRC decision was made to emphasize analyses relating to core meltdown conditions rather than to controlled LOCAs. As a consequence, the test facility is to undergo redesign, pending the development of a new listing of facility operational requirements. These requirements are to be specified by the code development team at Battelle Memorial Institute in consultation with ORNL and NRC. In the interim, the design effort will concentrate on establishing practical operating limits on the various structural components and on the detailed design of components which will be unaffected by operational constraints on the facility.

Transient Release from LMFBR Fuel

The efforts in the Chemical Technology Division are a part of the larger Breeder Reactor Aerosol Release and Transport (ART) Program at ORNL, sponsored by NRC, and are concerned with the safety factors involving the radionuclide release and transport from breeder reactors. The scope includes radionuclide release from fuel; transport to, and release from, the primary containment boundaries; and behavior within containments. The overall goal of the program is to provide the analytical techniques and experimental data necessary to assess the transient behavior and amounts of radionuclides released from breeder reactor cores as a result of postulated events of varying severity up to and including severe hypothetical core-disruptive accidents (HCDAs).

The program is divided into several related experimental and analytical activities, as detailed and summarized in other reports^{8,9} and listed as follows:

1. Development of a capacitor discharge vaporization (CDV) system for injecting electrical energy

8. I. S. Kress, G. W. Parker, and M. H. Fontana, *Work Plan: Transient Release Program*, ORNL TM-4875 (September 1975).

9. I. F. Parsley, *Work Plan: Transient Release Program, Addendum 1: Investigation of LMFBR Aerosol Behavior*, ORNL TM-4875, Addendum 1 (January 1976).

7. Reactor Safety Study, an Assessment of Accident Risk in U.S. Commercial Nuclear Power Plants, WASH-1400, Appendix VII, pp. VII-13 (October 1975).

internally in simulated (UO_2) and real breeder reactor fuel that will provide a nonnuclear technique for studying the fuel response to HCDA-like energy depositions.

2. Development of alternative techniques for generating fuel-simulant aerosols on a relatively continuous basis.
3. Study of the characteristics and transient behavior of fuel and fuel-simulant aerosols within several vessels for scale effects.
4. Production and study of fuel-simulant and sodium aerosols in the Nuclear Safety Pilot Plant (NSPP) for validation of models, with particular attention to the behavior of mixed aerosols and scale-up to containment size.
5. Study of the fuel interaction, expansion, and thermal behavior within the sodium pool as the resultant fuel vapor bubble is transported through the overlying sodium to the cover-gas region.

Our participation in the program, which included the initial development of the CDV nonnuclear high-energy transient simulator technique, was primarily concerned with only the first three of these activities.

1. Development of a CDV¹⁰ system (Fig. 8.2) was shown to be at a satisfactory state early this year. It has now been relocated and integrated into the Fuel Aerosol Simulant Test (FAST)¹¹ project, listed above as activity 5, being conducted mainly within the Engineering Technology Division at the Y-12 site.

10. 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*, ORNL NUREG TM-160 (in press).

11. A. L. Wright, A. M. Smith, and T. S. Kress, *Fuel Aerosol Simulant Test (FAST) Plan*, ORNL NUREG TM-129 (September 1977).

Fig. 8.2. Capacitor discharge vaporization system.

With the CDV technique, ceramic fuel can be put into HCDA-like mean-energy states of up to 3000 J/g, which is sufficient to effect prompt disassembly of a fuel pin and flash a significant portion of the superheated liquid fuel to vapor. The efficiency of the energy deposition, which was initially quite low, has been gradually improved by optimizing both the electrical circuitry and the physical configuration of the specimen until most of the power is expended in the vaporization process. The range of time intervals for disassembly can be adjusted to match HCDA theory within about 1 μ sec. This method of simulating fast reactor transients was initially developed at Karlsruhe¹² but has been further expanded at ORNL.

2. The effort toward the development of alternative techniques for generating fuel-simulant aerosols on a somewhat continuous basis has led to a relatively successful application of the dc electric arc in a cold-hearth furnace. Typically, the flow of current from a graphite-tipped electrode first melts uranium oxide and then continues to heat the liquid to local boiling, thereby vaporizing significant quantities. The equipment shown in Fig. 8.3 will vaporize about 50 g of UO_2 per minute; however, the

12. W. Schikarski, *The Karlsruhe Research Program on Nuclear Aerosols and Its Relation to the Plutonium Hazard of Fast Sodium Reactors*, KFK-795 (July 1968).

Fig. 8.3. Cold-hearth arc furnace.

relatively poor geometrical arrangement and the severe thermal gradient lead to rapid deposition on the cold furnace walls. Purging with large volumes of argon reduces this thermophoretic effect to some extent; however, the ultimate goal of achieving an instantaneous airborne concentration of 100 g m⁻³ in a 5-m³ vessel may not be attainable by this method.

An alternative method based upon the high-temperature ignition of powdered uranium metal in oxygen appears to offer two advantages: (1) it avoids the problem of internal wall losses, and (2) it appears to respond to a scale-up effort and is therefore adaptable to provide larger aerosol sources for larger vessels. The early work of Grosse and Conway¹³ has been used as a starting point in the design of a practical uranium oxygen torch; however, the requirement for an anhydrous aerosol to be generated in the presence of liquid sodium led to the application of a dc plasma arc as a preheater and ignitor for the uranium powder. Trial designs, consisting of a multijet concentric configuration for surface mixing of metal and oxygen around the plasma flame, have been relatively successful with a substitute aluminum powder for uranium. Initial trials, using uranium fuel and having suitable safeguards, are nearing completion.

3. The characterization of fuel-simulant aerosols in small vessels (activity 3) has been conducted in the 0.5-m³ CRI-III vessel (Fig. 8.2) and in the 4.5-m³ CRI-II vessel (Fig. 8.3). Detailed intercomparisons have been made of fine-particle morphology between two methods of continuous generation and two methods of instantaneous vaporization (capacitor discharge).

These studies have shown that primary particles are indeed somewhat unique to the generation process; conversely, agglomeration behavior is almost identical for the aerosols produced by all vapor-condensation processes.

8.2 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 of NRC with the technical information required to formulate appropriate ALARA guidelines for the

release of radioactive materials from various segments of the nuclear fuel cycle. Survey reports on the conversion of yellow cake to UF₆ by the "dry" process and the conversion of recycle uranium to UF₆ were completed and issued.^{14,15} We are evaluating the costs for the treatment of radioactive wastes and the environmental impact of waste effluents associated with converting yellow cake to UF₆ by the solvent extraction fluorination process. This evaluation will form the basis for the final report in the ALARA series.¹⁶ 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.

8.3 SAFETY REVIEW OF NUCLEAR FACILITIES

Federal regulations require that privately owned nuclear facilities be licensed by NRC prior to start of operation. In connection with the licensing process, the Chemical Technology Division is responsible for providing technical support to NRC in reviewing the safety of these facilities and in the preparation of safety evaluation and related generic reports. During

13. A. V. Grosse and J. B. Conway, "Combustion of Metals in Oxygen," *Ind. Eng. Chem.* 50(4), 663-72 (April 1958).

14. M. B. Sears, R. E. Blanco, B. C. Finney, G. S. Hill, R. E. Moore, 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 I. The Fluorination-Fractionation Process*, ORNL NUREG TM-7 (September 1977).

15. J. W. Roddy, R. E. Blanco, B. C. Finney, G. S. Hill, R. E. Moore, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle - Conversion of Recycle Uranium to UF₆*, ORNL NUREG TM-37 (August 1977).

16. M. B. Sears, R. E. Blanco, B. C. Finney, G. S. Hill, R. E. Moore, 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).

this report period, we participated in the safety reviews and the preparation of safety evaluation reports for the Allied General Nuclear Services' Barnwell Nuclear Fuel Plant Separations Facility, the Exxon Fuel Recovery and Recycling Center Separations Facility, the General Electric Morris Operation Modified Fuel Storage Facility, and the Stone and Webster Independent Spent Fuel Storage Facility.

Other significant activities included the following: (1) the preparation of expert witness testimony for the S-3 hearing on environmental considerations for the uranium fuel cycle, (2) an evaluation of the effects of a tornado on the Nuclear Fuel Services Fuel Reprocessing Plant, (3) a determination of decontamination and exposure costs resulting from the accidental release of radioactive materials from by-product manufacturing and fuel fabrication facilities,¹⁷ and (4) an analysis of the effects of a hydrogen explosion in a high-level radioactive liquid waste tank.¹⁸

8.4 SAFEGUARDS STUDIES

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 storage vaults that offer a high degree of protection for materials stored in them. Results of this study are being presented in a series of three reports 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, which discusses the desirability and feasibility of vault automation in special nuclear material storage, was published at ORNL and NRC during the year.¹⁹ The second report on the value impact of vault automation has been prepared, and a draft has been submitted to NRC for comment.²⁰ The completed work, incorporating their suggestions,

will then be published. The third report in the series sets forth design criteria for vault automation and is in preparation.²¹

Value impact studies indicate that the automation of storage vaults was more cost-effective in achieving comparable levels of safeguards worth than either of two other nonautomated concepts that were developed.²² A nonsafeguards benefit of reduced personnel exposure was also shown to be achieved in automated vault systems, since such systems are inherently operated remotely.

Two subcontracts were let and completed in developing information needed in preparing the report on design criteria.²³ One of these, with JBF Associates of Knoxville, Tennessee, dealt with a parametric study of the availability of Power and Free Conveyor (PAFC) systems being considered for use in a conceptual automated vault system; the other, with FMC Corporation of Santa Clara, California, was aimed at developing reliability and maintainability data from commercial applications of PAFC.

In the report on design criteria, the objective is to enlarge the method for evaluating vault concepts for safeguards worth that was developed initially in the earlier study on desirability and feasibility, with the goal of making application of the method more general. Minimum safeguards benefit values can then be set as criteria. All parts of a conceptual vault system can then be evaluated for the safeguards benefit value and compared with the criteria. An example is given of a vault concept based on the contemplated use of PAFC as the material handling and storage system.²⁴

8.5 ENVIRONMENTAL STATEMENT ON PLUTONIUM UTILIZATION (GESMO)

The Chemical Technology Division continued to provide technical support to NRC in connection with the Final Generic Environmental Statement on the Use of Recycle Plutonium in Mixed-Oxide Fuel in Light-Water-Cooled Reactors (GESMO) study. Reactor concepts²⁵ associated with plutonium

17. J. P. McBride, *Economic Consequences of Accidental Releases from Fuel Fabrication and Radioisotope Processing Plants* (in preparation).

18. H. W. Godbee et al., *Preliminary Consideration on Ignition of Hydrogen and/or Loss of Coolant in a High-Level Radioactive Liquid Waste Tank*, ORNL NUREG-12 (in preparation).

19. W. R. Hamel and I. B. Shappert, *Desirability and Feasibility of Vault Automation in Special Nuclear Material Storage*, ORNL NUREG-20 (NUREG-0318) (August 1977).

20. W. I. McDuffee and W. R. Hamel, *Value Impact of Vault Automation in Special Nuclear Material Storage*, ORNL NUREG-33 (NUREG-CR0019) (to be published).

21. W. I. McDuffee, W. R. Hamel, I. B. Shappert, and A. S. Pruitt, *Design Criteria for Vault Automation in Special Nuclear Material Storage*, ORNL NUREG-44 (in preparation).

22. J. W. Wachter, *Model Plutonium Recycle Reactors for the Environmental Analysis of the Mixed-Oxide Fuel Cycle*, ORNL NUREG-21 (in preparation).

utilization were developed, and computer-derived bases for estimating the radionuclides in spent fuel were provided for the various modes of fuel-cycle operations addressed in the GESMO study.

The impact on the fuel cycle of the recycling of uranium and of uranium and plutonium was studied using the projected growth of the industry during the last 25 years of this century for the GESMO study. The model reactors were utilized in this study to project the radioactivity and thermal power of the generated wastes, of the waste shipments, and the accumulated inventories at various stages of the fuel cycle.²³

8.6 WASTE MANAGEMENT PARAMETRIC STUDIES

The objective of the Waste Management Parametric Studies Program is to perform engineering and economic evaluations of alternative methods for the management of radioactive wastes in the nuclear fuel cycle. These studies are conducted to provide the Office of Nuclear Regulatory Research of NRC with the technical information required to assess the impact on fuel-cycle industries of licensing requirements that might be imposed for effluent control and waste management.

A study was conducted to determine (1) the dollar cost and effectiveness for decreasing the releases of ^{14}C and ^{85}Kr from a model nuclear fuel reprocessing plant that processes LWR fuels and (2) the best method for disposing of the resulting waste products.²⁴ The model plant is representative of plants that are in the testing or design stage and has an annual capacity of 1500 metric tons of LWR fuel. Four removal technologies were evaluated for cost-effectiveness: caustic treatment, molecular sieve adsorption, fluorocarbon absorption, and cryogenic distillation. The least expensive option for the removal and disposal of ^{14}C as CO_2 is the direct reaction of a $\text{Ca}(\text{OH})_2$ slurry with the CO_2 from the dissolver off-gas stream, followed by concretion of

the product in 210-liter (55-gal) drums and final disposal by shallow-land burial. The use of molecular-sieve adsorption for the removal of CO_2 is slightly more expensive and placement of the concreted CaCO_3 product in a federal repository adds about 10% to the annual costs. The estimated costs for the removal of ^{85}Kr from the gaseous radioactive effluents for the two options considered, cryogenic distillation and fluorocarbon adsorption, are nearly the same, with a slight cost advantage calculated for cryogenic distillation. The product gas is compressed, placed in 50-liter cylinders, and permanently stored in a federal repository.

8.7 WASTE MANAGEMENT GENERIC STUDIES

The updating continued on the three earlier generic reports done at ORNL on the status of evaporation,²⁵ ion exchange,²⁶ and solid radwaste practices²⁷ at nuclear power plants. Efforts have continued in the preparation of a new report on filtration for the Effluent Treatment System branch of NRC. The collating and analysis of the data obtained at the New Orleans Radwaste Management Workshop held in January 1977 and from the questionnaires circulated to the nuclear utilities have been completed, and draft sections of the reports have been prepared. The final reports should be available in the latter part of 1978.

23. J. W. Wachter, *Effect of Fuel Recycling on Radioactivity and Thermal Power of High-Level Wastes*, ORNL NUREG TM-146 (in preparation).

24. J. W. Roddy, E. L. Compere, and B. C. Finney, *Options in the Management of Carbon-14 and Krypton-85 Wastes from LWR Fuel Reprocessing* (in preparation).

25. H. W. Godbee, *Use of Evaporation for the Treatment of Liquids in the Nuclear Industry*, ORNL-4790 (September 1973).

26. K. H. Lin, *Use of Ion Exchange for the Treatment of Liquids in Nuclear Power Plants*, ORNL-4792 (December 1973).

27. A. H. Kibbey and H. W. Godbee, *A Critical Review of Solid Radwaste Practices at Nuclear Power Plants*, ORNL-4924 (March 1974).

9. Miscellaneous Programs

9.1 URANIUM-233 PROCESSING

Storage and Distribution of ^{233}U

Receipts during this report period include 69.0 kg of ^{233}U (10 ppm ^{232}U) as UO_2 in four shipments and 43.1 kg of uranium (91% ^{233}U , 2% ^{235}U) as metal, oxide, and dross in one shipment.

Disbursements from the facility consisted of 3.7 kg of ^{233}U (10 ppm ^{232}U) in two shipments and 0.3 kg of ^{233}U (38 ppm ^{232}U) as UO_2 and 0.1 kg of ^{233}U (220 ppm ^{232}U) as UO_2 in separate, single shipments. In addition, 100 g of plutonium as PuO_2 was distributed to another facility at ORNL.

Dissolution and Purification of ^{233}U

The UO_2 scrap dissolver was operated to recover 53.7 kg of ^{233}U from UO_2 during 13 dissolution cycles.

One run was conducted in the single-cycle solvent extraction system to recover 1.6 kg of ^{233}U that was contaminated with 2000 ppm plutonium. The plutonium contamination level was decreased to 3 ppm by using ferrous sulfate (0.1 M in the feed and 0.01 M in the scrub) as a reductant. A second run was conducted to recover 1.0 kg of ^{233}U from system flushing.

An inspection of head-end vessels revealed large quantities of sludge which had accumulated during the dissolution and processing of approximately 30 metric tons of $^{233}\text{UO}_2\text{-ThO}_2$ scrap from the LWBR fuel fabrication program. The solids were flushed from the vessels through a filter which will subsequently be removed and analyzed for ^{233}U by a nondestructive assay technique.

The high-pressure ion exchange system was operated to purify 9.0 kg of ^{233}U , which was subsequently converted to UO_2 .

Conversion of ^{233}U from Nitrate Solution to Ceramic-Grade UO_2 Powder

A total of 7.3 kg of ceramic-grade UO_2 powder was prepared. The uranium was processed through the

conversion facility in nominal 1.0-kg (uranium) batches. The system was checked each week to ensure operability, since we have a 100-kg (^{233}U) order from Argonne National Laboratory which will be produced within the next eight or nine months.

9.2 SHIPPING-CASK TEST PROGRAM

Drop-Test Pad

During this report period, the construction of a new drop-test pad was completed at the Tower Shielding Facility. This structure, which is shaped like an Aztec pyramid, measures 9.6 by 12.6 m at the base. A 2.4- by 5.4-m armor-plated steel plate is embedded flush with the top surface, which is 4.8 m wide by 7.6 m long. The combination of the 0.6-m-thick armor plate, which weighs 63.6 metric tons, and the 554.5 metric tons of associated concrete meets the International Atomic Energy Agency's criterion for an "essentially unyielding" surface.

In November, four 113.6-liter containers designed for shipping fissile material were subjected to two drops onto the test-pad surface: one from a distance of 1 m onto a 15-cm steel pipe, and one from a distance of 9 m at an oblique angle onto the bolt closure of the container. Posttest examination of the containers revealed that all four had remained closed and thus successfully withstood the stresses represented by the specified conditions.

Knapp Mills Cask

Arrangements were made for the Reynolds Electrical and Engineering Company at Mercury, Nevada, to decontaminate a 20-metric ton Knapp Mills spent fuel cask. This decontamination procedure was completed about midyear, and the cask was subsequently shipped to ORNL. A health physics survey of the cask upon its arrival at the cask storage area revealed gross contamination on the trailer saddle and on the corresponding points of the cask.

Sandblasting of the trailer and the cask was required to reduce the contamination to an acceptable level.

Drop Tests

A series of drop tests involving the 20-metric ton Knapp Mills cask are planned for the first half of 1978. These tests include:

1. a 9-m drop with a balsa-wood impact limiter attached to the closure end of the cask.
2. a 9-m drop on the cask closure end.
3. a 9-m drop with the cask positioned at its vertical center of gravity.
4. a 9-m drop with the cask at an oblique angle.
5. a 1-m drop onto a 15-cm steel spike.

9.3 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 a 5000-gal vessel in the Building 3019 facility. Although the vessel was packed with borosilicate glass rings prior to introduction of the solution nine years ago, the existence or integrity of these rings, or any leakage of the solution into the pit, cannot be verified; thus it is necessary to depend solely on soluble poisons for nuclear safety. The concentrations of soluble poisons have varied widely over the years, perhaps due to the difficulty of obtaining a representative sample of the solution in the vessel. In addition, the vessel cannot be inspected to determine the effect of corrosion.

We have prepared a preconceptual design, cost estimate, and schedule for the conversion of this uranium to U_3O_8 and its subsequent storage in an earthquake-proof, safeguarded facility. The storage facility is now under construction and is scheduled to be completed in FY 1978. The conversion facility is being reviewed by DOE; with adequate funding, the conversion operation could be performed in FY 1981.

9.4 NUCLEAR SAFETY ASSISTANCE

For a number of years the Chemical Technology Division has assisted the Nuclear Safety Information Center (NSIC) by providing editorship for the Plant

Safety Features section of *Nuclear Safety*, the bimonthly technical journal published by NSIC for the U.S. Nuclear Regulatory Commission. *Nuclear Safety* limits its scope to topics relevant to the analysis and control of hazards associated with nuclear reactors, operations involving fissionable materials, and the products of nuclear fission and their effects on the environment. The journal is divided into six sections: General Safety Considerations, Accident Analysis, Control and Instrumentation, Plant Safety Features, Consequences of Effluent Release, and Current Events.

The Plant Safety Features section covers a broad subject area which includes air handling, management of wastes, contamination control, fire safety, and other aspects of containing hazardous materials within the confines of the various types of plants in the nuclear fuel cycle. This section also covers the design, fabrication, testing, and performance of containment systems and of system components such as fuel elements, vessels, and the buildings to house them. The section editor seeks review articles on these topics from qualified authors worldwide, then edits for technical content and readability. Articles are submitted to at least two peer reviewers in the subject area before publication.

During this report period, the following articles appeared in the Plant Safety Features section of *Nuclear Safety*:

"Nuclear Safety Experiments in the Marviken (Sweden) Power Station"

"Continuing Challenges in Nuclear Air Cleaning"

"Fatigue-Crack Propagation in Pressure Vessel Steels"

"LOFT Emergency Core-Cooling System Experiments: Results from the LI-4 Experiments"

"Effect of Engineered Safety Features on the Risk of Hypothetical LMFBR Accidents"

Nuclear Safety recently won first place for the third consecutive year in the communication competition by the Society for Technical Communication.

9.5 BNFP APPLICABILITY STUDY

In November 1977, Congress directed that the Energy Research and Development Administration (now DOE) conduct a study to determine whether the Barnwell Nuclear Fuel Plant (BNFP) could be utilized in support of the nonproliferation objectives

of the United States. The sum of \$1 million was provided for this task, which was to be completed by April 1, 1978. A task team composed of personnel from ACDA (the State Department), DOE, ORNL, the Hanford Development Engineering Laboratory, the Savannah River Plant, Stanford Research Institute, and International Energy Associates Ltd. was assembled in November. Coordinated by the Pilot Plant Section of the Chemical Technology Division, this team immediately began to prepare material describing the BNFP and to evaluate (1) alternative operating modes to which the plant could be adapted for the reprocessing of LWR fuels; (2) other uses for the BNFP not involving reprocessing,

including "mothballing" and decommissioning; and (3) ownership and management options. Supporting studies included radioactive spiking, safeguards, waste management, and resource utilization. The final report consisted of an *Executive Summary* and the following three volumes: *Volume I—Summary of Major Findings and Conclusions*; *Volume II—BNFP Utilization Alternatives, Evaluations and Conclusions*; and *Volume III—Appendices*. Volume III contains detailed discussions which support the evaluations contained in Volume II.

The assignment was completed on schedule with delivery of the study to DOE by March 31, 1978.

Administrative Summary

PUBLICATIONS, ORAL PRESENTATIONS, AND PATENTS

Biochemical Technology

Bostick, W. D., "Automated Environmental Analyses Using a Centrifugal Analyzer," presented at the Gordon Research Conference on Analytical Chemistry, New Hampton School, New Hampton, N.H., Aug. 10, 1977.

Bostick, W. D., S. R. Dinsmore, J. E. Mroczek, and T. P. Waalkes,¹ "Separation and Analysis of Arylsulfatase Isoenzymes in the Body Fluids of Man," presented at the Tenth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, Oak Ridge National Laboratory, Mar. 16-17, 1978.

Bostick, W. D., and J. E. Mroczek, "Evaluation with the Centrifugal Fast Analyzer of a Chemical Activation Procedure for Creatine Kinase MB Isoenzyme," *Clin. Chem.* 23, 1633 (1977).

Burtis, C. A.,² J. E. Mroczek, and T. O. Tiffany, "The Centrifugal Analyzer and Its Use in Clinical Analyses," pp. 3-22 in *Methods for the Centrifugal Analyzer*, ed. J. Savory and R. E. Cross, American Association for Clinical Chemists, Winston Salem, N.C., 1978.

Snipe, A. L.,⁴ and W. L. Griffith,⁴ "Facultative Nature of Some Anaerobic Fixed-Film Protozoans," presented at the 77th Annual Meeting of the American Society for Microbiology, New Orleans, La., May 8-13, 1977.

Genung, R. K., and J. E. Mroczek, "A Microcomputer-Based Portable Centrifugal Fast Analyzer with Fast-Kinetics Monitoring Capability," presented at the 70th Annual Meeting of the American Institute of Chemical Engineers, New York, Nov. 13-17, 1977.

Holladay, D. W., C. W. Hancher, D. D. Chilcote,⁵ and C. D. Scott, "Biodegradation of Phenolic Waste Liquors in Stirred-Tank, Packed-Bed, and Fluidized-Bed Bioreactors," *AIChE Symp. Ser.* 74, 241 (1978).

Jolley, R. L., "Characterization of Chloro-Organics: Compounds of Environmental Concern Produced by Chlorination of Water," presented as an Oak Ridge Associated Universities Traveling Lecture at Southwest Texas Section of the American Chemical Society, Kingswood, Tex., Apr. 14, 1977; and at Catholic University, Ponce, Puerto Rico, May 24, 1977.

Jolley, R. L., "Identification of Organic Constituents in Natural and Process Waters Using High-Resolution Liquid Chromatography," presented as an Oak Ridge Associated Universities Traveling Lecture at Texas A&I University, Kingswood, Tex., Apr. 14, 1977; at the University of Puerto Rico, Rio Piedras, May 23, 1977; and at Atlanta University, Atlanta, Ga., Feb. 10, 1978.

1. Johns Hopkins University Oncology Center, Baltimore.

2. Center for Disease Control, Atlanta, Ga.

3. Instrumentation Laboratories, Inc., Spokane, Wash.

4. Chemistry Division; formerly with Chemical Technology Division.

5. Hanna Mining Co., Nashua, Minn.

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- Jolley, R. L., "Introductory Remarks as Session Chairman," presented at the Symposium on Disinfection, 175th National Meeting of the American Chemical Society, Anaheim, Calif., Mar. 12-17, 1978.
- Jolley, R. L., "Opening Remarks," presented at the Second Conference on Water Chlorination: Environmental Impact and Health Effects, Gatlinburg, Tenn., Oct. 31-Nov. 4, 1977.
- Jolley, R. L., *Water Chlorination: Environmental Impact and Health Effects*, p. 439, vol. I, Ann Arbor Science, Ann Arbor, Mich., 1978.
- Jolley, R. L., R. B. Cumming,⁶ W. W. Pitt, Jr., F. G. Taylor, Jr.,⁷ J. E. Thompson, and S. J. Hartmann, "Ecological Impact of Chloro-Organics Produced by Chlorination of Cooling Tower Waters," presented at the Symposium on Microbiology of Power Plant Effluents, University of Iowa, Iowa City, Sept. 19-20, 1977.
- Jolley, R. L., and W. W. Pitt, Jr., "Chloro-Organics in Surface Water Sources for Potable Water," presented at the Symposium on Disinfection Technology, 97th Annual Conference of the American Water Works Association, Anaheim, Calif., May 8, 1977; published in the *Proceedings*.
- Jolley, R. L., W. W. Pitt, Jr., F. G. Taylor, Jr.,⁷ S. J. Hartmann, G. Jones, Jr., and J. E. Thompson, "An Experimental Assessment of Halogenated Organics in Waters from Cooling Towers and Once-Through Systems," presented at the Second Conference on Water Chlorination: Environmental Impact and Health Effects, Gatlinburg, Tenn., Oct. 31-Nov. 4, 1977; to be published in the *Proceedings*.
- Jolley, R. L., W. W. Pitt, Jr., and J. E. Thompson, "Organics in Aqueous Process Streams of a Coal Conversion Bench-Scale Unit Using the Hydrocarbonization Process: HPLC and GC/MS Analysis," presented at the 23rd Annual Technical Meeting of the Institute of Environmental Sciences, Los Angeles, Apr. 25-27, 1977; published in the *Proceedings*, p. 25.
- Lee, D. D., and C. D. Scott, "A Tapered Fluidized-Bed Bioreactor for Treatment of Aqueous Effluents from Coal Conversion Processes," presented at the 70th Annual Meeting of the American Institute of Chemical Engineers, New York, Nov. 13-17, 1977; published in the *Proceedings*.
- Lee, N. E., R. K. Genung, W. F. Johnson,⁸ J. E. Mrochek, and C. D. Scott, "Automated System for Fractionation of Blood Samples," presented at the Tenth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, Oak Ridge National Laboratory, Mar. 16-17, 1978.
- Mrochek, J. E., W. D. Bostick, and S. R. Dinsmore, "New Liquid Chromatographic Techniques of Potential Interest to the Clinical Laboratory," presented at the Tenth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, Oak Ridge National Laboratory, Mar. 16-17, 1978.
- Pitt, W. W., Jr., "New Developments in Biomedical Engineering," published in the *Oak Ridger*, Feb. 17, 1978, and the Sunday Supplement of the *Knoxville News-Sentinel*, Feb. 19, 1978.
- Pitt, W. W., Jr., C. W. Hancher, and H. W. Hsu,⁹ "The Tapered Fluidized-Bed Bioreactor—An Improved Device for Continuous Cultivation," presented at the 84th National Meeting of the American Institute of Chemical Engineers, Atlanta, Ga., Feb. 24-Mar. 1, 1978.
- Pitt, W. W., Jr., and R. L. Jolley, "Characterization of Organics in Aqueous Streams of Coal Conversion Processes," presented at the Second Pacific Area Chemical Engineering Conference, Denver, Colo., Aug. 28-31, 1977; published in the *Proceedings*.
- Pitt, W. W., Jr., R. L. Jolley, and G. Jones, Jr., "Recent Results in High-Resolution Ion Exchange Chromatography in Aquatic Environmental Analysis," presented at the Gordon Research Conference on Ion Exchange, Brewster Academy, Wolfeboro, N.H., July 27, 1977.

6. Biology Division.

7. Environmental Sciences Division.

8. Instrumentation and Controls Division.

9. University of Tennessee, Knoxville.

- Scott, C. D., "Engineering Involvement in the Health Industry," presented at the 70th Annual Meeting of the American Institute of Chemical Engineers, New York, Nov. 13-17, 1977.
- Scott, C. D., "Metabolic Profile by High-Resolution Liquid Chromatography," in *Contemporary Topics in Analytical and Clinical Chemistry*, Plenum, New York, 1977.
- Scott, C. D., R. S. Melville,¹⁰ and D. S. Young,¹¹ "Introduction to the Proceedings of the Ninth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory," *Clin. Chem.* 23, 1385 (1977).
- Scott, C. D., R. S. Melville,¹⁰ and D. S. Young,¹¹ "Introduction to the Proceedings of the Tenth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory," presented at the Tenth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, Oak Ridge, Tenn., Mar. 16-17, 1978.
- Shumate, S. E., II, "Bioengineering: Exploitation of Microbial Talents," presented at the ORNL Bimonthly Colloquium, American Museum of Atomic Energy, Oak Ridge, Tenn., Mar. 14, 1978.
- Shumate, S. E., II, "Bioengineering Research—Bioprocess Development," seminar presented as Distinguished Visiting Lecturer, Virginia Polytechnic Institute and State University, Blacksburg, Va., May 2, 1977.
- Shumate, S. E., II, "Denitrification and Metal Toxicity Problems in Waste Management," presented at the International Workshop on Biosaline Research, Kiawah Island, S.C., Sept. 15-18, 1977.
- Shumate, S. E., II, C. W. Hancher, G. W. Strandberg, and C. D. Scott, "Biological Processes for Environmental Control of Effluent Streams in the Nuclear Fuel Cycle," presented at the Waste Management and Fuel Cycles 78 Symposium, Tucson, Ariz., Mar. 5-8, 1978.

Chemical Engineering Research

- Begovich, J. M., and J. S. Watson, "An Electroconductivity Technique for the Measurement of Axial Variation of Holdups in Three-Phase Fluidized Beds," *AIChE J.* 24, 351 (1978).
- Canon, R. M., and J. D. Hewitt, *Boiling Heat Transfer in a Bench-Scale, Molten-Salt Thermal Energy Storage Device*, ORNL/TM-5689 (May 1977).
- Hewitt, J. D., "Electrophoretic Mass Transport Analyzer: Operational Characteristics with Aqueous Solutions and Applicability to Organic Liquid-Solid Systems," presented at the 19th Technicians Symposium, 174th National Meeting of the American Chemical Society, Chicago, Aug. 28-Sept. 2, 1977.

Coal Technology

- Cochran, H. D., Jr., "Heats of Coal Hydrogenation by Differential Scanning Calorimetry," Letter to the Editor, *Fuel* 57, 124 (1978).
- Cochran, H. D., Jr., and J. M. Holmes, "Hydrocarbonization of Western Coal with Zero Net Hydrogen Consumption," presented at the Thermal Hydrocarbon Chemistry Symposium, Anaheim, Calif., Mar. 12-17, 1978.
- Cochran, H. D., Jr., and J. M. Holmes, "Mild Hydrocarbonization of Western Coal," presented at the Fourth International Conference on Coal Gasification, Liquefaction, and Conversion to Electricity, University of Pittsburgh, Pittsburgh, Pa., Aug. 4, 1977.
- DeCarlo, V. A., 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).

10. National Institute of General Medical Sciences, National Institutes of Health, Bethesda, Md.

11. Mayo Clinic, Rochester, Minn.

- Forrester, R. C., III, "Macroscopic Sample Effects on the Pyrolysis of Bituminous and Subbituminous Coals at Underground Coal Gasification Heating Rates," *Proceedings of the Third Annual Underground Coal Gasification Symposium*, Fallen Leaf Lake, Calif., June 6-9, 1977, CONF-770652.
- Holmes, J. M.,¹² D. A. Dyslin,¹³ M. S. Edwards, D. S. Joy, G. R. Peterson,¹⁴ C. B. Smith,¹⁵ and P. M. Lantz,¹⁵ "Evaluation of a Commercial-Scale Hydrocarbonization Process to Produce Clean Char, Oil, and Pipeline Gas from Coal," presented at the Second Pacific Chemical Engineering Congress (Pachec 77), Denver, Colo., Aug. 26-31, 1978.
- Holmes, J. M.,¹² D. A. Dyslin,¹³ M. S. Edwards, D. S. Joy, G. R. Peterson,¹⁴ C. B. Smith,¹⁵ and P. M. Lantz,¹⁵ *Hydrocarbonization Process Evaluation Report, Vol. I: Conceptual Design and Cost Estimate of a Commercial-Scale Facility*, ORNL-5212 (July 1977).
- Holmes, J. M.,¹² D. A. Dyslin,¹³ M. S. Edwards, D. S. Joy, G. R. Peterson,¹⁴ C. B. Smith,¹⁵ and P. M. Lantz,¹⁵ *Hydrocarbonization Process Evaluation Report, Vol. II: Evaluation of Process Feasibility*, ORNL-5213 (July 1977).
- Klein, J. A., and R. E. Barker, "Assessment of Environmental Control Technology for Hydrocarbonization," presented at the Second Pacific Chemical Engineering Congress (Pachec 77), Denver, Colo., Aug. 28-31, 1977.
- Lantz, P. M.,¹⁵ *The University of Utah's Continuous Coal Hydrogenation Process*, ORNL TM-5737 (April 1977).
- Rodgers, B. R., "Clean Energy from Coal," presented to the Mountain Empire Community College (Va.) Excursion Group, American Museum of Atomic Energy, Oak Ridge, Tenn., April 1977.
- Rodgers, B. R., "Coal Conversion—Its Relation to the National Energy Picture," presented to the Scientific Research Society of America (Sigma Xi), Kings Mountain, N.C., Feb. 16, 1978.
- Rodgers, B. R., "Coal Liquefaction—Removing the Bottleneck," pp. 35-39 in *ORNL Review*, Winter 1977.
- Rodgers, B. R., "Electrokinetic and Physical Properties of Coal Liquids," presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., Mar. 13, 1978.
- Rodgers, B. R., "Filtration of Micron-Sized Particles from Coal Liquids—Carbonaceous Precoats," presented at the Second Pacific Chemical Engineering Congress (Pachec 77), Denver, Colo., Aug. 28-31, 1977; published in the *Proceedings*, pp. 651-55, vol. 1 (1977).
- Rodgers, B. R., "National Coal Energy Perspective," presented at a meeting of the League of Women Voters, Oak Ridge, Tenn., July 20, 1977.
- Rodgers, B. R., "Separation of Micron-Sized Particles from Coal Liquids," presented at the Illinois Institute of Technology, Chicago, Oct. 26, 1977.
- Rodgers, B. R., "Separation of Micron-Sized Particles from Coal Liquids—The Effect of Surface Charge," presented at the 84th National Meeting of the American Institute of Chemical Engineers, Atlanta, Ga., Feb. 27, 1978.
- Rodgers, B. R., "Separation of Mineral and Organic Solids from Liquefied Coal," presented at the University of Michigan, Ann Arbor, Oct. 28, 1977.
- Rodgers, B. R., "The Coal Research Program at ORNL with Emphasis on Solid-Liquid Separations," presented at Sandia Laboratories, Albuquerque, N.M., Sept. 2, 1977.

12. Engineering Technology Division; formerly with Chemical Technology Division.

13. UCC-ND General Engineering.

14. Development Division, Y-12 Plant.

15. Health and Safety Research Division.

- Rodgers, B. R., "Zeta Potential of Particles in Liquefied Coal Solutions," presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., Mar. 15, 1978.
- Rodgers, B. R., S. Katz, and P. R. Westmoreland, *Supporting Research and Development on Separations Technology: Final Report*, ORNL/TM-5843 (October 1977).
- Salmon, R., M. S. Edwards, and W. C. Ulrich, *Evaluation of the Synthoil Process: Volume I—Process Design and Cost Estimate of a 100,000 Barrel/Stream Day Facility*, ORNL-5209 (June 1977).
- Salmon, R., M. S. Edwards, W. C. Ulrich, et al., *Evaluation of the Synthoil Process: Volume II—Status of Development*, ORNL-5210 (June 1977).
- Salmon, R., M. S. Edwards, and W. C. Ulrich, *Evaluation of the Synthoil Process: Volume III—Unit Block Flow Diagrams for a 100,000 Barrel/Stream Day Facility*, ORNL-5211 (June 1977).
- Spence, R. D., and J. R. Hightower, Jr., "Behavior in an Electric Field of Ash Particles Suspended in a Coal-Derived Liquid," *J. Tenn. Acad. Sci.* 53(1), 28 (1978).
- Ulrich, W. C., *Evaluation of In Situ Coal Gasification Processes on a Regional Basis*, ORNL-5279 (December 1977).
- Westmoreland, P. R., R. C. Forrester III, and A. P. Sikri,¹⁶ "In Situ Gasification: Recovery of Otherwise Inaccessible Coal Reserves," presented at the Miami International Conference on Alternative Energy Sources, Miami Beach, Fla., Dec. 5-7, 1977; published in the *Proceedings*.

Development of the Thorium Fuel Cycle

- Fitzgerald, C. L., V. C. A. Vaughn, and C. E. Lamb, *Determination of Fission Product and Heavy Metals Inventories in FTE-4 Fuel Rods by a Grind-Burn-Leach Flowsheet*, ORNL/TM-5756 (July 1977).
- Forsberg, C. W., *Separation of Radioactive Krypton from Carbon Dioxide and Oxygen with Molecular Sieves*, ORNL/TM-5826 (October 1977).
- Forsberg, C. W., *Theoretical Analysis and Preliminary Experiments on the Feasibility of Removing CO₂ Containing ¹⁴C Selectively with a Ca(OH)₂ Slurry from a ⁸⁵Kr-Contaminated HTGR Reprocessing Plant Off-Gas Stream*, ORNL/TM-5825 (October 1977).
- Gilliam, T. M., V. L. Fowler, and D. J. Inman, *Krypton Absorption in Liquid CO₂ (KALC): Campaign III in the Experimental Engineering Section Off-Gas Decontamination Facility*, ORNL/TM-5655 (September 1977).
- Gilliam, T. M., V. L. Fowler, and D. J. Inman, "Removal of Krypton-85 from HTGR Reprocessing Plant Off-Gas Streams," presented at the 1977 Winter Meeting of the American Nuclear Society, San Francisco, Nov. 27-Dec. 2, 1977; published in *Trans. Am. Nucl. Soc.* 27, 480-81 (1977).
- Gilliam, T. M., V. L. Fowler, and D. J. Inman, *The Experimental Engineering Section Off-Gas Decontamination Facility's Fractionator Column: Installation and Performance*, ORNL/TM-5869 (March 1978).
- Haas, P. A., *Resin-Based Preparation of HTGR Fuels: Operation of an Engineering-Scale Uranium Loading System*, ORNL-5300 (October 1977).
- Haas, P. A., and J. P. Drago, "Separates Spherical Particles from Nonspherical," *Chem. Process.* 40(10), 152 (1977).
- Haas, P. A., J. P. Drago, D. L. Million, and R. D. Spence, *Development, Design, and Preliminary Operation of a Resin-Feed Processing Facility for Resin-Based HTGR Fuels*, ORNL/TM-6061 (January 1978).

¹⁶ Department of Energy, Washington, D.C.

- Holladay, D. W., *Experiments with a Lime Slurry in a Stirred Tank for the Fixation of Carbon-14-Contaminated CO₂ from Simulated HTGR Fuel Reprocessing Off-Gas*, ORNL/TM-5757 (March 1978).
- Holladay, D. W., G. L. Haag, and A. D. Ryon, "The Fixation of CO₂ in Simulated HTGR Fuel Reprocessing Off-Gas," presented at the 1977 Winter Meeting of the American Nuclear Society, San Francisco, Nov. 27-Dec. 2, 1977.
- Levins, D. M.,¹⁷ R. W. Glass, M. M. Chiles,¹⁸ D. J. Inman, and D. C. Watkins,¹⁹ "β-Scintillation Monitor for Krypton-85 at High Pressures," *Nucl. Instrum. Methods* 146, 517-25 (1977).
- Lin, K. H., *Process Alternatives for HTGR Fuel Reprocessing Wastes: An Engineering Evaluation*, ORNL/TM-5823 (May 1977).
- Lin, K. H., and W. E. Clark, "High-Level Solid Wastes from HTGR Fuel Reprocessing," presented at the 1977 Winter Meeting of the American Nuclear Society, San Francisco, Nov. 27-Dec. 2, 1977; published in *Trans. Am. Nucl. Soc.* 27, 442 (1977).
- Shaffer, J. H., W. E. Shockley, and R. B. Evans III,¹⁸ *The Reaction of Uranyl Nitrate Solutions with Amberlite IRC-72 Cation Exchange Resin at 30°C: A Kinetic Investigation for the HTGR Fuel Recycle Plant*, ORNL/TM-5866 (January 1978).
- Spence, R. D., and P. A. H. Has, *Tests of a Higgins Contactor for the Engineering-Scale Resin Loading of Uranium*, ORNL/TM-5973 (January 1978).

Fusion Energy Studies

- Clinton, S. D., and J. S. Watson, "Tritium Removal from Liquid Metals by Sorption of Yttrium," presented at the Seventh Symposium on Engineering Problems of Fusion Research, University of Tennessee, Knoxville, Oct. 25-28, 1977; published in the *Proceedings*.
- Compere, E. L., J. S. Watson, and J. T. Bell,¹⁹ "Tritium in Fission and Fusion Reactor Systems," presented at the 107th Annual Meeting of the AIME, Denver, Colo., Feb. 26-Mar. 2, 1978.
- Fisher, P. W., "Introduction to Cryogenic Vacuum Pumping (to be included in class notes)," presented at the Basic Vacuum Technology Course of the American Vacuum Society, Boston, Mass., Nov. 7-11, 1977; published in the *Proceedings*.
- Fisher, P. W., and J. S. Watson, "Cryosorption Pumping of Deuterium by MS-5A at Temperatures Above 4.2 K for Fusion Reactor Applications," presented at the 24th National Vacuum Symposium, Boston, Nov. 7-11, 1977.
- Fisher, P. W., and J. S. Watson, "Cryosorption Pumping of 95% Deuterium-5% Helium on Molecular Sieve-5A at 4.2 K," presented at the Seventh Symposium on Engineering Problems of Fusion Research, University of Tennessee, Knoxville, Oct. 25-28, 1977; published in the *Proceedings*.
- Fisher, P. W., and J. S. Watson, "Cryosorption Pumping of Helium at 4.2 K by Type 5A Molecular Sieve," presented at the 107th Annual Meeting of the American Nuclear Society, New York, June 12-17, 1977.
- Garber, H. J.,²⁰ and J. S. Watson, "Tritium Systems Preliminary Design for TNS," presented at the Seventh Symposium on Engineering Problems in Fusion Research, University of Tennessee, Knoxville, Oct. 25-28, 1977.

17. Australian Atomic Energy Commission.

18. Deceased.

19. Chemistry Division.

20. Westinghouse Electric Corp., Pittsburgh, Pa.

Talbot, J. B., and F. W. Wiffen,²¹ "Recovery of Tritium from Solid Li-Al and Sintered Aluminum Product (SAP) Blanket Materials," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 27-Dec. 2, 1977.

Watson, J. S., "Engineering Problems in Fusion Power," presented to nuclear engineering and chemical engineering students at the University of Virginia, Charlottesville, October 1977.

Watson, J. S., "Mass Transfer Processes in Hydride Beds," presented at the Hydride Symposium, Albuquerque, N.M., Mar. 8-9, 1978.

Watson, J. S., and F. W. Fisher, "Cryosorption Pumping Under Fusion Reactor Conditions," presented at the Seventh International Vacuum Congress, Vienna, Sept. 12-16, 1977; published in the *Proceedings*.

Watson, J. S., and H. J. Garber,²⁰ "Fuel Handling System for TNS," presented at the 1977 Winter Meeting of the American Nuclear Society, San Francisco, Nov. 27-Dec. 2, 1977.

HTGR Technology

Dyer, F. F.,²² R. P. Wichner, and A. P. Malinauskas, "A Study of Radionuclides in the Peach Bottom HTGR Primary Circuit," presented at the 1977 Annual Meeting of the American Nuclear Society, New York, June 12-17, 1977.

Homan, F. J.,²¹ T. B. Lindemer, F. L. Long,²¹ T. N. Tiegs,²¹ and R. L. Beatty,²¹ "Stoichiometric Effects on Performance of High-Temperature Gas-Cooled Reactor Fuels from the U-C-O System," *Nucl. Technol.* 35, 428-41 (1977).

Lindemer, T. B., "Measurement and Interpretation of CO and Kr + Xe in Irradiated ThO₂-Containing HTGR Fuel Particles," *J. Am. Ceram. Soc.* 60(9-10), 409-16 (1977).

Malinauskas, A. P., F. F. Dyer,²² L. L. Fairchild, W. J. Martin, and R. P. Wichner, "Fission Product Behavior in the Peach Bottom HTGR," presented at the Japan-U.S. Seminar on HTGR Safety Technology, Brookhaven National Laboratory, Sept. 15-16, 1977; published in the *Proceedings*.

Morgan, M. T., and A. P. Malinauskas, "Cesium Release and Transport in BISO-Coated Fuel Particles," *Nucl. Technol.* 35, 457 (1977).

Pearson, R. L., and T. B. Lindemer, "Simulation of Fission Product Behavior in HTGR Fissile Fuel Particles," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 25-27, 1977.

Pearson, R. L., and T. B. Lindemer, "The Interaction of LaC₂ and NdC₂ with SiC in HTGR Particles," presented at the American Nuclear Society Thermal Reactor Safety Meeting, Sun Valley, Idaho, July 31-Aug. 4, 1977; published in the *Proceedings*.

Stark, W. A., Jr.,²³ and A. P. Malinauskas, "Surface Area—Burnoff Correlation for the Steam-Graphite Reaction," presented at the Japan-U.S. Seminar on HTGR Safety Technology, Brookhaven National Laboratory, Upton, N.Y., Sept. 15-16, 1977.

Wichner, R. P., F. F. Dyer,²² and A. P. Malinauskas, "Distribution of Cesium and Other Fission Products in Peach Bottom HTGR Fuel Elements," presented at the 1977 Annual Meeting of the American Nuclear Society, New York, June 12-17, 1977.

Wichner, R. P., F. F. Dyer,²² W. J. Martin, and L. C. Bate, *Distribution of Fission Products in Peach Bottom HTGR Fuel Element E11-07*, ORNL-5214 (April 1977).

Wichner, R. P., F. F. Dyer,²² W. J. Martin, and L. L. Fairchild, *Distribution of Fission Products in Peach Bottom HTGR Fuel Element E14-01*, ORNL/TM-5730 (August 1977).

21. Metals and Ceramics Division.

22. Analytical Chemistry Division.

23. Los Alamos Scientific Laboratory, Los Alamos, N.M.

Miscellaneous

- Baumann, C. D.,²⁴ C. J. Barton,²⁴ E. L. Compere, and T. K. Row,²⁵ *Very High Temperature Gas Reactor Environmental Impacts Assessment*, ORNL/TM-5914 (August 1977).
- Besmann, T. M., *SOLGASMIX-PV, a Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems*, ORNL/TM-5775 (April 1977).
- Brooksbank, R. E., "Nuclear Fuel Cycle," presented at the Oak Ridge Associated Universities, Oak Ridge, Tenn., Apr. 19, 1977, and Mar. 20, 1978.
- Brooksbank, R. E., "Safeguards in the Nuclear Industry," presented at the Oak Ridge Associated Universities, Oak Ridge, Tenn., Apr. 26, 1977.
- Brooksbank, R. E., "The Status of the Nuclear Fuel Cycle—1977," presented at the WATtec Fifth Annual Energy Conference and Exhibition, Knoxville, Tenn., Feb. 24, 1978.
- Brooksbank, R. E., J. E. Bigelow, D. O. Campbell, F. G. Kitts, and R. B. Lindauer, "Fuel Cycles Using Adulterated Plutonium," presented at the 18th Annual ASME Symposium on Non-Proliferation: Reality and Illusion of a Plutonium-Free Economy, University of New Mexico, Albuquerque, Mar. 16–17, 1978; to be published in the *Proceedings*.
- Canon, R. M., K. W. Wall,²⁶ A. W. Smith,²⁶ and G. K. Patterson,²⁶ "Turbulence Level Significance of the Coalescence-Dispersion Rate Parameter," *Chem. Eng. Sci.* 32(11), 1349 (1977).
- Dickens, J. K.,²⁷ G. L. Morgan,²⁷ G. T. Chapman,²⁷ T. A. Love,²⁷ E. Newman, and F. G. Perey,²⁷ "Cross Sections for Gamma-Ray Production by Fast Neutrons for 22 Elements Between Z-3 and Z-82," *Nucl. Sci. Eng.* 62, 515 (1977).
- Feldman, M. J., "An Overview of Foreign Programs," presented at the American Institute of Chemical Engineers Annual Symposium on Closing the Nuclear Fuel Cycle, Oak Ridge, Tenn., Sept. 20–22, 1977.
- Feldman, M. J., "Public Awareness and the Professional Society," presented at the IAEA Conference on Nuclear Power and Its Fuel Cycle, Salzburg, Austria, May 2–13, 1977.
- Feldman, M. J., "The Role of Nuclear Centers in the Utilization of the Nuclear Option," presented at the WATtec Fifth Annual Energy Conference and Exhibition, Knoxville, Tenn., Feb. 23–25, 1978.
- Feldman, M. J., "The U.S. Nonproliferation Policy and the Reactions of the Technical Community," presented at the Congress of International Technology, Pittsburgh, Pa., Oct. 9–14, 1977; published in the *Proceedings*.
- Feldman, M. J., J. B. van Erp,²⁸ and O. H. Klepper, "Nuclear Safety at Salzburg," *Nucl. Saf.* 18(6), 756 (1977).
- Haire, R. G.,²⁹ M. H. Lloyd, W. O. Milligan,²⁹ and M. L. Beasley,²⁹ "Lattice Parameters of $^{244}\text{Cm}(\text{OH})_3$ and the Effect of Self-Irradiation on Crystalline $^{241}\text{Am}(\text{OH})_3$ and $^{244}\text{Cm}(\text{OH})_3$," *J. Inorg. Nucl. Chem.* 39, 834 (1977).
- Jones, J. E.,³⁰ W. R. Gambill, R. H. Cooper,³¹ E. C. Fox,³¹ L. C. Fuller,³⁰ C. C. Littlefield,³¹ and M. D. Silverman,³⁰ *Assessment of Very High-Temperature Reactors in Process Applications. Appendix II—VHTR Process Heat Application Studies*, ORNL/TM-5410 (June 1977).

24. Retired.

25. Energy Division.

26. University of Missouri, Rolla.

27. Neutron Physics Division.

28. Argonne National Laboratory, Argonne, Ill.

29. Baylor University, Waco, Tex.

30. Engineering Technology Division.

- Jubin, R. T., and J. G. Moore, *A User's Guide for the Computer Program DASAVOR—Data Storage and Variable Output Recovery System*, ORNL/TM-5807 (May 1977).
- Kim, J.,³¹ R. C. Davis,³¹ W. R. Gambill, and H. H. Haselton,³¹ "A Heat Transfer Study of Water-Cooled Swirl Tubes for Neutral Beam Targets," presented at the Seventh International Symposium on Engineering Problems in Fusion Research, University of Tennessee, Knoxville, Oct. 25-28, 1977.
- Lloyd, M. H., book review of *Chemistry of Americium*, by W. W. Schulz, *Nucl. Sci. Eng.* 65, 199 (1977).
- Leuze, R. E., "Technology of the Light Water Reactor Fuel Cycle," presented at the Oak Ridge Associated Universities, Oak Ridge, Tenn., July 13, 1977.
- Rodgers, B. K., and T. M. Reed,³² "Carbon Tetrafluoride and Carbon in Ionizing Radiation," *Ind. Eng. Chem., Prod. Res. Dev.* 16(1), 87 (1977).
- Roogers, B. R., T. M. Reed,³² S. N. Subbanna,³² and E. H. Meadows,³² "Perfluoroalkanes from Sulfur Hexafluoride/Carbon Reactions," *Ind. Eng. Chem., Prod. Res. Dev.* 16(2), 191 (1977).
- Scott, C. D., "Engineering Involvement in the Health Industry," presented at the 70th Annual Meeting of the American Institute of Chemical Engineers, New York, Nov. 13-17, 1977.
- Tedder, D. W., and D. F. Rudd,³³ "Parametric Studies in Industrial Distillation: Part I. Design Comparisons; Part II. Heuristic Optimization; Part III. Design Methods and Their Evaluation," *AIChE J.* 24(2), 303 (1978).
- Vondra, B. L., and G. D. Lehmkuhl,³⁴ "Product Conversion Options Under Revised Energy Policies," presented at the 84th National Meeting of the American Institute of Chemical Engineers, Atlanta, Ga., Mar. 1, 1978.
- Wymer, R. G., "Closing the Nuclear Fuel Cycle: The Status of Technical Problems," presented at the Annual Symposium of the Knoxville-Oak Ridge Section of the American Institute of Chemical Engineers, Oak Ridge, Tenn., Sept. 20-22, 1977.
- Wymer, R. G., "The Nuclear Energy Crisis," presented at the University of Lowell, Lowell, Mass., May 6, 1977.
- Youngblood, E. L., I. J. Urza,³⁵ and G. I. Cathers,³⁴ *Laboratory and Pilot-Plant Studies on the Conversion of Uranyl Nitrate Hexahydrate to UF₆ by Fluidized-Bed Processes*, ORNL/TM-5912 (June 1977).

Nuclear Regulatory Commission Programs

- Blanco, R. E., et al., "A Cost/Benefit Analysis of Methods for Controlling the Release of Radioactive Materials in the Nuclear Fuel Cycle," presented at the International Conference on Nuclear Power and Its Fuel Cycle, Salzburg, Austria, May 11, 1977; published as IAEA-CN-36/429 (1977).
- Davis, Wallace, Jr., *A Model of Iodine Transport and Reaction Kinetics in a Nuclear Fuel Reprocessing Plant*, ORNL/NUREG-16 (August 1977).
- Davis, Wallace, Jr., "Carbon-14 Production in Nuclear Reactors," presented at the Symposium on Management of Low-Level Radioactive Waste, Georgia Institute of Technology, Atlanta, May 23-27, 1977.
- Godbee, H. W., "U.S. Nuclear Fuel Cycle: An Introductory Overview," presented at the American Society of Mechanical Engineers Short Course on Radioactive Waste Management for Nuclear Power Reactors, Chicago, Oct. 3-7, 1977.

31. Fusion Energy Division.

32. University of Florida, Gainesville.

33. University of Wisconsin, Madison.

34. Atomics International, Golden, Colo.

35. Exxon Nuclear Company.

- Godbee, H. W., and A. H. Kibbey, "Ignition of Hydrogen and/or Loss of Coolant in a High-Level Radioactive Liquid Waste Storage Tank: Resultant Thermal Transients, Radioactive Releases, and Associated Population Doses," presented to the Nuclear Regulatory Commission, Washington, D.C., July 1977.
- Godbee, H. W., and A. H. Kibbey (compilers), *Informal Proceedings of the Radwaste Management Workshop, New Orleans, La., Jan. 12-14, 1977* (April 1977).
- Hamel, W. R.,⁴ and L. B. Shappert, *Desirability and Feasibility of Vault Automation in Special Nuclear Material Storage*, ORNL/NUREG-20 (NUREG-0318) (October 1977).
- Kibbey, A. H., "Summary of the ORNL-Sponsored Reactor Radwaste Management Workshop," presented at the 1977 Joint Power Generation Conference, Long Beach, Calif., Sept. 18-21, 1977; published as 77-JPGC-NE-14.
- Kibbey, A. H., "The Chemistry and Properties of Solidification Agents," presented at the American Society of Mechanical Engineers Short Course on Radioactive Waste Management for Nuclear Power Reactors, Chicago, Oct. 3-7, 1977.
- Kibbey, A. H., H. W. Godbee, and G. S. Hill,¹⁵ "Estimated Radiological Doses from the Gaseous Effluents of a Model High-Level Waste Solidification Facility," presented at the National Topical Meeting of the American Nuclear Society on the Back End of the LWR Fuel Cycle, Savannah, Ga., Mar. 19-22, 1978.
- McBride, J. P., R. E. Moore,¹⁵ J. P. Witherspoon,¹⁵ and R. E. Blanco, *Radiological Impact of Airborne Effluents of Coal-Fired and Nuclear Power Plants*, ORNL-5315 (August 1977).
- Roddy, J. W., R. E. Blanco, B. C. Finney, G. S. Hill,¹⁵ R. E. Moore,¹⁵ and J. P. Witherspoon,¹⁵ *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle—Conversion of Recycle Uranium to UF₆*, ORNL/NUREG/TM-37 (August 1977).
- Sears, M. B., "Nuclear Waste Management in the Front End of the Nuclear Fuel Cycle," presented at the Division of Science and Technology Conference Course on Nuclear Waste Management, College of Lifelong Learning, Wayne State University, Detroit, Apr. 23-24, 1977.
- Sears, M. B., "Radioactive Waste Treatment Costs and Environmental Impact for Milling of Uranium Ore," presented at the National Convention of the Society of Women Engineers, Cincinnati, Ohio, June 24, 1977.
- Sears, M. B., R. E. Blanco, B. C. Finney, G. S. Hill,¹⁵ R. E. Moore,¹⁵ and J. P. Witherspoon,¹⁵ *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 I. The Fluorination-Fractionation Process*, ORNL/NUREG/TM-7 (September 1977).
- Witherspoon, J. P.,¹⁵ M. B. Sears, and R. E. Blanco, "Releases of Radioactivity from Uranium Mills and Radwaste Effluent Costs," *Trans. Am. Nucl. Soc.* 27, 151 (1977).

Patents

- Campbell, D. O., and S. R. Buxton, "Recovery of Transplutonium Elements from Nuclear Reactor Waste," U.S. Patent 4,025,602 (May 24, 1977).
- Clark, W. E., and C. T. Thompson, "Immobilization of Iodine in Concrete," U.S. Patent 4,017,417 (Apr. 12, 1977).
- Hancher, C. W., and C. D. Scott, "Tapered Bed Bioreactor," U.S. Patent 4,032,407 (June 28, 1977).
- Lindemer, T. B., E. L. Long, Jr.,²¹ and R. L. Beatty,²¹ "Pyrolytic Carbon-Coated Nuclear Fuel," U.S. Patent 4,077,838 (Mar. 7, 1978).
- Notz, K. J., R. H. Rainey, C. W. Greene, and W. W. Shockley, "Method for Loading Resin Beds," U.S. Patent 4,070,438 (Jan. 24, 1978).

Rodgers, B. R., and M. S. Edwards, "Filtering Coal-Derived Oil Through a Filter Media Precoated with Particles Partially Solubilized by Said Oil," U.S. Patent 4,046,690 (Sept. 6, 1977).

Shumate, S. E., II, "Filter Type Rotor for Multistation Photometer," U.S. Patent 4,035,156 (July 12, 1977).

Tallent, O. K., "Method for Dissolving Plutonium Dioxide," U.S. Patent 4,069,293 (Jan. 17, 1978).

Watson, C. D., and B. S. Weil, "Method for Shearing Spent Nuclear Fuel Assemblies," U.S. Patent 4,056,052 (Nov. 1, 1977).

Power Reactor Fuel Processing

Besmann, T. M., and T. B. Lindemer, "Equilibria in the U-C-O System," presented at the 1977 Fall Meeting of the American Ceramic Society, Hyannis, Mass., Sept. 25-28, 1977.

Besmann, T. M., and T. B. Lindemer, "Thermodynamics of the Conversion of Plutonium Dioxide to Plutonium Monocarbide," *J. Nucl. Mater.* 67, 77-87 (1977).

Besmann, T. M., and K. E. Spear,³⁶ "Analysis of the Chemical Vapor Deposition of Titanium Diboride. I. Equilibrium Thermodynamic Analysis. II. Modeling the Kinetics of Deposition," *J. Electrochem. Soc.* 124(5), 786-90 (1977).

Brooksbank, R. E., W. T. McDuffee, and R. H. Rainey, "A Review of Thorium Fuel Reprocessing Experience," presented at the 84th National Meeting of the American Institute of Chemical Engineers, Atlanta, Ga., Feb. 26-Mar. 2, 1978.

Campbell, D. O., "Hot-Cell Studies of Light Water Reactor Fuel Reprocessing," presented at Battelle-Pacific Northwest Laboratories, Richland, Wash., July 21, 1977.

Campbell, D. O., "Nuclear Fuel Reprocessing—Recent Research," presented at the 79th Annual Meeting of the American Ceramic Society, Chicago, Apr. 23-28, 1977.

Campbell, D. O., "Solids from Fuel Dissolution, Process Solutions, and Waste Evaporation," presented at the American Nuclear Society Topical Meeting on the Back End of the LWR Fuel Cycle, Savannah, Ga., Mar. 19-22, 1978; published in the *Proceedings*.

Campbell, D. O., W. L. Pattison, and S. R. Buxton, "Batch Extraction and Stripping Tests of Coprocessing," presented at the American Nuclear Society National Topical Meeting on the Back End of the Nuclear Fuel Cycle, Savannah, Ga., Mar. 19-22, 1978; published in the *Proceedings*.

Carter, W. L., R. H. Rainey, and D. R. Johnson,³⁷ "Thorium Fuel Cycles for LWRs: Fuel Diversion Assessments and Recycle Requirements," presented at the American Nuclear Society National Topical Meeting on the Back End of the LWR Fuel Cycle, Savannah, Ga., Mar. 19-22, 1978; published in the *Proceedings*.

Carter, W. L., R. H. Rainey, D. R. Johnson,³⁷ and J. A. Horak,³⁷ *Preliminary Analysis of Alternative Fuel Cycles for Proliferation Evaluation*, ORNL/TM-6036 (September 1977).

Clark, W. E., "The Isolation of Radioiodine with Portland Cement. Part I: Scoping Leach Studies," *Nucl. Technol.* 36, 215 (1977).

Counce, R. M., *A Literature Review of Nitrogen Oxide Absorption into Water and Dilute Nitric Acid*, ORNL/TM-5921 (August 1977).

Cox, R. L.,³⁷ *Radiative Heat Transfer in Arrays of Parallel Cylinders*, ORNL-5239 (June 1977).

36. Pennsylvania State University, University Park.

37. ORGDP; formerly with Chemical Technology Division.

- Hampson, D. C., "Safety Aspects of Fast Breeder Fuel Cycles," presented at the LMFBR Safety Institute, Argonne National Laboratory, Argonne, Ill., Feb. 9, 1978.
- Hannaford, B. A., "Iodox Process—Iodine Removal from Air with Hyperazeotropic Nitric Acid," presented at the 1977 Winter Meeting of the American Nuclear Society, San Francisco, Nov. 27-Dec. 2, 1977.
- Horner, D. E., D. J. Crouse, and J. C. Mailen, *Cerium-Promoted Dissolution of PuO_2 and $PuO_2 \cdot UO_2$ in Nitric Acid*, ORNL/TM-4716 (August 1977).
- Horner, D. E., and J. C. Mailen, "Solvent Extraction Kinetics of Uranium and Fission Products," presented at the 1977 Winter Meeting of the American Nuclear Society, San Francisco, Nov. 27-Dec. 2, 1977; published in *Trans. Am. Nucl. Soc.* 27, 484 (1977).
- Horner, D. E., J. C. Mailen, and H. R. Bigelow,³⁸ "Solubility of PdI_2 in Nitrate and Perchlorate Solutions," *J. Inorg. Nucl. Chem.* 39, 1656 (1977).
- Irvine, A. R., and E. L. Nicholson, Jr., *Impact of Proliferation-Resistant Fuel Cycles on Hot Experimental Facility Design and Objectives*, ORNL/TM-6117 (January 1978).
- Joy, D. S., and B. D. Holcomb,³⁹ *Logistics Models for the Transportation of Radioactive Waste and Spent Fuel*, ORNL/TM-6192 (March 1978).
- Kirkman, J. Q., and J. P. Drago, "Development of a Continuous Rotary Dissolver," presented at the American Nuclear Society National Topical Meeting on the Back End of the LWR Fuel Cycle, Savannah, Ga., Mar. 19-22, 1978; published in the *Proceedings*.
- Lloyd, M. H., "Chemical Behavior of Plutonium in LWR Fuel Reprocessing Solutions," presented at the American Nuclear Society National Topical Meeting on the Plutonium Fuel Cycle, Miami Beach, Fla., May 2-4, 1977; published in the *Proceedings*.
- Mailen, J. C., and D. E. Horner, "Removal of Iodine from Reactor Fuel Solutions as Insoluble PdI_2 ," *Nucl. Technol.* 33, 260 (1977).
- Morse, L. E., *A Conceptual Study for the Reprocessing of Spent Carbide and Nitride Fast Reactor Fuels in Relation to Gasborne Radiological Releases*, ORNL/TM-6100 (December 1977).
- Nicholson, E. L., Jr., *The PuO_2 Dissolution Problem for LWR: Pu Recycle and LMFBR Fuels: Fabrication and Reprocessing Problems and Their Resolution*, ORNL/TM-5903 (July 1977).
- Notz, K. J., and R. L. Beatty,²¹ "Remote Fabrication for Alternate LWR Fuels by Sol-Gel Sphere-Pac Technology," presented at the American Nuclear Society National Topical Meeting on the Back End of the LWR Fuel Cycle, Savannah, Ga., Mar. 19-22, 1978; published in the *Proceedings*.
- Rainey, R. H., W. L. Carter, et al., *Preliminary Analysis of Alternative Fuel Cycles for Proliferation Evaluation*, ORNL/TM-6036 (August 1977).
- Seagren, R. D., "Transportation of Radioactive Waste," presented at the University Studies and Weekend College, Wayne State University, Detroit, Apr. 24, 1977.
- Shappert, L. B., W. J. Bryan, et al., *The Obsolete Cask Program: End-On Drop Tests With and Without an Impact Limiter and the 40-Inch Puncture Test*, ORNL/TM-1312, vol. 19 (July 1977).
- Shappert, L. B., D. S. Joy, and M. M. Heiskell, *Radioactive Waste Transportation Systems Analysis and Program Plan*, ORNL-5352 (March 1978).
- Stacy, R. G., and J. H. Goode, "Voloxidation and Dissolution of Irradiated LWR Fuel," presented at the American Nuclear Society National Topical Meeting on the Back End of the LWR Fuel Cycle, Savannah, Ga., Mar. 19-22, 1978; published in the *Proceedings*, CONF-780304.

38. Co-op student, University of Tennessee, Knoxville.

39. Computer Sciences Division.

Tallent, O. K., and J. C. Mailen, "Effects of Metal Ion Impurities on PuO_2 Dissolution in Nitric-Hydrofluoric Acid Solution," *Nucl. Technol.* 34, 416 (1977).

Tallent, O. K., J. C. Mailen, and K. D. Williams, "Study of the Dissolution of Refractory PuO_2 in Aqueous Hydriodic Acid Solutions," presented at the American Nuclear Society National Topical Meeting on the Plutonium Fuel Cycle, Miami Beach, Fla., May 2-4, 1977; published in the *Proceedings*.

Vondra, B. L., and D. J. Crouse, "Present Status of LWR Fuels Reprocessing Technology," presented at the Winter Meeting of the American Institute of Chemical Engineers, New York, Nov. 13-17, 1977; published in the *Proceedings*.

Whitley, M. E., *A Dimensional Analysis of Solids Transport and Dispersion in a Rotary Kibn*, ORNL/TM-5898 (July 1977).

Yarbro, O. O., J. Q. Kirkman, and A. R. Irvine, "The Application of the Rotary Dissolver Concept to Various Fuel Cycles," presented at the 84th National Meeting of the American Institute of Chemical Engineers, Atlanta, Ga., Feb. 26-Mar. 1, 1978.

Yarbro, O. O., J. C. Mailen, and M. J. Stephenson, "Retention of Gaseous Isotopes," presented at the International Conference on Nuclear Power and Its Fuel Cycle, Salzburg, Austria, May 2-13, 1977.

Progress Reports

Blomeke, J. O., and D. W. Tedder, *Actinide Partitioning and Transmutation Program Progress Report for Period October 1, 1976 to March 31, 1977*, ORNL/TM-5888 (June 1977).

Burch, W. D., M. J. Feldman, W. S. Groenier, B. L. Vondra, and W. E. Unger, *LMFBR Fuel Reprocessing Program Progress Report for Period January 1 to March 31, 1977*, ORNL/TM-5879 (May 1977).

Burch, W. D., M. J. Feldman, W. S. Groenier, B. L. Vondra, and W. E. Unger, *Advanced Fuel Recycle Program Progress Report for Period April 1 to June 30, 1977*, ORNL/TM-5993 (September 1977).

Burch, W. D., M. J. Feldman, W. S. Groenier, B. L. Vondra, and W. E. Unger, *Advanced Fuel Recycle Program Progress Report for Period July 1 to September 30, 1977*, ORNL/TM-6092 (November 1977).

Burch, W. D., M. J. Feldman, W. S. Groenier, B. L. Vondra, and W. E. Unger, *Advanced Fuel Recycle Program Progress Report for Period October 1 to December 31, 1977*, ORNL/TM-6221 (February 1978).

King, L. J., J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1976*, ORNL-5305 (October 1977).

King, L. J., J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June 30, 1977*, ORNL-5358 (December 1977).

Malinauskas, A. P., R. A. Lorenz, R. P. Wichner, J. L. Collins, S. K. Whatley, O. L. Kirkland, and R. L. Towns, *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period January-March 1977*, ORNL/NUREG/TM-122 (June 1977).

Malinauskas, A. P., R. A. Lorenz, R. P. Wichner, J. L. Collins, S. K. Whatley, O. L. Kirkland, and R. L. Towns, *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period April-June 1977*, ORNL/NUREG/TM-139 (September 1977).

Malinauskas, A. P., R. A. Lorenz, R. P. Wichner, J. L. Collins, S. K. Whatley, O. L. Kirkland, and R. L. Towns, *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period July-September 1977*, ORNL/NUREG/TM-170 (January 1978).

- Malinauskas, A. P., R. A. Lorenz, R. P. Wichner, J. L. Collins, S. K. Whatley, O. L. Kirkland, and R. L. Towns, *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period October-December 1977*, ORNL/NUREG/TM-186 (March 1978).
- Pitt, W. W., Jr., and J. E. Mrochek, *Experimental Engineering Section Semiannual Progress Report for the Period March 1 to August 31, 1976. Volume 2: Biotechnology and Environmental Programs*, ORNL/TM-5865/V2 (March 1978).
- Ryon, A. D., *Experimental Engineering Section Semiannual Progress Report for the Period March 1, 1976 to August 31, 1976. Volume 5: Reactor Programs*, ORNL/TM-5865/V5 (March 1978).
- Scott, C. D., C. A. Burtis,² W. S. Groenier, W. W. Pitt, Jr., A. D. Ryon, C. D. Watson, and J. S. Watson, *Experimental Engineering Section Semiannual Progress Report (Excluding Reactor Programs), September 1, 1975 to February 29, 1976*, ORNL/TM-5533 (July 1977).
- Scott, C. D., S. D. Clinton, R. Hightower, Jr., J. E. Mrochek, W. W. Pitt, Jr., A. D. Ryon, and J. S. Watson, *Experimental Engineering Section Semiannual Progress Report for the Period March 1 to August 31, 1976. Volume 1: Summary Report*, ORNL/TM-5865/V1 (September 1977).
- Tedder, D. W., and J. O. Blomeke, *Actinide Partitioning and Transmutation Program Progress Report for Period April 1 to June 30, 1977*, ORNL/TM-6056 (October 1977).
- Tedder, D. W., and J. O. Blomeke, *Actinide Partitioning and Transmutation Program Progress Report for Period July 1 to September 30, 1977*, ORNL/TM-6174 (February 1978).
- Vondra, B. L., et al., *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period January 1 to March 31, 1977*, ORNL/TM-5864 (May 1977).
- Vondra, B. L., et al., *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period April 1 to June 30, 1977*, ORNL/TM-5987 (August 1977).
- Vondra, B. L., et al., *Alternate Fuel Cycle Technologies Program Quarterly Report for Period July 1 to September 30, 1977*, ORNL/TM-6076 (November 1977).
- Vondra, B. L., et al., *Alternate Fuel Cycle Technologies/Thorium Fuel Cycle Technology Programs Quarterly Report for Period October 1 to December 31, 1977*, ORNL/TM-6206 (February 1978).

Reactor Safety Research

- Albrecht, H.,⁴¹ M. F. Osborne, and H. Wild,⁴¹ "Experimental Determination of Fission and Activation Product Release During Core Meltdown," presented at the American Nuclear Society Meeting on Thermal Reactor Safety, Sun Valley, Idaho, July 31-Aug. 5, 1977.
- Besmann, T. M., "Assessment of Oxygen Behavior in U-Pu-C Nuclear Fuel," presented at the 79th Annual Meeting of the American Ceramic Society, Chicago, Apr. 23-28, 1977.
- Besmann, T. M., and T. B. Lindemer, *Chemical Thermodynamics of the System Cs-U-Zr-H-I-O in the LWR Fuel-Clad Cap*, ORNL/TM-6130 (January 1978).
- Fischer, M.,⁴¹ and M. F. Osborne, "LWR Fuel-Behavior Research in the Federal Republic of Germany," *Nucl. Saf.* 19(2), 176 (1978).
- Kelly, M. J., J. M. Rochelle,¹ and G. W. Parker, "A Nonnuclear Method of Reaching the Fuel Thermodynamic State Postulated in Prompt Critical Excursions," presented at the 79th Annual Meeting of the American Ceramic Society, Chicago, Apr. 23-28, 1977.

41. GFK Karlsruhe, Federal Republic of Germany.

Lorenz, R. A., "Fission Product Source Term Correlations for Spent Fuel Transportation Accidents and Controlled Loss-of-Coolant Accidents," presented at the Fifth Water Reactor Research Information Meeting, Gaithersburg, Md., Nov. 7-11, 1977.

Lorenz, R. A., and J. L. Collins, "Behavior of Simulated Fission Products Under LWR Accident Conditions," presented at the 79th Annual Meeting of the American Ceramic Society, Chicago, Apr. 23-28, 1977.

Parker, G. W., "Fast Reactor HCDA Fuel Aerosols: Physical and Chemical Behavior," presented at the 79th Annual Meeting of the American Ceramic Society, Chicago, Apr. 23-28, 1977.

Parker, G. W., M. J. Kelly, and G. E. Creech,⁴² "Comparative Behavior of Instantaneously and Continuously Generated Reactor Fuel Aerosols," presented at the Tenth Aerosol Technology Meeting, Albuquerque and Los Alamos, N.M., Sept. 27, 1977.

Parker, G. W., and R. Van Houten,⁴³ "Fuel Behavior, Fission Product Behavior, and Research on Core Meltdown; Summary Review of Meeting Highlights," presented at the American Nuclear Society Meeting on Thermal Reactor Safety, Sun Valley, Idaho, July 31-Aug. 5, 1977.

Separations Chemistry

Bahner, C. T.,⁴⁴ R. R. Shoun, and W. J. McDowell, *Impurities That Cause Difficulty in Stripping Actinides from Commercial Tetraalkylcarbamoylmethylphosphonates*, ORNL/TM-5878 (September 1977).

Bond, W. D., Y. Jao,⁴⁵ and J. R. Peterson,⁴⁶ "The Oxidation-Reduction Kinetics Involved in the $\text{Np(V)} \rightarrow \text{Np(IV)} + \text{Fe(III)}$ System in Nitric Acid Solutions," *J. Inorg. Nucl. Chem.* 39, 1395-1402 (1977).

Bouwer, E. J.,⁴⁷ J. W. McKlveen,⁴⁷ and W. J. McDowell, "Uranium Assay of Phosphate Fertilizers and Other Phosphatic Materials," presented at the 22nd Annual Meeting of the Health Physics Society, Atlanta, Ga., July 3-8, 1977.

McDowell, W. J., F. G. Seeley, and M. T. Ryan,⁴⁸ "Penetration of HEPA Filters by Alpha Recoil Aerosols," *Health Phys.* 32(5), 445 (1977).

McDowell, W. J., and R. R. Shoun, "An Evaluation of Crown Compounds in Solvent Extraction of Metals," presented at the International Solvent Extraction Conference, Toronto, Sept. 12-16, 1977.

McDowell, W. J., R. R. Shoun, and Boyd Weaver,⁴⁹ "Crown Compounds as Solvent Extraction Reagents," presented at the First Symposium on Macrocyclic Compounds, Brigham Young University, Provo, Utah, Aug. 15-17, 1977.

Ryon, A. D., K. B. Brown, and F. G. Seeley, "Evaluation of Nitric Acid Leaching as a Means of Separating Radium and Other Significant Radionuclides from Uranium Ores and Tailings," presented at the Workshop on Radionuclide Leaching from Uranium Ores and Tailings, Ottawa, Oct. 15, 1977.

Ryon, A. D., F. J. Hurst,¹⁹ and F. G. Seeley, *Nitric Acid Leaching of Radium and Other Significant Radionuclides from Uranium Ores and Tailings*, ORNL/TM-5944 (August 1977).

Seeley, F. G., "Problems Associated with the Separation of Radium from Uranium Ore Tailings," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 23-27, 1977.

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49. Science Applications, Inc., Oak Ridge, Tenn.

Seeley, F. G., "Problems in the Separation of Radium from Uranium Ore Tailings," *Hydrometallurgy* 2, 249 (1977).

Shoun, R. R., "A Comparative Study of Organophosphorus Bidentate Extractants and Characterization of Their Impurities," presented at the Second Annual Workshop on Removal of Actinides from Aqueous Waste Solutions, Richland, Wash., May 18-19, 1977.

Shoun, R. R., W. J. McDowell, and Boyd Weaver,⁹ "Bidentate Organophosphorus Compounds as Extractants from Acidic Waste Solutions: A Comparative and Systematic Study," presented at the International Solvent Extraction Conference, Toronto, Sept. 9-16, 1977.

Transuranium-Element Processing

Collins, E. D., and D. E. Benker, "Iodox Process Tests in a Transuranium-Element Production Campaign," presented at the American Nuclear Society National Topical Meeting on the Back End of the LWR Fuel Cycle, Savannah, Ga., Mar. 19-22, 1978; published in the *Proceedings*.

Davis, W. C., *Stable Isotope Customer List and Summary of Shipments—FY 1976 (July 1, 1975–September 30, 1976)*, ORNL/TM-5853 (April 1977).

Fellows, R. L., and J. R. Peterson,⁹ "The First Preparation of an Einsteinium(II) Compound, EsCl_2 ," presented at the 12th Annual Rare-Earth Research Conference, Oglebay Park, W. Va., Oct. 17-19, 1977.

Whitson, W. R., *ORNL Shielded Facilities Capable of Remote Handling of Highly Radioactive Beta-Gamma Emitting Materials*, ORNL/TM-5971 (September 1977).

Waste Management

Alexander, C. W., and J. O. Blomeke, "Origin and Characteristics of Low-Level Nontransuranic Waste from the Nuclear Fuel Cycle," presented at the Symposium on the Management of Low-Level Radioactive Waste, Atlanta, May 23-27, 1977; to be published in the *Proceedings*.

Alexander, C. W., C. W. Kee, A. G. Croff, and J. O. Blomeke, *Projections of Spent Fuel to Be Discharged by the U.S. Nuclear Power Industry*, ORNL/TM-6008 (October 1977).

Blomeke, J. O., *1972 Preliminary Safety Analysis Report Based on a Conceptual Design of a Proposed Repository in Kansas*, ORNL/TM-5764 (August 1977).

Blomeke, J. O., "Partitioning of High-Level Wastes," presented at the UCC-ND Waste Management Technology Conference, Y-12 Plant, Jan. 25-26, 1978.

Blomeke, J. O., "Reactor Waste Disposal," presented at the Oak Ridge Associated Universities, Oak Ridge, Tenn., Aug. 10, 1977.

Blomeke, J. O., "Reprocessing and the Storage of Radioactive Waste," presented to the Nuclear Engineering Department, University of Wisconsin, Madison, June 23, 1977.

Blomeke, J. O., "Waste Disposal," presented at the Nuclear Safety Seminar, Georgia Institute of Technology, Atlanta, Mar. 13-17, 1978.

Blomeke, J. O., D. E. Ferguson, and A. G. Croff, "Disposal of Spent Fuel," presented at the Waste Management '78 Conference, University of Arizona, Tucson, Mar. 5-8, 1978; to be published in the *Proceedings*.

Croff, A. G., D. W. Tedder, J. P. Drago, J. O. Blomeke, and J. J. Perona,⁹ *A Preliminary Assessment of Partitioning and Transmutation as a Radioactive Waste Management Concept*, ORNL/TM-5808 (September 1977).

- Culler, F. L.,⁵⁰ J. O. Blomeke, H. E. Goeller, and A. M. Platt,⁵¹ "Management of High-Level and Alpha-Bearing Wastes," pp. 125-42 in *Nuclear Power and Its Fuel Cycle*, IAEA, Vienna, 1977.
- Jenks, G. H., and C. D. Bopp, *Storage and Release of Radiation Energy in Salt in Radioactive Waste Repositories*, ORNL-5058 (October 1977).
- Leuze, R. E., W. D. Bond, and D. W. Tedder, "Conceptual Methods for Actinide Partitioning," *Proceedings of the First Technical Meeting on the Nuclear Transmutation of Actinides, Ispra, Italy, March 16-18, 1977*, pp. 115-17 (1978).
- Moore, J. G., H. E. Devaney, M. T. Morgan, and G. C. Rogers, "The Fixation of Iodine Waste in Cement," presented at the 107th Annual Meeting of the AIIME, Denver, Colo., Feb. 26-Mar. 2, 1973.
- Newman, E., "The Incorporation of Radioactive Wastes in Concrete," presented at the UCC-ND Waste Management Technology Conference, Y-12 Plant, Jan. 25-26, 1978.
- Salmon, R., and C. W. Kee, *KWIKPLAN—A Computer Program for Projecting the Annual Requirements of Nuclear Fuel Cycle Operations*, ORNL/TM-5880 (June 1977).
- Tedder, D. W., "An Overview of the ORNL Actinide Partitioning Program," presented at the Second Annual Workshop on the Removal of Actinides from Aqueous Wastes, Richland, Wash., May 18-19, 1977.
- Tedder, D. W., "Material Balance Flowsheets for a PWR-U Reprocessing Plant," presented at the Second Annual Workshop on the Removal of Actinides from Aqueous Wastes, Richland, Wash., May 18-19, 1977.
- Weeren, H. O., "Waste Disposal by Shale Fracturing at ORNL," presented at the Symposium on Management of Low-Level Radioactive Waste, Georgia Institute of Technology, Atlanta, May 23-27, 1977.
- Weeren, H. O., "Waste Disposal by Shale Fracturing at ORNL," *Nucl. Eng. Des.* 44, 291 (1977).

50. Electric Power Research Institute, Palo Alto, Calif.

51. Battelle Pacific Northwest Laboratories, Richland, Wash.

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	Engineering Aspects of Solidification Methods	H. W. Godbee

January 18	Waste Partitioning Process Development OPIX Hot-Cell Bidentate Extractions	F. W. Forsberg S. Katz
January 25	Fundamental Studies of Solids Separation from Coal-Derived Liquids Mass Transfer in Agitated, Low-Entrainment Liquid-Liquid Contactors	B. R. Rodgers C. H. Brown, Jr.
February 1	Experimental Requirements of the Thorium Fuel Cycle Tritium Recovery from Voloxidation Off-Gases	A. D. Kelmers W. D. Holland
February 8	Hydrocarbonization of Bituminous Coal Carbonization of Coal Liquefaction Residues	E. L. Youngblood R. E. Barker
February 15	Iodox Engineering Development High-Level Demonstration	B. A. Hannaford D. E. Benker
February 22	State of the Art of High-Temperature, High-Pressure Gas Filtration H ₂ S Removal from Low-Btu Coal-Gas Coal Beneficiation	J. P. Meyer M. S. Edwards S. P. N. Singh
March 1	Fuel Cycle Studies Properties of Crushed Irradiated Graphite Determined by the Jenike Test Method Batch Extraction and Stripping Tests of Coprocessing	C. L. Fitzgerald W. L. Pattison
March 8	Waste Transportation Program OWI Logistics Modeling	L. B. Shappert D. S. Joy
March 15	KALC—Final Status Report Fixation of ¹⁴ CO ₂	T. M. Gilliam G. L. Haag
March 29	Analyses of Mixed DBP-MBP Plutonium Complexes from Solution Absorption Spectrum Extraction Behavior of Plutonium Polymer Formed During Low Acid Costripping	R. L. Fellows J. B. Knauer

**DIVISIONAL PERSON-POWER AND FINANCIAL SUMMARY
FY 1978**

	Funding (in thousands)	Person-years
DOE PROGRAMS		
Coal	\$ 5,238	21.0
Fusion	65	1.0
Fission	21,523	117.0
Physical Research	6,046	77.0
ANFLOW	334	3.5
Biology and Environment	1,597	17.0
Biomedical Applications	132	1.0
TRUST and ²³³ U Dispensing Facility	2,051	13.0
TOTAL DOE PROGRAMS	\$36,786	250.5
WORK FOR OTHERS PROGRAMS		
Nuclear Regulatory Commission	\$ 1,464	15.0
Savannah River Operation and Pacific Northwest Laboratory	4,888	33.0
Office of Waste Isolation	469	6.0
Other federal agencies	139	2.5
Miscellaneous	415	4.0
TOTAL WORK FOR OTHERS	\$ 7,375	60.5
TOTAL FINANCIAL PLANS	\$44,161	311.0

CHEMICAL TECHNOLOGY DIVISION

MAR 23 1978

INTELLIGENCE
ANALYSIS
PLANNING
OPERATIONS
COMBAT