152
11-23-81
gpc

(2)
B8463/8

LH. 93

ORNL-5757

ornl

OAK
RIDGE
NATIONAL
LABORATORY

UNION
CARBIDE

MASTER

**Chemical Technology Division
Progress Report
for the Period April 1, 1979,
to March 31, 1981**

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Contract No. W-7405-eng-28

CHEMICAL TECHNOLOGY DIVISION PROGRESS REPORT
for the Period April 1, 1979, to March 31, 1981

D. E. Ferguson	—Division Director
C. D. Scott	—Associate Division Director
R. G. Wymer	—Associate Division Director
R. W. Glass	—Engineering Coordination and Analysis Section Head
J. R. Hightower	—Advanced Technology Section Head
R. E. Leuze	—Pilot Plant Section Head
A. P. Malinauskas	—Chemical Development Section Head
E. Newman	—Isotope Separations Section Head
W. W. Pitt, Jr.	—Experimental Engineering Section Head

Date Published: November 1981

DISCLAIMER

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

Reports previously issued in this series are as follows:

ORNL-2392 Period Ending August 31, 1957
ORNL-2576 Period Ending August 31, 1958
ORNL-2788 Period Ending August 31, 1959
ORNL-2993 Period Ending August 31, 1960
ORNL-3153 Period Ending May 31, 1961
ORNL-3114 Period Ending May 31, 1962
ORNL-3452 Period Ending May 31, 1963
ORNL-3627 Period Ending May 31, 1964
ORNL-3830 Period Ending May 31, 1965
ORNL-3945 Period Ending May 31, 1966
ORNL-4145 Period Ending May 31, 1967
ORNL-4272 Period Ending May 31, 1968
ORNL-4422 Period Ending May 31, 1969
ORNL-4572 Period Ending May 31, 1970
ORNL-4682 Period Ending March 31, 1971
ORNL-4794 Period Ending March 31, 1972
ORNL-4883 Period Ending March 31, 1973
ORNL-4966 Period Ending March 31, 1974
ORNL-5050 Period Ending March 31, 1975
ORNL-5172 Period Ending March 31, 1976
ORNL-5295 Period Ending March 31, 1977
ORNL-5383 Period Ending March 31, 1978
ORNL-5542 Period Ending March 31, 1979

Contents

1. INTRODUCTION AND DIVISIONAL OVERVIEW	1
2. FISSION ENERGY	4
2.1 Consolidated Fuel Reprocessing Program	4
2.2 HTGR Technology Program	4
3. NUCLEAR WASTE MANAGEMENT	5
3.1 Cement and Concrete Technology	5
3.2 Partitioning and Transmutation	12
3.3 Alternate Waste Forms Development	13
3.4 Removal and Segregation of Radioactive Nuclides and Nitrate from Liquid Waste Streams	16
3.5 Updating of the ORIGEN Computer Code	20
3.6 Integrated Data Base	21
3.7 Carbon-14 Immobilization	23
3.8 Krypton Hydrofracture Studies	25
3.9 Assistance to Office of Nuclear Waste Isolation	26
3.10 Transportation Technology Program	28
3.11 FUSRAP Stabilization Technology Development and Applications	31
4. FOSSIL ENERGY	33
4.1 Coal Conversion Process Development	33
4.2 Coal Conversion Engineering Evaluation and Economic Assessments	42
5. BASIC SCIENCE AND TECHNOLOGY	53
5.1 Separations Science	53
5.2 Fuel Cycle Chemistry	59
5.3 Chemical Engineering Research	68
5.4 Fundamental Processes in Sorption Pumping and Transfer Operations Using Deep Beds of Sorbents	74
5.5 Resource Recovery	74
5.6 Actinide Oxides, Carbides, and Nitrides	78

5.7	Fusion Energy Studies	78
5.8	Uranium Recovery from Low-Level Aqueous Sources	80
5.9	Chemical Thermodynamic Assessments for Fluidized-Bed Coal Combustors	80
6.	BIOTECHNOLOGY AND ENVIRONMENTAL PROGRAMS.....	81
6.1	Bioprocess Research and Development	81
6.2	Monitoring and Measurement Research and Development	84
6.3	Environmental Control Technology	102
6.4	Flue Gas Desulfurization Studies	114
7.	SPECIAL ISOTOPE PRODUCTION AND SEPARATIONS	119
7.1	Transuranium-Element Processing	119
7.2	Isotopic Separations.....	121
8.	NUCLEAR REGULATORY COMMISSION PROGRAMS	125
8.1	Reactor Safety Research	125
8.2	Regulatory Differences Between Thorium and Current Uranium Fuel Cycles.....	125
8.3	Safety Review of Nuclear Facilities.....	130
8.4	Definition of Parameters for Major Accidents in Spent Fuel Storage, Fuel Reprocessing, and Waste Solidification Facilities	130
9.	THREE MILE ISLAND SUPPORT STUDIES.....	132
10.	MISCELLANEOUS PROGRAMS.....	134
10.1	Conversion of Consolidated Edison Uranium from a Nitrate Solution to U_3O_8	134
10.2	$^{233}U_3O_8$ Packet Loading for Argonne National Laboratory	134
10.3	Uranium-233 Processing	134
10.4	Improvements to Safeguards in Building 3019	135
10.5	Safeguards Engineering	135
10.6	Removal of Hazardous Radionuclides from Uranium Mill Tailings	136
10.7	Chattanooga Shale as a Source of Oil and Valuable Metals	137
10.8	Post-Accident Sampling in Nuclear Reactors (Support to TVA).....	139
	ADMINISTRATIVE SUMMARY.....	141
	Publications, Oral Presentations, and Patents	143
	Seminars	185
	Divisional Person-Power and Financial Summary	188
	Chemical Technology Division Author Index	189

1. Introduction and Divisional Overview

The Chemical Technology Division (CTD) is one of the largest research and development (R&D) divisions within the Oak Ridge National Laboratory (ORNL). Its staff consists of approximately 180 engineers and scientists plus about 140 supporting technical and administrative personnel, who occupy buildings located at the ORNL and Y-12 sites. The scope of the CTD programs is exceptionally broad, encompassing basic and applied scientific and engineering research, engineering development and assessments, and the operation of pilot plants and small production facilities. These programs include the development of processes that find application in the nuclear, fossil, and solar energy areas, as well as in waste management and environmental control technology. Other activities range from studies in biochemical technology to the production of important research materials.

While most of the programs are funded by the U.S. Department of Energy (DOE), important activities are also carried out for other governmental agencies and some support is derived from industrial sources.

The Division is organized into the following sections:

1. *Advanced Technology*, where R&D leading to new chemical engineering processes for nonnuclear energy technology is conducted;
2. *Chemical Development*, where R&D in the chemical sciences and reactor fuel chemistry is performed;
3. *Engineering Coordination and Analysis*, where process evaluations and engineering assessments are made;
4. *Experimental Engineering*, where bench-scale engineering studies are pursued;
5. *Isotope Separations*, where stable and radioactive isotopes are separated electromagnetically (this section was transferred to the Operations Division on October 1, 1981);
6. *Pilot Plant*, where integrated processes are studied and special production commitments are met.

Fuel Recycle, previously a section of the CTD, became an ORNL division in early 1981. Thus the major portion of the work under the Consolidated Fuel Reprocessing Program (CFRP) is now the responsibility of the Fuel Recycle Division. However, the product conversion program as well as the hot-cell and laboratory chemical development activities of the CFRP remain within the CTD.

Work related to waste management continues to be high on our list of priorities. Efforts in the concrete encapsulation program are concentrated in five areas: (1) ORNL fixation of wastes in concrete, (2) studies of FUETAP (formed under elevated temperature and pressures) concrete immobilization, (3) hydrofracture mix development, (4) a cooperative project with the Federal Republic of Germany, and (5) thermal property measurements. In another program, sol-gel technology is being applied to the incorporation of high-level nuclear waste for permanent disposal in a form with superior leach resistance. A new program has been established to develop a system of computer codes capable of maintaining a data base of current waste inventories and of gathering information to enable projections of these inventories according to agreed-upon bases.

The major emphasis in fossil energy is focused on R&D activities that are related to direct coal liquefaction processes. A number of projects are also being carried out in support of the Major Plants Program. Economic assessments and evaluations are continuing; several important studies related to environmental control technology for coal conversion processes have been performed.

The chemical separations and chemical engineering research programs serve as a source of new ideas and provide impetus and direction for the more applied programs. Our efforts in this area involve the development of new and improved separations methods, the study of new engineering concepts in separations science, and the behavior of materials in chemical engineering systems. These efforts support mission-oriented energy development activities,

investigations of fundamental chemical behavior which might be useful in devising more effective techniques (or improving existing techniques) for separating actinides and fission products, and the evaluation of novel methods for the recovery of metals and minerals from low-grade ores and solid industrial wastes.

Current projects and new initiatives in our biotechnology and environmental programs are addressing (1) the conversion of biomass to chemicals and fuel; (2) the treatment of gaseous, liquid, and solid wastes from fossil energy combustion and conversion processes; and (3) the accelerated transfer of emphasis in the measurement technology area from biomedical/clinical analysis to environmental/process monitoring applications.

We have continued to operate the facilities for transuranium-element processing and stable-isotope separations. (The stable-isotope separations activity was transferred to the Operations Division on October 1, 1981.) The materials produced by these facilities are supplied to investigators for use in research projects at ORNL and elsewhere.

Under the programs being administered for the U.S. Nuclear Regulatory Commission (NRC), we have performed reactor safety research studies principally concerned with fission product release and transport in nuclear reactors. This effort was expanded during the latter part of the report period in response to the Three Mile Island reactor accident. Assistance has also been provided to the NRC in the safety review of nuclear facilities.

In summary, the CTP was engaged in a variety of important, challenging tasks and activities throughout April 1, 1979–March 31, 1981. The highlights of our accomplishments include:

1. Demonstrating the feasibility of a codecontamination flowsheet for uranium and plutonium recovery from spent fuel.
2. Developing a process which utilizes the $\text{CO}_2\text{-Be(OH)}_2$ reaction to remove and immobilize ^{14}C directly from specific off-gas streams at nuclear facilities.
3. Using the internal gelation process to prepare multiple batches (to 200 g) of $\text{UO}_2\text{-PuO}_2$ microspheres. This process was developed to produce microspheres which could be converted to acceptable fuel pellets.
4. Demonstrating in laboratory studies that FUETAP concrete is thermally stable to at least 900°C . The amount of radiolytic gas generated in FUETAP concrete by specimens containing ^{244}Cm was found to be $\leq 5\%$ of that generated in normal concrete.
5. Completing an evaluation of partitioning-transmutation of long-lived isotopes as a strategy for reducing waste storage risks. Although this approach appears to be technically feasible, the increased short-term risks due to nonradiological factors and the excessive costs for relatively small long-term benefits make it unattractive.
6. Developing an indirect liquefaction reactor capable of vapor phase or slurry phase operation and a thermal conductivity monitor capable of continuous measurement at process temperatures and pressures.
7. Performing the first direct measurement of the simultaneous photoproduction of hydrogen and oxygen from water.
8. Developing a bioreactor system for producing ethanol at a high rate using immobilized cells of *Zymomonas mobilis*.
9. Developing, constructing, and testing a fluidized-bed bioreactor pilot plant for high-rate biological denitrification.
10. Designing and constructing a 2-L/s (50,000-gpd) ANFLOW pilot plant.
11. Determining, as part of the environmental controls technology assessment for indirect liquefaction processes, that the addition of pollutant controls to ensure conformance to current guidelines for releases in analogous industries increased the required selling price for the product by $\sim 12\%$.
12. Installing and operating a 445-mm-diam continuous annular chromatograph, which is fabricated of stainless steel, with a design pressure of 1.1 MPa (150 psig).
13. Developing the HCl leaching process for the recovery of metals from coal residue and adding the capability for ion exchange and HCl sparge crystallization as separation steps. In addition, estimates of the cost of a production plant were made, and this system was extended to the processing of oil shale retort residue.
14. Expanding the computer-retrievable Separations Systems Data Base (SEPSYS) and placing it in the Department of Energy/Remote Console (DOE/RECON) computer system, where it is publicly available.
15. Completing the isotopic enrichment of a large quantity of ^{201}Tl . This isotope is the precursor of ^{201}Tl , which has found application in medical diagnostic studies.

16. Completing the commitments for the Zero Reactor criticality studies by loading the remaining 1128 (of a total of 1743) packets with $^{235}\text{U}_2\text{O}_8$.

In addition, two I-R 100 Awards were received from *Industrial Research and Development* during

this report period. These awards were granted for our development of a portable fluorescence spotter (1980) and our development of extractive scintillators and photon-electron-rejecting alpha liquid scintillation (PERALS) spectrometry (1981).

2. Fission Energy

2.1 CONSOLIDATED FUEL REPROCESSING PROGRAM

This year ORNL management formed a new division, the Fuel Recycle Division, from the Fuel Recycle Section in the Chemical Technology Division. However, many of the fuel fabrication programs and all of the hot-cell and laboratory development activities remained within the Chemical Technology Division. The hot-cell efforts deal primarily with the characterization of dissolver residues and the use of the Solvent Extraction Test Facility in the Transuranium Processing Plant for processing irradiated light-water reactor fuel. Plans are also being developed to process breeder reactor fuels. The laboratory chemical development activities include studies of the chemistry of selected fission products and the actinides in fuel reprocessing operations and of the cleanup of recycle streams. Fuel fabrication studies have included development of gel microsphere formation and direct thermal denitration for coconversion of uranium-plutonium solutions to mixed oxides. The products from each of these processes offer advantages for the subsequent formation of fuel pellets, and the selection of the favored process can be made soon for further development.

The results of studies to develop reprocessing technology for reactor fuels are not included here

because regulations stipulate that such information must be distributed only under category UC-86. All work is reported under the Consolidated Fuel Reprocessing Program in topical reports and in a series of quarterly progress reports, the most recent of which is the *Consolidated Fuel Reprocessing Program Quarterly Progress Report for Period Ending March 31, 1981*, ORNL/TM-7773 (June 1981).

2.2 HTGR TECHNOLOGY PROGRAM

The work done in support of high-temperature gas-cooled reactor (HTGR) technology is not reported here in compliance with regulations which stipulate that such information must be distributed only under category UC-77—Gas-Cooled Reactor Technology. The results of our investigations in this area have been summarized in internal documents and in annual reports. The most recent of the latter publications are the *High-Temperature Gas-Cooled Reactor Base Technology Program Annual Progress Report for Period Ending December 31, 1979*, ORNL-5643 (July 1980) and *High-Temperature Gas-Cooled Reactor Base Technology Program Annual Progress Report for Period Ending December 31, 1980*, ORNL-5753 (in press).

3. Nuclear Waste Management

3.1 CEMENT AND CONCRETE TECHNOLOGY

During this reporting period, the Cement and Concrete Technology Program consisted of six subprograms: (1) the use of cementitious materials as alternative waste forms for high-specific-activity defense and commercial radioactive waste, (2) the immobilization of TRU waste in FUETAP concrete, (3) the development of grouts suitable for the disposal via hydraulic fracturing of the waste sludges generated at ORNL, (4) a cooperative research and development program between the United States and the Federal Republic of Germany on the use of cementitious materials in radioactive waste management, (5) the development and testing of cementitious mixtures suitable for plugging holes in the vicinity of a repository, and (6) thermal property measurements of cementitious and natural materials. The last two programs were sponsored by the Office of Nuclear Waste Isolation (ONWI).

Fixation of Defense Waste

Work continues on the evaluation of concretes formed under elevated temperatures and pressures (FUETAP concretes) as alternative hosts for the Savannah River Plant (SRP) defense waste. In this process, SRP solids are blended with cementitious mixtures containing specific admixtures to fix the radionuclides. A small amount (1%) of the water reducer D-65 is added so that a flowable grout may be formed with a minimum amount of water. A ceramiclike solid is formed on curing the mixture for 24 h at 100°C and 0.1 MPa. To diminish the potential for future canister pressurization by radiolysis or heat after placement in a storage site or repository, the free water is removed by heating the concrete at 250°C for 24 h (Fig. 3.1).

The results from many of the laboratory studies on the encapsulation of SRP waste in FUETAP concrete were summarized in a recent publication,¹ the abstract of which follows:

Fig. 3.1. FUETAP flowchart.

1. J. G. Moore, G. C. Rogers, S. Katz, M. T. Morgan, and E. Newman, "FUETAP Concretes—Tailored Autoclaved Concretes for the Fixation of Radioactive Waste," presented at the American Nuclear Society Topical Meeting on Waste Management, Tucson, Ariz., Feb. 23-26, 1981; published in the proceedings.

FUETAP concretes are cement-based waste hosts containing special admixtures to fix specific radionuclides in the waste. They are formed under elevated temperature and pressure. Laboratory results suggest that these specially tailored autoclaved concretes are promising alternative waste forms for defense, commercial, and TRU wastes. Cementitious mixes containing 15 to 25 wt % simulated defense waste when cured for 24 h at 100 to 250°C and at 0.1 to 4.1 MPa produced strong, thermally stable solids with compressive strengths of >60 MPa. The thermal conductivity was >1 W/(m·K). The leachabilities of cesium and plutonium from the solids were comparable to those from borosilicate glass. Although the strontium leach rates from the solids are higher than from glass, initial data indicate that formulation adjustments may lower these rates.

To prevent canister pressurization by either heat or radiolysis in or to the repository, the autoclaved solids are dewatered at 250°C for 24 h. Small-scale laboratory tests show that the resulting material is stable to at least 900°C. Specimens containing 0.6 mg $^{244}\text{Cm/g}$ demonstrated that after 1 year the amount of radiolytic gas generated in FUETAP concrete is <5% of that generated in normal concrete. These FUETAP concretes offer considerable potential as low-temperature alternative waste hosts for the immobilization of all levels of radioactive waste.

Laboratory studies are currently in progress to determine the thermal stability and leachability of FUETAP concretes containing SRP waste. The thermal studies examine the effect of short-term heating at 800°C and long-term storage at 250°C. In the short-term tests, specimens decreased in length about 1.7% after being heated at $\leq 4^\circ\text{C/min}$ to 800°C then cooled at the same rate back to ambient temperature. For the time periods examined (a few minutes to 24 h) the shrinkage was essentially independent of the time the specimen was held at 800°C. In the 250°C tests, the specimens showed a 1.4% weight loss and a 10% reduction in compressive strength after one month but no additional change after the second month.

All leach tests must now be performed using the MCC-1 test method² proposed by the Material Characterization Center. This is a static leach test at 90°C using three standard leachants for 3- to 28-d leach periods. Results obtained in participating in MCC-1 round robin leach tests involving NBS and PNL-76-68 glass indicated that some changes should be made in the cleaning procedure of the Teflon containers, the preparation of the silicon water leachant, and the number of blanks used in the test. The leach results obtained from this test are primarily useful for short-term comparisons of specimens, with little if any value for long-term extrapolations or the determination of leach mechanisms. Examples of the leach rates obtained for cesium and strontium from PNL-76-68 glass into deionized water are shown in Table 3.1.

Table 3.1. Cesium and strontium leachability from PNL-76-68 glass into deionized water at 90°C

Leach period (d)	Average leach rate (g/cm ² ·d)	
	Cesium	Strontium
3	1.4×10^{-6}	4.3×10^{-7}
7	8.6×10^{-7}	2.6×10^{-7}
14	9.4×10^{-7}	1.4×10^{-7}
28	7.8×10^{-7}	4.0×10^{-8}

Similar studies showed that the leach rates of cesium, strontium, and iron into deionized water from FUETAP concrete containing simulated calcined SRP waste incorporating zeolite were 2×10^{-6} , 2×10^{-8} , and 2×10^{-8} g/cm²·d, respectively. Work is in progress to improve the cesium retention. Previous studies showed that the leachability of strontium from concretes containing actual waste is usually one to two orders of magnitude less than values obtained with simulated wastes.³

Immobilization of TRU Waste

A laboratory investigation was started in FY 1981 on the fixation of TRU waste in FUETAP concrete. These tailored concretes offer a number of advantages as a host for these wastes. The process and resulting products have the degree of flexibility required to handle the wide variety of TRU wastes; the final waste form has a low leachability and negligible radiolytic gasification.

The initial studies emphasized the development of tailored cementitious mixtures for the fixation of slagging pyrolysis incinerator (SPI) fly ash, municipal waste slag frit (MWSF), and simulated Rocky Flats sludge. One formulation involving the fixation of SPI fly ash is given in Table 3.2. A sample prepared using this formulation was cured for 24 h at 250°C. The resulting sample had a compressive strength of 95 MPa, a density of 1.71 g/cm³, a porosity of 29%, and a thermal conductivity of 0.56 W/(m·K).

2. D. M. Strachan, B. O. Barnes, and R. P. Turcotte, "Standard Leach Tests for Nuclear Waste Materials," p. 347 in *Scientific Basis for Nuclear Waste Management*, vol. 3, J. G. Moore (ed.), Plenum, New York, 1981.

3. J. A. Stone, *Evaluation of Concrete as a Matrix for Solidification of Savannah River Plant Waste*, DP-1448 (June 1977).

Table 3.2. Composition of
FUETAP concrete containing
SPI fly ash

Ingredient	Wt %
Type I cement	40.0
SPI fly ash	40.0
Ottawa sand	1.0
D-65 water reducer	1.0
Water	18.0

The substitution of 5 wt % amorphous silica for part of the cement in FUETAP specimens containing 40 and 45 wt % SPI fly ash produced only slight changes in the physical properties of the resulting solids cured and dewatered in the same manner. Compressive strengths and densities ranged from 65 to 72 MPa and 1.51 to 1.66 g/cm³, respectively. The thermal conductivities and porosities of these solids were 0.58 to 0.64 W/(m·K) and 31.5 to 35.5%, respectively.

A trial specimen containing 42.75 wt % MWSF was made using the FUETAP process. Although the workability and set time of the material were good, there was a certain amount of particle segregation. Subsequent formulations containing 50 and 60 wt % MWSF resulted in no particle segregation and excellent physical properties. Compressive strengths ranged from 60 to 90 MPa, the porosities were approximately 17%, and thermal conductivities were about 1 W/(m·K).

Future laboratory studies will focus on Rocky Flats sludge, since the SPI project was cancelled. An initial FUETAP formulation containing 20 wt % simulated Rocky Flats sludge had satisfactory physical properties. However, the set time was short (<2 h). Formulation studies are in progress to control the set time and improve the physical properties at waste loadings ≥20 wt %. Specimens as large as 75 L will be prepared with this waste to determine the dewatering characteristic on an engineering scale.

Hydrofracture Mix Development Studies

On completion of the new hydrofracture facility, the Gunit tanks currently used for waste sludge will be emptied and retired. The ~1500 m³ of sludge will be slurried with water, formed into a grout by blending with a suitable cementitious dry mix, and disposed of by hydraulic fracturing at the new facility. During this report period, in addition to assistance with routine injections of aqueous waste, laboratory studies continued on problems associated

with sludge disposal. The major tasks addressed were:

1. the effect of slurry viscosity on the pumpability of slurry-grout mixtures,
2. the evaluation of alternative cesium sorbents,
3. the leachability of hydrofracture grouts,
4. the difference between laboratory- and field-blended grouts, and
5. the feasibility of the disposal of cellulosic and other trash materials or waste oil by hydraulic fracturing.

Properties of sludge-slurry grouts. Since the sludges stored in the Gunit tanks are quite variable, methods were devised to ensure that the sludge remained suspended in the aqueous slurries and that the resulting grouts had satisfactory flow properties. Bentonite clay was found to be the best suspending agent for the solids. Slurries containing 15 wt % simulated sludge solids were easily suspended with 2 wt % bentonite clay in a 0.1 M NaNO₃ solution. The settling rate was ≤5.0 vol % in 24 h. The slurry viscosity was dependent on the composition of the sludge and the pH. Nomograms were developed relating this viscosity to the ratio of dry solids mix to slurry necessary for an acceptable grout. Thus by monitoring the viscosity of the slurry, adjustments may be made in the solid-to-liquid ratio to maintain satisfactory pumping characteristics.⁴

A number of chemical additives were found that could be used in an emergency to control the flow properties of slurry grouts. For example, Q-Broxin, a thinner from Baroid Petroleum Services (Houston, Tex.) reduced the velocity required for turbulent flow of a grout in a 5.0-cm-diam tube from 1.76 to 1.20 m/s; FX-32C, a plasticizer supplied by Fox Industries, Inc. (Baltimore, Md.) reduced the requisite velocity from 1.76 to 0.75 m/s.

Alternative clays. Three alternative commercial clays for cesium sorption were found that could be substituted for Indian red pottery clay if it was no longer available. These were Cedar Heights, Bandy black, and Todd dark clay. Leach data from grout mixes made with dry mixes (Table 3.3) containing 7.7 wt % of either Bandy black, Todd dark, or Indian red clay indicated effective cesium diffusivities into distilled water of 2.0×10^{-13} , 6.1×10^{-13} , and 3.7×10^{-14} cm²/s, respectively. In each case the grout was prepared using a solid-to-liquid (W-7 simulated waste) ratio of 719 g/L. The specimens were cured in

4. E. W. McDaniel, *Rheology of Sludge-Slurry Grouts*, ORNL/TM-7497 (October 1980).

Table 3.3. Composition of dry mix used to evaluate clays

Ingredient	Wt %
Type I portland cement	38.5
Kingston fly ash	38.5
Attapulgite clay	15.3
Clay for cesium sorption	7.7

≥90% relative humidity for 28 d at ambient temperature and pressure.

Leachability of hydrofracture grouts. Results from short-term demineralized water leach tests at room temperature using the modified International Atomic Energy Agency method⁷ showed that the leachability of strontium from hydrofracture grouts containing simulated sludges decreased with increasing curing time. However, pressure curing had no effect. Effective diffusivities of 2.29×10^{-10} , 3.26×10^{-11} , and 1.38×10^{-11} cm²/s were obtained for grouts cured 28, 91, and 182 d, respectively. In the pressure tests, the specimens were cured 28 d at either 4.1 MPa or ambient pressure. The leach results were almost identical. In both series of tests the specimens were prepared using the standard dry mix for sludges at a solids-to-slurry ratio of 719 g/L (Table 3.4). Sufficient strontium was added to the simulated sludge to be equivalent to a ⁹⁰Sr concentration of about 24 Ci/L.

Laboratory vs field grouts. Studies were reinstated to determine the reasons for the differences between laboratory and plant grouts made with the same ingredients and at the same solid-to-liquid ratio. Grouts prepared with solids blended in the plant usually have a lower viscosity and a higher phase

separation than grouts prepared with laboratory-blended solids.

Recent results indicate that physical action on the dry solids mix prior to grout preparation changes the viscosity and phase separation of grouts made from these solids. The viscosity and phase separation of grouts prepared in the laboratory from dry solids mixes that were subjected to shearing in a Waring blender prior to grout preparation had lower viscosities and higher phase separation than usual batch-mixed laboratory grouts. The phase separation and, to a lesser extent, the viscosity were functions of the amount of shear time; thus, grouts could be made to duplicate the values normally obtained for plant grouts (Table 3.5).

Table 3.5. Effect of shearing dry solids prior to grout preparation on grout viscosity and phase separation^a

Shear time ^a (min)	Viscosity (Pa·s)	Phase separation (vol %)
0	0.0140	5.6
30	0.0075	6.7
60	0.0075	9.8
120	0.0075	11.8
Plant blend	0.0085	12.3

^aDry solids consisting of 38.5 wt % type I cement, 38.5 wt % Kingston TVA fly ash, 15.3 wt % Attapulgite-150 clay, 7.7 wt % Indian red pottery clay, and 0.04 wt % CFR-1 (a set regulator) mixed in the ratio of 719 g/L with W-7 simulated waste solution.

^bSheared at 5000 rpm in a commercial-size Waring blender.

Table 3.4. Formulation used for leach specimens

Ingredient	Composition (wt %)	
	Dry mix	Grout
Type I portland cement	46.0	17.41
Kingston fly ash	46.0	17.41
Indian red pottery clay	8.0	3.03
Simulated dry sludge ^a		9.51
Aqueous solution ^b		52.64

^aFreshly precipitated hydrous iron oxides, dried to 150°C then screened through a 150-μm screen.

^b0.1 M NaNO₃ solution containing 2.0 wt % bentonite clay.

Disposal of waste materials. Scoping studies were made to determine the feasibility of the disposal of waste diffusion pump oils, biodegraded cellulosic waste material, or pelletized shredded waste by hydrofracture. Grouts were made using the standard dry mix and a solids-to-liquid ratio of 719 g/L in the case of the oil and biodegraded material. Pumpable, acceptable grouts were formed with aqueous waste solution containing 1 vol % of the oil. However, the biodegraded waste solution gave a higher phase

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

separation and viscosity than the standard control grout made with W-7 simulated intermediate-level waste solution. Additional tests will be made to determine what adjustments have to be made in the grout formulation to produce grouts suitable for hydraulic fracturing.

Grouts containing pelletized shredded wastes that were suitable for a demonstration injection were made by mixing cement containing 60 or 70 wt % fly ash with slurries containing 12 wt % pelletized waste suspended with 1 or 2 wt % bentonite clay. At a solids-to-slurry ratio of 360 g/L, the grouts had acceptable flow characteristics although all grouts prepared with the pelletized shredded waste thickened with time and shear.

U.S.-F.R.G. Cooperative Program

Meetings with the Federal Republic of Germany (F.R.G.) at Karlsruhe Kernforschungszentrum in February 1980 established a series of initial work tasks for a U.S.-F.R.G. cooperative research program on the characterization and evaluation of cementitious waste forms. The tasks, with the associated lead country, are as follows:

1. Verification of short-term leach mechanisms and diffusion coefficients of radioactive waste fixed in cementitious materials (U.S.).
2. Corrosion of cementitious materials at elevated temperatures and pressures (F.R.G.).
3. Radiolysis studies on cementitious pellet and matrix formulation (U.S.).
4. Kinetics of the dewatering of cementitious materials (F.R.G.).
5. Determination of mineral phases involved in the fixation of radioactive wastes in cementitious materials (U.S. and F.R.G.).

Subsequent meetings in Germantown, Maryland (June 1980), and Oak Ridge (November 1980) confirmed these research tasks and expressed an interest in expanding the cooperative tasks to include:

1. development programs in granulation technology, in situ exposure studies in the Asse, and applications of special admixtures;
2. joint technology development programs in waste handling, transportation, and disposal;
3. development of in situ monitoring techniques for assuring the quality of cementitious waste forms; and
4. cooperative demonstration projects.

These proposals have met with a great deal of enthusiasm by researchers and administrators in both countries because such coordinated, parallel development programs save time and money by eliminating costly duplications of effort and because there is a mutual gain in the exchanging of complementary technology developments. The project is scheduled to start in April 1981 pending approval of FY 1981 funding by DOE.

Borehole Plugging

This program was supported by ONWI through FY 1979 to assist in devising, developing, and testing cementitious mixtures suitable for plugging holes that may represent a hazard to a waste isolation repository. During the final year the program was subdivided into three activities: (1) systematic study of pozzolanic (fly ash)-cement and salt-cement mixtures, (2) development of techniques for measuring the permeability of cementitious solids and plug-wall rock junctions, and (3) laboratory evaluation of borehole plug formulations proposed for the Bell Canyon field tests. These studies are summarized in three reports.⁶⁻⁸ The abstract of the fly ash study⁶ follows:

Results of initial studies of a systematic investigation to determine the effects of fly ash and salt on the physical properties of pozzolanic concretes and saltcretes are reported. The objective of this program is to develop cementitious mixes that will form thermodynamically stable solids for plugging boreholes in various geologic media. In this first phase of the investigation, some of the problems and major effects in such cementitious systems have been identified and laboratory techniques have been developed.

The addition of fly ash to mortars decreased the set time and bleed characteristics and increased the compressive strength and permeability, but it had very little effect on the density or the thermal conductivity of the solids. The magnitude of these effects was only slightly related to the lime content of the fly ash.

In the case of saltcretes, the addition of a low-lime fly ash slightly decreased the set time and the bleed characteristics of the wet mix.

6. J. G. Moore, M. T. Morgan, E. W. McDaniel, H. B. Greene, and G. A. West, *Cement Technology for Borehole Plugging: Interim Report on the Effects of Fly Ash and Salt on the Physical Properties of Cementitious Solids*, ORNL/TM-7106 (March 1980).

7. E. W. McDaniel, *Cement Technology for Borehole Plugging: An Interim Report on Permeability Measurements of Cementitious Solids*, ORNL/TM-7092 (January 1980).

8. J. G. Moore, M. T. Morgan, E. W. McDaniel, H. B. Greene, and G. A. West, *Cement Technology for Plugging Boreholes in Radioactive Repository Sites: Progress Report for the Period October 1, 1978 to September 30, 1979*, ORNL-5610 (August 1980).

However, a high-lime fly ash doubled the set time and decreased the bleed characteristics to essentially zero. The compressive strength of saltcretes was increased by the addition of fly ash and was independent of the lime content. Such additions had little effect on the thermal conductivity or density.

The thermal conductivities of cement pastes containing fly ash showed a near-linear relationship with the density of the resulting solids. In the case of mortars, the thermal conductivity decreased with increasing temperature and showed some hysteresis in the initial heating cycle. After the first cycle, the thermal conductivity decreased from about 1.32 W/m·K at 350 K to 1.27 W/m·K at 475 K.

These interim results have shown the need for more detailed studies on the effect of water and fly ash composition in these formulations and the necessity for developing a more accurate means of measuring time-dependent volume changes that occur in cementitious specimens.

Techniques were developed to measure gaseous and liquid permeabilities in the microdarcy range of cementitious solids and plug-wall rock junctions.

The abstract from the publication⁷ describing these techniques and the associated data follows:

The permeability of borehole plug solids and plug-wall rock junctions is a property of major interest in the Borehole Plugging Program. This report describes the equipment and techniques used to determine the permeabilities of possible borehole plugging materials and presents results from tests on various cementitious solids and plug-rock combinations. The cementitious solids were made from mixtures of cement, sand, salt, fly ash, and water. Three different types of cement and four different fly ashes were used. Permeabilities ranged from a high value of 3×10^{-4} darcy for a neat cement paste to a low of 5×10^{-8} darcy for a saltcrete containing 30 wt % sodium chloride.

Miniature boreholes were made in the following four different types of rock: Westerly granite, Dresser basalt, Sioux quartzite, and St. Cloud granodiorite. These small holes were plugged with a mix consisting of 23 wt % type I portland cement, 20 wt % bituminous fly ash, 43.2 wt % sand, and 13.8 wt % water. After curing for 91 d at ambient temperature, the permeability of the plug-wall rock junctions ranged from 3×10^{-5} to $< 1 \times 10^{-8}$ darcy. Three of the four miniature plugged boreholes exhibit permeabilities of < 10 microdarcys.

Cementitious plug formulations proposed by Sandia Laboratories for the Bell Canyon borehole plugging field test⁹ were evaluated in laboratory tests using core specimens from the actual site. The abstract of the report⁸ presenting the results of this investigation follows:

Laboratory evaluations were made of several borehole plug formulations proposed for the Bell Canyon field test. Measurements included compressive strength, permeability, density, and thermal conductivity. A few preliminary tests with saltcrete formulations showed no significant difference in physical properties of the solid as a function of fly ash or cement composition. The saltcrete proposed for the field test gave acceptable pushout strength and permeability values using miniature borehole plugs in anhydrite. Similar laboratory tests made with a freshwater formulation indicated high permeability. Electron micrographs showed dissolution cavities or cracks at the plug-wall interface. These studies showed that the reactions

occurring between the borehole plug and the adjacent rock wall are an important factor in obtaining a good seal and that laboratory tests are useful to indicate the possibility of success or failure of field tests.

Abstracts of separate reports on permeability experiments and systematic studies of pozzolanic cement and saltcretes are included.

Thermal Property Measurements

The objective of this program is to develop techniques for obtaining accurate thermal property data for a variety of geologic media and to provide ONWI with a referee capability for comparison with results from contractors making routine determinations of thermal properties.

Thermal conductivity measurements of Cypress Creek rock salt and caprock showed significant differences between results obtained by ORNL and those by the Energy Materials Testing Laboratory (EMTL) of Fiber Materials, Inc. Further investigations on the Pyroceram 9606 reference material revealed that approximately half of the difference in the results could be attributed to a difference in the values used for the Pyroceram 9606. EMTL used values derived from thermal diffusivity measurements, whereas ORNL used values from the NBS data series which were obtained by steady-state radial heat flow measurements. A summary of the thermal conductivities for rock salt and caprock is given in Table 3.6. In this summary, values determined by ORNL, EMTL, and other installations are compared. The results from the comparative method used by ORNL, EMTL, and Dynatech are given relative to both the NBS steady-state Pyroceram data¹⁰ and the pulsed laser diffusivity Pyroceram data.¹¹

Thermal conductivities for the Pyroceram 9606 over the range 293 to 573 K derived from the averages

9. C. L. Christensen, *Test Plan, Bell Canyon Test, WIP, Experimental Program, Borehole Plugging, SAND-79-0139* (June 1979).

10. R. W. Powell, C. Y. Ho, and P. F. Lilly, *Thermal Conductivity of Selected Materials*, NBS-MON-8 (November 1966).

11. Averages of data from the following sources: J. F. Lagedrost, Energy Materials Testing Laboratory, Fiber Materials, Inc., Biddeford, Me., personal communication, Feb. 24, 1981; R. L. Rudkin, *Thermal Diffusivity Measurements on Metals and Ceramics at High Temperatures*, USAF Report No. ASD-TDR-62-24, Part II (January 1963), pp. 1-16; R. L. Gibby, *Thermal Diffusivity and Thermal Conductivity of Stoichiometric (U, Pu) O₂*, BNWL-704 (May 1968), pp. 1-39.

Table 3.6. Thermal conductivity of rock salt and caprock

Research agency	Source	No. of samples measured	Density (g/cm ³)	Thermal conductivity ^a λ , (W/m-K) at 373 K			Coefficients ^c for $\lambda = AT^b$	
				NBS	Diff.	Other ^b	A	B
Salt								
ORNL ^d	Avery Island	4	2.12	3.58	3.27		163	-1.94
	Jefferson Island	2		3.53	3.22		108	-0.966
	Cypress Creek (1701 ft)	1	2.21	4.34	3.96		823	-1.27
EMTL	Cypress Creek (1701 ft)	1	2.21	3.78	3.44		530	-0.850
	Cypress Creek	3	2.21	3.76	3.43		966	
	Randall City	3	2.16	3.78	3.45		1,296	-1.00
	Swisher City	2	2.18	3.68	3.35		958	-0.955
	Vacherie Dome	1	2.18	4.53	4.13		151	-1.39
Dynatech ^f		9		3.90	3.56		3,333	-1.14
Sandia and LASL ^g		6				4.68	4,000	-1.14
NBS ^h						5.12	4,092	-1.13
Caprock								
EMTL ⁱ		1	2.96	3.84	3.50		2,719	-1.12
ORNL ^j		1	2.96	4.53	4.13		20,301	-1.42
ORNL ^k				4.11	3.75		3,973	-1.16

^aValues at 373 K obtained by comparative measurements are calculated based on both steady-state (NBS) Pyroceram data and Pyroceram data from thermal diffusivity measurements (Diff.).

^bSandm used a linear steady-state heat flow conductivity system with a heat flow transducer. LASL used a heat probe, which is a line source transient heat flow method.

^cDynatech and ORNL used NBS steady-state Pyroceram data for these measurements. Conversions relative to diffusivity data can be made by multiplying by factor $0.9689 \exp(-22.5/T)$. EMTL (Fiber Materials, Inc.) used diffusivity-based data. Conversions relative to steady-state data can be made by multiplying by factor $1.032 \exp(22.5/T)$.

^dM. T. Morgan, *Thermal Conductivity of Rock Salt from Louisiana Salt Domes*, ORNL/TM-6809 (June 1979).

^eJ. F. Lagedrost, *Thermal Property and Density Measurements of Samples Taken from Drilling Cores from Potential Geological Media*, ONWI/Sub/79/E-15-00800-1 through -16 (August 1979-March 1980).

^fJ. N. Sweet and J. E. McCreight, *Thermal Conductivity of Rock Salt and Other Geologic Materials from the Site of the Proposed Waste Isolation Pilot Plant*, SAND 79-1665 (March 1980).

^gJ. M. Yang, "Thermophysical Properties," pp. 209-11 in *Physical Properties Data for Rock Salt*, NBS Monograph 161 (January 1981). Yang derived recommended values from several experiments (including Russian) and concluded that values above 100 K were accurate within 5%.

of the thermal diffusivities may be described by the expression

$$\lambda = 2.676 \exp(88.00/T).$$

Thermal conductivities for the Pyroceram 9606 obtained by radial heat flow measurements over the same range follow the relation

$$\lambda = 2.762 \exp(110.5/T).$$

The thermal conductivities of eight standard rocks obtained from the Bureau of Mines were reported in ORNL/TM-7502.¹² The results are summarized in Table 3.7. The thermal conductivity decreased as a

result of annealing as is evidenced by the difference between preheat and postheat values. These coefficients were obtained by least-squares fit to experimental data over the range 363 to 533 K. The measurements were made by the cut bar comparative method using Pyroceram 9606 as a reference and NBS data¹⁰ for the thermal conductivity of the Pyroceram.

In other work, a thermal conductivity cell for fragmented or friable material was developed, and several coating formulations were tested to improve interface conductivity.

12. M. T. Morgan and G. A. West, *Thermal Conductivity of the Rocks in the Bureau of Mines Standard Rock Suite*, ORNL/TM-7052 (January 1981).

Table 3.7. Coefficients for the calculation of thermal conductivities of standard rocks before and after heating to 533 K

	Coefficients ^a			
	Preheat ^b		Postheat ^c	
	A (W/m·K)	B (W/m)	A (W/m·K)	B (W/m)
Sioux quartzite	-0.434	2225	0.272	1840
Dresser basalt	2.044	365.7	2.062	350.1
St. Cloud gray granodiorite	1.250	534.9	1.525	374.4
Barre granite	1.112	515.5	1.334	314.3
Holston limestone	0.050	948.6	0.442	689.4
Westerly granite	1.157	450.1	1.492	259.4
Berea sandstone	0.476	641.7	0.753	484.7
Salem limestone	0.109	603.6	0.475	412.3

^aFor equation $\lambda = A + B/T$, where λ = thermal conductivity (W/m·K) and T = temperature (K), the coefficients were calculated from averages of individual values for x, y, and z samples.

^bFrom data measured before heating to maximum temperature of 533 K.

^cFrom data measured after heating to maximum temperature.

3.2 PARTITIONING AND TRANSMUTATION

Transmutation of the long-lived radioisotopes in fuel cycle wastes to short-lived or stable products is an approach that could be used to reduce the future risk incurred by geologic repositories. A prerequisite for transmutation is that the species of interest first be partitioned from the wastes and recovered in a form suitable for bombardment with neutrons. Since the difficulties of effecting the necessary separations are expected to be as great as, or greater than, those associated with reprocessing the fuels to recover uranium and plutonium, any realistic evaluation of this approach must consider partitioning and transmutation jointly. During fiscal years 1977 through 1980 we undertook, with the participation of several other organizations,¹³ an assessment of partitioning and transmutation (P-T) to establish technical feasibility and identify any incentives for its implementation.¹⁴

Feasibility was assessed by formulating credible partitioning flowsheets based on experimental evidence and by devising transmutation strategies that could be verified with relatively sophisticated calculations. The incentives were defined by cost-risk-benefit analysis. Only conventional chemical processes having a reasonably high assurance of success and availability were considered and light-water reactors were assumed to be the primary transmutation devices. Although the actinides were taken as the principal candidates for P-T, the long-

lived fission products ⁹⁹Tc and ¹²⁹I were also considered.

The approach used in this assessment was to perform an incremental analysis of a reference fuel cycle and a P-T fuel cycle that were based on a self-generated plutonium recycle pressurized-water reactor. They were identical except that the reference cycle provided for the recovery and recycle of only the economic values of uranium and plutonium, whereas the P-T cycle used additional partitioning processes to recover actinides from the fuel fabrication and fuel reprocessing plant waste, and to recycle them to the reactor.¹⁵ Chemical flowsheets were generated based on solvent extraction, HNO₃-HF and Ce(IV)-HNO₃ leaching, and cation exchange chromatography and having the potential to reduce unrecovered actinides in the fuel fabrication and

13. Other organizations that participated in this assessment are Argonne National Laboratory, Brookhaven National Laboratory, Sandia National Laboratory, Idaho National Engineering Laboratory, Savannah River Laboratory, Mound Facility, Rocky Flats Plant, The Ralph M. Parsons Company, Science Applications, Inc., and Los Alamos Technical Associates.

14. A. G. Croff, J. O. Blomeke, and B. C. Finney, *Actinide Partitioning-Transmutation Program Final Report, I. Overall Assessment*, ORNL-5566 (June 1980).

15. J. W. Wachter and A. G. Croff, *Actinide Partitioning-Transmutation Program Final Report, III. Transmutation Studies*, ORNL/TM-6983 (July 1980).

reprocessing plant wastes to $<0.25\%$.¹⁶ Waste treatment facilities utilizing these flowsheets were designed conceptually, and their costs were estimated.¹⁷ A P-T fuel shipment cask was also conceptually designed, and its cost was estimated.¹⁸ Finally the short-term (contemporary) risks from fuel cycle operations and the long-term (future) risks from a repository (assumed to be located at the presently proposed Waste Isolation Pilot Plant site) were estimated for cases with and without P-T.^{19,20}

A summary of the costs, risks, and benefits of P-T is presented in Table 3.8. The incremental cost of P-T (\$9.2 million/GW(e)-year) is equivalent to 1.28 mills/kWh(e), an increase of 5% to the cost of nuclear-generated electricity. The increase in short-term risk to the general public was found to be 2850 man-rem/GW(e)-year, 99.4% of which was attributable to nonradiological risks arising principally from the steam plant off-gas and from physical damage during transportation. As a basis of comparison, natural background causes about 5000 man-rem/GW(e)-year to the same population. The reduction in long-term risk, estimated over a 1 million-year period, represents the benefit derivable from P-T. This was found to be only 300 man-rem/GW(e)-year, and is less than 0.001% of natural background. The cost/benefit ratio based only on the reduction of radiological risk is \$32,400/man-rem, which is considerably in excess of the \$1000/man-

rem criterion that is used to determine whether additional effluent control systems on nuclear power plants are justified. There is actually a *negative* total benefit if nonradiological risks are included.

We concluded that, while both partitioning of the actinides from wastes and their subsequent transmutation in power reactors were feasible using currently identified and studied technology, implementation of this concept cannot be justified because of the small radiological benefits and substantially increased costs. Greater than 99% of the long-term risk from the repository is due to ^{99}Tc and ^{129}I , and while we believe that partitioning and transmutation of these species is feasible, it would almost certainly not be cost-effective. If a policy decision should nevertheless be made to implement P-T, we estimate that research and development funding of ~\$900 million over a 20-year period would be needed. On the other hand, it should be pointed out that some of the technology identified during this program can be effectively utilized to improve future waste management practices within conventional fuel cycle operations.

3.3 ALTERNATE WASTE FORMS DEVELOPMENT

A program has been under way at ORNL for about two years to apply the sol-gel technology developed for reactor fuel preparation²¹ to the incorporation of high-level nuclear waste (HLW) for permanent disposal in a form that has superior leach resistance. It is a part of the HLW Technology Program administered through the HLW Program Office at

Table 3.8. Summary of the costs, risks, and benefits of P-T per GW(e)-year

	Reference case	P-T case	Increment
<i>Costs</i>			
Fuel cycle costs, \$10 ⁶	181.9	181.1	9.2
<i>Short-term risk</i>			
Radiological dose, man-rem	4	20	16
Total risk, man-rem	1,700	4,550	2,850
Natural background, man-rem (for comparison)	5,000	5,000	0
<i>Long-term benefit</i>			
Radiological dose, man-rem	25,800	25,500	300
Natural background,	33.5×10^6	33.5×10^6	0

^aIncludes nonradiological risks expressed as equivalent radiological impact using a conversion factor of 5000 man-rem/health effect.

^bExpected dose integrated over 1 million years.

16. D. W. Tedder, B. C. Finney, and J. O. Blomeke, *Actinide Partitioning-Transmutation Program Final Report, II. Partitioning Process for LWR Fuel Reprocessing and Refabrication Plant Wastes*, ORNL TM-6982 (June 1980).

17. Ralph M. Parsons Co., *Actinide Partitioning-Transmutation Program Final Report, V. Preconceptual Designs and Costs of Partitioning Facilities and Shipping Casks*, ORNL TM-6985 (June 1980).

18. C. W. Alexander and A. G. Croff, *Actinide Partitioning-Transmutation Program Final Report, IV. Miscellaneous Aspects*, ORNL TM-6984 (October 1980).

19. Science Applications, Inc., *Actinide Partitioning-Transmutation Program Final Report, VI. Short-Term Risk Analysis of Reprocessing, Refabrication and Transportation*, ORNL TM-6986 (June 1980).

20. Los Alamos Technical Associates, Inc., *Actinide Partitioning-Transmutation Program Final Report, VII. Long-Term Risk Analysis of the Geologic Repository*, ORNL TM-6987 (September 1980).

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

Savannah River Laboratory (SRL) and is aimed at processing high-level defense wastes that exist as sludges in tank storage at installations throughout the country, particularly at Savannah River. The program at ORNL is a cooperative effort between the Chemical Technology Division and the Metals and Ceramics Division. Gel spheres containing waste and suitable matrix materials are prepared in the Chemical Technology Division and dried, sintered, and coated in the Metals and Ceramics Division.

Sphere Preparation

Most of the spheres have been prepared by internal gelation, although some work was done with external gelation in the earlier stages of the program. A generic flowsheet for the internal gelation process is shown in Fig. 3.2. The waste sludge is partially dissolved in nitric acid, and a solution of the matrix elements is added to provide a feed solution. Some finely divided solids (e.g., MnO_2) can be tolerated in the system. Urea is dissolved in the feed solution to neutralize excess acid and prevent premature gelation. The adjusted feed is then cooled to 0°C and

mixed with a solution of hexamethylenetetramine (HMTA), precooled to 0°C. The chilled feed broth is fed through a vibrating nozzle into a column of circulating, immiscible forming liquid (approximately equal volumes of trichloroethylene and 2-ethylhexanol) at 55°C. Ammonium hydroxide for precipitation and gelation is provided by the thermally activated decomposition of HMTA as the spherical droplets fall through the forming liquid. The gelled spheres are transferred hydraulically in the forming liquid to a tank where they are aged for about 1 h. At the end of the aging period, the spheres are rinsed with a solution of 50 vol % isopropanol-0.5 M NH_4OH to remove entrained forming liquid and are then washed with 0.5 M NH_4OH to remove residual urea, HMTA, and dissolved salts (nitrate, chlorides).

Two internal gelation systems have been operated in the laboratory. Small-scale exploratory tests are made in a 2.5-cm (1-in.)-diam column at a scale of about 1 g metal oxides per batch. Batches of spheres up to 150 g are prepared in a system with a 10-cm (4-in.)-diam column. More than 5 kg of spheres were prepared in this system for drying, sintering, and coating tests. A larger system, capable of producing spheres at the rate of 1 kg/d, was installed and tested for leaks.

A variety of matrix systems has been used, from the complex Synroc²² system, in which the final composition of the spheres is tailored to the composition of highly stable titanium minerals, to simpler nontailored systems that use ZrO_2 or Al_2O_3 as the matrix. Gel spheres were prepared with the Synroc maxtrix system at waste loadings of 1 wt % waste oxides (Synroc B), 55% (Synroc D), and 70% (70/30). Gelation with the nontailored matrix systems is simpler and requires substantially less urea

Fig. 3.2. Flowsheet for incorporating high-level waste in gel spheres by internal gelation.

22. A. E. Ringwood, S. C. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, "Immobilisation of High Level Nuclear Reactor Wastes in SYNROC," *Nature* 278, 219 (1978).

Tabl. 3.9. Typical internal gelation parameters for gelation of various compositions

Waste form	Feed solutions			Used in gelation (mol/mol metal)	
	Metal oxides (g/mL)	Metal (mol/L)	H ⁺ (mol/L)	HMTA	Urea
Synroc B	0.161	2.1	N.D.	2.2	9.9
Synroc D	0.272	4.0	1.4	2.0	4.0
Synroc 70/30	0.313	4.6	0.7	1.5	3.6
ZrO ₂ 90/10	0.224	3.0	1.5	2.0	2.3

(Table 3.9), and these systems have the additional advantage of not adding chloride to the system (titanium is added to the Synroc matrix as TiCl_3). Gel spheres have been prepared with a ZrO_2 matrix at waste loadings of 50 to 100%. The 90% waste-loaded material was superior to the other zirconia-based spheres from the standpoint of less cracking in the wash cycle and better appearance after drying and sintering. Spheres prepared with Al_2O_3 or ZrO_2 - Al_2O_3 matrix appeared to be softer than those prepared with the 10% ZrO_2 matrix.

Numerous types of simulated composite SRP waste have been used, including sludge material prepared by the Southwestern Chemical Company, solutions prepared from soluble salts, sludge prepared at ORNL by a SRL procedure, and SRL-supplied sludge. Gelation conditions were independent of the waste source if the feed solutions were prepared to have the same composition. Gel spheres were also prepared at the 90% waste oxide-10% ZrO_2 composition from a high-iron sludge and a high-aluminum sludge prepared by SRL.

Detailed compositions of the SRP composite waste and some of the waste form products prepared from it are shown in Table 3.10. The Synroc D and

Synroc 70/30 spheres were dried, sintered, and coated with carbon in the Metals and Ceramics Division and subjected there to standard leaching tests with deionized water at 90°C. The concentrations of all metals in the leach solutions were below the detection limits with inductively coupled plasma emission spectroscopy (ICP) or atomic absorption, indicating leach rates of less than 10^{-2} to 10^{-4} g/m²-d for the various metals. The ZrO_2 90/10 spheres have also been successfully coated and are expected to have equally low leach rates.

Cesium Retention

Cesium is present in the waste tanks in the supernatant solution above the sludge. It is separated from the solution by sorption on the weak acid phenolic ion exchange resin Duolite ARC-59 and then eluted from the resin with 2 M $(\text{NH}_4)_2\text{CO}_3$ - NH_4OH .²³ After removal of NH_3 and CO_2 by steam stripping, the eluate contains 2 M Na_2CO_3 and 0.007 M Cs. This solution is usually sorbed on the zeolite

23. J. R. Wiley and R. M. Wallace, *Removal of Cesium from Savannah River Plant Waste Supernate*, DP-1388 (July 1975).

Table 3.10. Composition of waste, matrix and product
Values are expressed in weight percent

Component	Synroc B product	SRP ^a waste	High waste-loaded SRP waste forms					
			Synroc D ^b		Synroc 70/30 ^c		ZrO ₂ 90/10 ^d	
			Matrix	Product	Matrix	Product	Matrix	Product
Fe ₂ O ₃		49.9		27.4		35.8		44.9
Al ₂ O ₃	10.9	9.8	33.6	20.6		7.0		8.8
MnO ₂		13.7		7.5		9.9		12.4
U ₃ O ₈		4.5		2.5		3.2		4.1
CaO	13.8	3.7	10.3	6.7	18.0	7.7		3.3
NiO		6.2		3.4		4.4		5.6
SiO ₂		1.2	15.8	7.8	21.2	6.7		1.1
Na ₂ O		7.0		3.8	9.9	7.9		6.3
Na ₂ SO ₄		1.3		0.7		0.9		1.2
Ce ₂ O ₃		1.1		0.6		0.8		0.8
Nd ₂ O ₃	0.3	1.1		0.6		0.8		0.9
SrO	0.2	0.5		0.3		0.4		0.5
TiO ₂	59.7		31.8	14.3	39.1	11.0		
ZrO ₂	9.8		8.5	3.8	11.8	3.3	100	10.0
BaO	4.2							
Mo ₂ O ₃	0.3					0.2		
Ru ₂ O ₃	0.3							
Cs ₂ O	0.5							

^aComposite SRP waste with aluminum removal normalized to compensate for removal of zeolite and addition of Ce₂O₃, SrO, and Nd₂O₃.

^bSynroc D: 70 wt % composite SRP waste without aluminum removal plus 30 wt % additives.

^cSynroc 70/30: 70 wt % composite SRP waste with aluminum removal plus 30 wt % additives.

^dZrO₂ 90/10: 90 wt % composite SRP waste with aluminum removal plus 10 wt % ZrO₂.

Ionsiv IE-95, and the loaded zeolite is incorporated in the high-level waste form.

Ionsiv IE-95, a synthetic chabazite, was by far the most effective adsorbent tested in our program for cesium removal from 2 M Na_2CO_3 -0.007 M Cs (Fig. 3.3). The gel spheres (washed and air dried) had very low cesium adsorption power. This was increased slightly, but not enough to be of practical use, by coating the dried spheres with *p*-chloro-*o*-benzyl phenol, a water-immiscible phenol that extracts cesium strongly from alkaline solution²⁴ or by adding pulverized Ionsiv IE-95 to the feed broth before the spheres were gelled. Cesium adsorption with zeolite types 4A, 5A, and 13X was lower by a factor of ~10 than with Ionsiv IE-95.

A sample of Ionsiv IE-95 was loaded with 5 wt % Cs from a 2 M Na_2CO_3 solution, and the loaded zeolite was coated with pyrolytic carbon in the Metals and Ceramics Division. The cesium concentration in leach solutions from standard leach tests was below the analytical detection limit, indicating a maximum leach rate of 10^{-3} g $\text{m}^{-2}\cdot\text{d}$.

Fig. 3.3 Cesium adsorption from 2 M Na_2CO_3 -0.007 M CsCl solution.

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

Basic research conducted during this period concentrated on the elucidation of mechanisms involved in the removal of trace heavy metals from aqueous streams by microorganisms. The removals of U, ^{226}Ra , and ^{137}Cs were considered, with work on radium and cesium biased toward existing waste handling problems at Weldon Springs, Missouri, and the Savannah River Plant, respectively. Process development efforts concentrated on the design, construction, operation, and evaluation of pilot plants based on fluidized-bed bioreactors containing fixed films of denitrifying bacteria. These pilot plants were developed at ORNL under contracts to Goodyear Atomic Cooperation (which operates a gaseous diffusion plant in Portsmouth, Ohio) and National Lead of Ohio (which operates the Feed Material Processing Center in Cincinnati) to reduce the nitrate discharges from those facilities to acceptable levels.

Removal of Heavy Metals from Aqueous Streams by Microorganisms

Earlier work demonstrated that uranium uptake by *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa* was not inhibited by the metabolic inhibitors 2,4-dinitrophenol and sodium azide, and thus that cellular metabolism was not required for uranium accumulation. In an extension of this work, uptake rates by cells of each species were measured after treatment with lethal agents such as mercuric chloride and formaldehyde. Uranium uptake rates with *P. aeruginosa* were relatively unaffected by treatment with either agent. This finding further demonstrated that the previously observed rapid uptake rates with this species could not be attributed to a metabolically mediated active transport.

As shown in Fig. 3.4, uptake rates with dead cells of *S. cerevisiae* were higher than those with untreated cells. Formaldehyde treatment may have increased the rate of uranium uptake by reducing the overall positive charge of cationic sites on the cell surface, but there are no apparent reasons for the enhancing effect of mercuric chloride.

The effect of environmental conditions on cellular uranium uptake during growth was investigated with

24. W. D. Arnold, D. J. Crouse, and K. B. Brown, "Solvent Extraction of Cesium (and Rubidium) from Ore Liquors with Substituted Phenols," *Ind. Eng. Chem. Process Des. Dev.* 4, 249 (1965).

Fig. 3.4. Effect of mercuric chloride and formaldehyde pre-treatment on uranium uptake by *S. cerevisiae*.

S. cerevisiae yeast cells. Such cells grown in a synthetic media of yeast and malt extract had a uranium uptake rate 2.5 times greater than that of cells grown on a rich organic medium. Evidence reported in the literature suggests that this difference is due to an increase in the protein and phosphate content (presumed metal-binding sites) of yeast walls induced by the slower growth rate that occurs in a synthetic medium.

Uranium accumulation by *S. cerevisiae* is a cell-surface-associated phenomenon occurring over a period of several hours. In contrast, uranium uptake by *P. aeruginosa* and a mixed culture of denitrifying bacteria involves a very rapid intracellular accumulation. To quantify this phenomenon, several methods for rapid contact and subsequent separation of the phases (i.e., cells with accumulated uranium from the solution with the remaining uranium) were tested. Although all methods (filtration, quenching by chemical complexation, etc.) tested during this

period were too slow to permit study of the rapid transition between initial contact and equilibrium conditions, a physical-chemical separation technique was devised which demonstrated that uranium complexation by *P. aeruginosa* occurs in <5–10 s. In this method, the two phases were rapidly forced by air pressure through a small bed of Bio-Rad AG50W-X12 cation exchange resin. The resin-bound uranium was subsequently eluted with nitric acid and analyzed by the Arsenazo III colorimetric technique. It was shown by using cell-free solutions that the 5- to 10-s residence time in the resin bed was sufficient to remove essentially all of the soluble uranium.

The microbial population responsible for denitrification in an ORNL-developed fixed-film, fluidized-bed bioreactor designed for the removal of nitrate from wastewaters was also found to be effective in removing uranium from solution. In support of process development efforts to utilize these denitrifying microorganisms as a biosorbent for uranium isolation, a study was made to determine the best method for storing them for subsequent use. As shown in Table 3.11, preservation by freezing (-20°C) resulted in a progressive decrease in uptake capacity over 3-week storage interval. However, the decrease was significantly less than that observed with bacteria refrigerated at 4°C .

The ability of microorganisms to remove ^{137}Cs from solution was considered in regard to a potential treatment process for a select high-level radioactively contaminated waste solution at the Savannah River Plant. The actual waste solution was simulated for our laboratory studies using a mixture of reagent-grade chemicals. It contains several metal species other than cesium and high concentrations of nitrate.

Table 3.11. The effect of storage temperature on uranium uptake by the mixed culture of denitrifying bacteria

Storage interval (weeks)	Assay time (h)	Solution uranium concentration (g/m^3) ^a at indicated storage temperature	
		4°C	-20°C
0	0.5	3.8	3.8
	22.5	2.0	2.0
1	0.5	33.9	5.5
	22.5	4.3	2.6
2	0.5	17	5.5
	22.5	8.9	4.6
3	0.5	21.7	6.7
	22.5	22.8	6.7

^aInitial solution uranium concentration, 100 g m^{-3} .

Both unlabeled and labeled CsCl were added to the Savannah River simulated sludge waste (SRSSW) and other test solutions; resulting concentrations are shown in Table 3.12. After exposure of the cells to ^{137}Cs under the conditions indicated, the cells were removed from solution, and the remaining soluble ^{137}Cs was assayed by γ -radiation counting.

As shown in Table 3.12, the distribution coefficients obtained were relatively low, and in all cases the bulk of the cesium (as evidenced by soluble radioactivity measurements) remained in solution. Little if any growth of the denitrifying bacteria occurred in the presence of cesium (ethanol as a carbon source, incubated anaerobically under a nitrogen atmosphere).

Radium-226 incorporation by microbial cells was considered with regard to another radioactive waste problem, namely, contaminated waste storage ponds at Weldon Spring, Missouri. In addition to ^{226}Ra , the water contains a variety of other metal species and 1.3% nitrate. Samples of the pond water were treated as indicated in Tables 3.13 and 3.14. Radium-226 incorporation was determined for resting cells and under growth conditions. Soluble ^{226}Ra remaining after cell contact (cells removed by centrifugation) was assayed using γ -radiation counting.

It can be seen from Table 3.13 that some organisms could accumulate ^{226}Ra under resting cell or growth

Table 3.13. Uptake of ^{226}Ra from contaminated pond water^a

Organism ^b	Conditions (pH)	Distribution coefficient ^c
<i>Pseudomonas aeruginosa</i>	4	<<1 ^d
	6.9	<<1 ^d
<i>Saccharomyces cerevisiae</i>	4	<<1 ^d
	6.9	<<1 ^d
<i>Ashbya gossypii</i>	7.7	344
<i>Penicillium chrysogenum</i>	7.7	624
Mixed culture of denitrifying bacteria	3.9	7
	5.7	95
	7.7	38

^aConcentration of ^{226}Ra : 354 pCi/L.

^bResting cells (washed and resuspended in H_2O) were added to the waste solution, and the mixture shaken at 25–27°C.

^cDistribution coefficient: (pCi ^{226}Ra /g cells) $\div$ (pCi ^{226}Ra /g solution).

^dThat is, pCi ^{226}Ra /g cells essentially equivalent to background.

(Table 3.14) conditions. However, the distribution coefficients were relatively low. Other researchers²⁵ have found 95% of the ^{226}Ra to be removed during long-term growth (over a period of months) of denitrifying microorganisms in the same pond water

25. P. A. Taylor, Chemical Process Department, Development Division, Y-12 Plant, Oak Ridge, Tenn., unpublished data.

Table 3.12. Cesium uptake by microorganisms

Culture and phase	Medium and conditions	Cesium concentration (g/m ³)	Cell concentration (g/100 mL)	Distribution coefficient ^a
<i>Pseudomonas aeruginosa</i> Resting	SRSSW - pH 4 pH 7 pH 10.2	0.12	0.4	11
		0.12	0.4	12
		0.12	0.4	9
		0.017	0.2	16
<i>Saccharomyces cerevisiae</i> Resting Growth ^b	Water - pH 6	0.006	0.6	26
		0.017	0.4	37
Mixed culture of denitrifying bacteria Growth	Denitrifying medium, ^c	0.013	0.002, 0.003	228,469
		0.013	0.04	9
		0.013	0.04	15
		0.013	0.006, 0.1010	95,137
		0.013	0.03	21
		0.013	0.05	49

^aDistribution coefficient: (cpm ^{137}Cs per g cells) $\div$ (cpm ^{137}Cs per g solution).

^bComplex organic medium.

^cEthanol (0.5% v/v) as carbon source.

Table 3.14. Radium-226 content of microorganisms cultured in contaminated pond water

	Total pCi ²²⁶ Ra			Distribution coefficient ^a
	Initial	Solution	CeLs	
Mixed culture denitrifying bacteria				
Glucose grown ^b	48	41.35	3.5,2.6	104,119
Ethanol grown ^b	48	32.34	1.9,3.1	124,126
<i>Chlorella pyrenoidosa</i>				
Shake culture ^c	48	40	0.45	51
Static culture ^c	48	56	0.63	41
WS algae ^d				
Shake culture ^c	48	42	0.37	46
Static culture	48	60	0.60	32

^aDistribution coefficient: (pCi ²²⁶Ra/g cells) ÷ (pCi ²²⁶Ra/g solution).

^b20-d incubation; 10-fold increase in cell mass.

^c17-d incubation.

^dMixed algal, blue-green algal population isolated from pond water.

examined in this work. Methanol was used as a carbon source. In contrast, very little ²²⁶Ra removal was observed in this work either by biosorption or during short-term growth experiments (over a period of weeks). Further experimentation is planned to resolve these differences.

Biodenitrification Pilot Plant

ORNL was contracted by Goodyear Atomic Corporation (GAT) and National Lead of Ohio (NLO), both facilities having difficulty meeting expected concentration limits for nitrate discharge,

to develop pilot plants based on fluidized-bed bioreactors for biodenitrification of process wastewaters.

A schematic drawing of the pilot plant developed by ORNL for GAT is shown in Fig. 3.5; the biodenitrification section consisted of two fluidized-bed bioreactors (each 20 cm in diam and 6.4 m in height) operated in series. This system was operated for 6 months beginning in January 1980.

A schematic drawing of the pilot plant developed for NLO is shown in Fig. 3.6; the biodenitrification section consisted of a single fluidized-bed bioreactor

Fig. 3.5. Flowsheet for Goodyear Atomic Corporation pilot plant.

Fig. 3.6. Flowsheet for the National Lead of Ohio pilot plant.

(50 cm in diam and 6.4 m in height). This system was operated for 10 weeks beginning in August 1980.

A summary of denitrification rates achieved with these systems during the development period is given in Table 3.15. Calculations of denitrification rates were based on empty reactor volumes. The hydraulic residence time in the 50-cm-diam bioreactor and in each of the 20-cm-diam bioreactors was approximately 11 min. For equivalent inlet concentrations, a single 20-cm-diam bioreactor produced the same denitrification rate as the 50-cm-diam bioreactor, indicating that the denitrification rate was independent of the bioreactor diameter. The ability to use bioreactors in series to reduce high nitrate concentrations to acceptable levels was also implied by the data in Table 3.15.

Figure 3.7 graphically summarizes the denitrification rates achieved in the 50-cm-diam bioreactor for

Fig. 3.7. Denitrification rates vs average nitrate concentrations for the 0.5-m-diam bioreactor.

varying average nitrate concentrations in the bioreactor. First-order kinetics were implied for average nitrate concentrations ≤ 500 g/m³. For higher average nitrate concentrations, an approximately constant denitrification rate of 30 kg of nitrate nitrogen per day per m³ of empty reactor was observed.

Upon completion of testing, the modular pilot plants described above were shipped to GAT for on-site usage. A complete project report is to be published elsewhere.²⁶

3.5 UPDATING OF THE ORIGIN COMPUTER CODE

The effort to update the ORIGIN computer code²⁷ 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

26. J. F. Walker, Jr., C. W. Hancher, and B. D. Patton, "Biological Treatment of Nitrate Wastewater Using Fluidized-Bed Bioreactors," presented at the Third Symposium on Biotechnology in Energy Production and Conservation in Gatlinburg, Tenn., May 12-15, 1981; to be published in the Proceedings.

27. M. J. Bell, ORIGIN: The ORNL Isotope Generation and Depletion Code, ORNL-4628 (May 1973).

Table 3.15. Comparison of denitrification rates for 20- and 50-cm bioreactors at different feed concentrations

Feed/effluent concentrations of NO ₃ (g/m ³)			Denitrification rate kg N(NO ₃)/d·m ³		
20-cm bioreactor	50-cm bioreactor	Two 20-cm bioreactors in series	20-cm bioreactor	50-cm bioreactor	Two 20-cm bioreactors in series
860/27	860/34	1715/40	26	24	23
10006/110	1100/27	2080/5	28	27	29
2027/1000	1741/455	4011/1430	32	30	33
2668/1340	2100/1025	5730/2110	38	38	43

bases on as firm a theoretical basis as possible. This involves modification of the original ORIGIN code to yield the ORIGIN2 code, which more accurately reflects the neutronic behavior of the actinides during irradiation. It also includes calculation of effective cross sections using more sophisticated reactor physics codes^{28,29} and updating the other data libraries. Progress prior to this report period included completing the modification of the computer code itself, developing and documenting updated models for uranium-plutonium cycle pressurized-water and boiling-water reactors,³⁰ and generating and documenting updated decay and photon libraries.³¹

During this report period ORIGIN2 reactor models for alternative fuel cycles in pressurized-water reactors were completed and documented.³² The fuels considered are (1) denatured ²³³UO₂ in ThO₂, (2) PuO₂ in ThO₂, (3) low-enrichment ²³⁵UO₂ irradiated to a burnup of 50,000 MWd per metric ton of heavy metal (MTHM), and (4) self-generated, denatured ²³³UO₂ in ThO₂.

The development of two CANDU reactor models was initiated, completed, and documented³³ during this report period. The fuel cycles considered are both once-through, one using natural UO₂ and the second using slightly enriched UO₂ (1.2 wt % ²³⁵U).

The development of eight ORIGIN2 liquid-metal fast breeder reactor (LMFBR) models was initiated and completed during this report period. The fuel cycles that were developed are listed in Table 3.16. Documentation of these models is not yet complete.

A user's manual³⁴ for the ORIGIN2 computer code and summary documentation³⁵ for the code were completed and issued during the report period.

Based on this documentation, a code package was made available through ORNL's Radiation Shielding Information Center.³⁶ By the end of the reporting period, 50 organizations had acquired the ORIGIN2 code package.

3.6 INTEGRATED DATA BASE

This program was begun in FY 1980 for the purpose of establishing and maintaining a computerized,

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

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

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

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

32. A. G. Croff and M. A. Bjerke, *Alternative Fuel Cycle PWR Models for the ORIGIN Computer Code*, ORNL TM-7005 (February 1980).

33. A. G. Croff and M. A. Bjerke, *Once-Through CANDU Reactor Models for the ORIGIN2 Computer Code*, ORNL TM-7177 (November 1980).

34. A. G. Croff, *A User's Manual for the ORIGIN2 Computer Code*, ORNL TM-7175 (July 1980).

35. A. G. Croff, *ORIGIN2: A Revised and Updated Version of the Oak Ridge Isotope Generation and Depletion Code*, ORNL-5621 (July 1980).

36. Code Package CCC-371, obtainable from Codes Coordinator, Radiation Shielding Information Center, Bldg. 6025, P.O. Box X, Oak Ridge National Laboratory, Oak Ridge, TN 37830, phone (615) 574-6176, FTS 624-6176.

Table 3.16. Fuel cycles considered in ORIGIN2 LMFBR* models

Core fissile material	Fertile material			Core burnup (GWd/MTHM ^b)
	Core	Axial blanket	Radial blanket	
LWR PuO ₂	UO ₂	UO ₂	UO ₂	100
LWR PuO ₂	UO ₂	UO ₂	UO ₂	6
Recycle PuO ₂	UO ₂	UO ₂	UO ₂	100
LWR PuO ₂	UO ₂	UO ₂	ThO ₂	100
LWR PuO ₂	ThO ₂	ThO ₂	ThO ₂	100
Recycle ²³³ UO ₂	ThO ₂	ThO ₂	ThO ₂	100
14% denatured ²³³ UO ₂	ThO ₂	ThO ₂	ThO ₂	100
40% denatured ²³³ UO ₂	ThO ₂	ThO ₂	ThO ₂	100

*Liquid-metal fast breeder reactor.

^bMetric tons of heavy metal.

LWR, light-water reactor

integrated data base of current and projected nuclear wastes in the United States. A consistent set of evaluated information on waste inventories, characteristics, sources, package descriptions, and locations of interim storage and disposal sites is needed by DOE and other agencies and contractors for use in waste program planning and systems analysis. The data base will also include costs and will be capable of taking into account the effects of different methods of chemical treatment and packaging on the characteristics of final waste forms.

A series of computer codes and data files called ORGENTRE is being developed to maintain this information and to project nuclear waste generation and treatment options. It consists of the following major components:

1. A series of waste generation codes and data bases comprising characteristics of the existing inventory, a nuclear materials projection code to calculate the fissile and fertile materials throughputs of all fuel cycle facilities for any given nuclear power buildup and reactor mix, a defense waste projection code, and an institutional-industrial waste projection code.
2. A waste treatment simulation code to calculate the characteristics of secondary wastes that are

generated as a consequence of any proposed treatment process.

3. A system data base composed of several libraries containing fuel cycle facility and waste treatment process flowsheet data, and tables of pertinent nuclear and engineering conversion constants.
4. An economics data file and code to determine the costs of various treatment options.
5. An output file containing the identity and characteristics of all the wastes that have been finally generated and projected, and a data base manager program to supply tabular and graphical representations of these data.

During the past 18 months, two reports were prepared to document the information on waste inventories that has been acquired thus far. The first³⁷ reported the quantity of spent fuel and wastes generated through 1979 and that projected through the year 2000. A second, draft report³⁸ updated the previous document and presented data on nuclear characteristics as well. A summary of these data is presented in Table 3.17. Many of the characteristics

37. *Spent Fuel and Waste Inventories and Projections*, ORO-778 (August 1978).

38. *Spent Fuel and Waste Inventories and Projections as of December 31, 1980*, ORNL NFW-81-9 (March 1981).

Table 3.17. Summary of current and projected inventories of nuclear fuels and wastes in the United States

Category	Inventory on December 31, 1980			Accumulated through CY 2000		
	Volume (10 ³ m ³)	Radioactivity (MCi)	Thermal power (MW)	Volume (10 ³ m ³)	Radioactivity (MCi)	Thermal power (MW)
Spent fuel	(6,900 MTHM) ^a	9,900	37	(75,000 MTHM) ^{a,b}	62,000	220
High-level wastes						
Defense	290	1,300	3.8	340	1,600	4
Commercial	2.2	37	0.1	2.2	23	0.1
Transuranic wastes						
Defense	320	0.8	0.004	400	1.5	0.011
Other	360	0.05		370	0.03	
Low-level wastes						
Defense	1,500	27		3,100	c	c
Other	760	6.2		5,100	2.2	0.03
Remedial action wastes						
Inactive mill tailings	15,000	~0.3		15,000	~0.3	
Other	46	c		2,000	c	
Active mill tailings	82,000	0.6		343,000	2.5	

^aAmounts in parentheses are given as metric tons of heavy metal (MTHM).

^bBased on installed nuclear capacities of 53.8, 137.5, and 179.7 MW(e) in calendar years 1980, 1990, and 2000, respectively.

^cNot available.

were calculated and projected using newly developed ORGENTRE codes. The waste inventory data are being acquired principally through the lead offices that were established by the DOE to oversee the management of the various types of waste, and it is expected that future reports containing additional information in a more sophisticated format will be published periodically as the ORGENTRE system becomes fully developed and operational.

A bibliographic file is also being created with emphasis on inventories, projections, and characteristics. Abstracts, key words, and other pertinent information are stored in a computer file that is designed to facilitate machine searches. A two-volume bibliography (abstracts and indexes) has been published³⁹ and will be updated periodically. A dictionary of waste management terms is also being prepared.

3.7 CARBON-14 IMMOBILIZATION

Introduction

Although no restrictions have been placed on the release of ^{14}C , it has been identified as a potential health hazard due to the ease with which it may be assimilated into the biosphere and its long half-life (5730 years). The intent of the Carbon-14 Immobilization Program is to develop and demonstrate a novel process for restricting off-gas releases of ^{14}C from various nuclear facilities. The process utilizes the $\text{CO}_2\text{-Ba(OH)}_2$ hydrate gas-solid reaction to directly remove and immobilize ^{14}C . Program emphasis is directed toward the treatment of an air-based off-gas stream containing small amounts of ^{14}C as $^{14}\text{CO}_2$. The reaction product, BaCO_3 , possesses both the thermal and chemical stability desired for long-term waste disposal.

Laboratory studies and a literature review were conducted to determine the feasibility of using beds of Ba(OH)_2 hydrate for $^{14}\text{CO}_2$ removal and fixation. The product, BaCO_3 , possesses excellent thermal and chemical stability for incorporation into cement and subsequent long-term disposal. Experimental studies have been conducted on both fixed and fluidized beds of Ba(OH)_2 hydrates. Although three stable hydrates exist— $\text{Ba(OH)}_2\cdot\text{H}_2\text{O}$, $\text{Ba(OH)}_2\cdot 3\text{H}_2\text{O}$, and $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ —we have identified $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ as the active species. Furthermore, we have observed that when flakes of $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ are contacted under proper conditions with a 330-ppm CO_2 gas stream, removal efficiency (<100 ppb), high reactant utilization (>99%), and an acceptable pressure drop (3.4 kPa/m for a 13-cm/s superficial velocity) are possible. Therefore, with reference to a September

30, 1980, program milestone, we have concluded that the use of packed beds of $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ flakes is the preferred mode of gas-solid contacting for the treatment of dilute CO_2 -bearing off-gas streams.

Experimental Studies

Experimental studies have been conducted on fixed and fluidized beds of Ba(OH)_2 hydrates. For these studies, commercial-grade $\text{Ba(OH)}_2\cdot\text{H}_2\text{O}$, $\text{Ba(OH)}_2\cdot 5\text{H}_2\text{O}$, and $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ and analytical-grade $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ have been examined. Studies at ambient conditions have indicated $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ to be the active species. Therefore, process operating conditions that favor the formation of $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ will likely be required. The dissociation water vapor pressure for $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ at 25°C is 8.26 mm Hg. Although both commercial- and analytical-grade $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ have been found to be reactive toward CO_2 , they are considerably less reactive than either $\text{Ba(OH)}_2\cdot\text{H}_2\text{O}$ or commercially designated $\text{Ba(OH)}_2\cdot 5\text{H}_2\text{O}$ that has been hydrated to $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$. We have observed that during the fixed-bed treatment of humidified air streams, the two reactants undergo a conditioning period during which the CO_2 -removal efficiency of the bed dramatically improves. However, this activation step is accompanied by a twofold increase in bed volume and degradation of the reactant particles. The resultant bed is extremely active for CO_2 removal, but gas throughput is restricted because of increased pressure drop. For the operation of a fluidized bed, this reduction would probably not present a problem. However, because of the many merits of the simpler fixed-bed concept, considerable effort has been directed toward reducing the magnitude of the pressure-drop problem.

Present efforts are directed toward the use of the flakes of commercial $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ in packed-bed reactors. Although designated as $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ by the vendor, our analysis has indicated a stoichiometry of $\text{Ba(OH)}_2\cdot 7.50\text{H}_2\text{O}$. X-ray patterns of the material have indicated $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ to be present. We now believe the flakes to be composed of $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ and a $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ - $\text{Ba(OH)}_2\cdot 3\text{H}_2\text{O}$ eutectic, the stoichiometry of the eutectic being $\text{Ba(OH)}_2\cdot 7.12\text{H}_2\text{O}$. Therefore, the flake appears to be composed of 53% $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ and the remainder eutectic.

Although these flakes possess considerably less reactivity than hydrated $\text{Ba(OH)}_2\cdot\text{H}_2\text{O}$, the material

39. C. A. Johnson and P. A. Garland, *Radioactive Waste Management Integrated Data Base: A Bibliography*, ORNL/TM-7385/V1 and V2 (September 1980).

has been found to have sufficient reactivity for the treatment of dilute CO_2 gas streams. Most of these runs have been conducted on 10.2-cm-ID $\times$ 51-cm-long (4- $\times$ 20-in.) packed beds which contain 4200 g of reactant. The large bed size was required to obtain unbiased pressure-drop information. A typical run would last 11 d. The bed of flakes is initially 52% void. However, negligible bed expansion has been noted upon complete conversion to the carbonate, and the final void volume is 77% due to the lower molar volume of the product. Although several gas superficial velocities have been examined, a nominal superficial velocity of 10 cm/s has been established as the reference condition based upon desired scale-up criteria. The bulk of the data to date have been obtained at a superficial velocity of 13 cm/s. For these studies, variables of particular interest are the effect of water vapor pressure and column temperature upon the removal efficiency of the bed, and the final pressure drop across the bed upon 100% reactant conversion.

Shown in Fig. 3.8 are the results of a run operated at near optimal conditions. The CO_2 breakthrough was reasonably sharp with a mass transfer zone of approximately 18 cm. The initial pressure drop across the bed was 1.0 kPa/m (0.04 lb-in.⁻²-ft⁻¹) and gradually increased to 2.8 kPa/m (0.11 lb-in.⁻²-ft⁻¹).

Fig. 3.8. Loading curve of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ flake bed.

The final product was a free-flowing solid that was easily removed from the column (Fig. 3.9).

As previously mentioned, it is believed that the conditions for the preceding run were near optimal as results have indicated an operating envelope to exist. The relative humidity for this run was 40%, which corresponded to an inlet water pressure of 1129 Pa (8.47 mm Hg). The dissociation vapor pressure of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at these conditions is 918 Pa (6.89 mm Hg). Results obtained under similar conditions with water vapor pressures less than that of the dissociation vapor pressure for $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ have resulted in bed deactivation and early CO_2 breakthrough, indicating $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ to be considerably less reactive than $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. This deactivation step appears to be kinetically controlled.

ORNL-PHOTO 4313-81

Fig. 3.9. Commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ reactant and BaCO_3 product flakes.

Studies are presently under way to develop a better understanding of the deactivation phenomenon. However, prolonged operation at vapor pressures below the dissociation vapor pressure of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ does not appear to be feasible.

Experimental studies have also indicated that there may be an upper relative humidity or water vapor pressure, above which it may not be desirable to

operate as pressure-drop problems are compounded. As previously cited, the flakes of commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ are composed of 53 mol % $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and 47 mol % $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ - $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ eutectic. Results have indicated that, when a flake is exposed to a high-humidity gas stream, a transformation takes place whereby the flake preferentially curls on one side and becomes a more active species (Fig. 3.10). Studies are under way to develop a better understanding of the mechanism for this transformation, although conversion of

$\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ and capillary condensation appear to be likely candidates. The resulting material is more active, but pressure-drop problems are also much greater due to ensuing particle degradation. Studies are under way to determine the severity of the problem as the humidity or water vapor pressure is increased while other system parameters remain constant.

Microbalance Analytical System

To aid in the understanding and development of a model for the packed-bed macrosystem, an understanding or at least an awareness of phenomena that occur on the microscale is required. Therefore, a microbalance analytical system has been constructed and has undergone initial calibration and testing. Typical sample sizes for these studies will be 200 mg. The microbalance is situated in a vacuum system capable of being evacuated to 10^{-4} Pa. Precise pressure and temperature control about the sample is provided for. The system as designed will enable the determination of the surface morphology of the solids, the dissociation vapor pressures of the hydrates as a function of temperature, and the rate of the CO_2 - $\text{Ba}(\text{OH})_2$ hydrate reaction (i.e., physical, thermodynamic, and kinetic properties of the solid).

Conclusion

For the treatment of an air-based off-gas stream, the use of packed beds of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ flakes has been demonstrated and is the preferred mode of gas-solid contacting. However, results indicate that an operating envelope exists. If the water vapor pressure in the gas is less than the dissociation vapor pressure of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, the bed will deactivate. If the vapor pressure is considerably greater, pressure-drop problems will increase with increasing humidity as the particles curl and degrade. Results have indicated that, when operated in the proper regime, the bulk of the increase in pressure drop results from the conversion of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ to BaCO_3 and not from the hydration of the commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ [i.e., $\text{Ba}(\text{OH})_2 \cdot 7.50\text{H}_2\text{O}$] to $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

3.8 KRYPTON HYDROFRACTURE STUDIES

These experimental studies are a part of the assessment of radioactive krypton disposal by hydrofracture techniques. The complete experimental program will determine the solubility and diffusivity of krypton in water, in simulated waste

ORNL-PHOTO 4314-81 R

(a)

ORNL-PHOTO 4315-81 R

(b)

Fig. 3.10. Top and bottom views of commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ subjected to high humidity. Original photograph, 72 × 95 mm; 16.5× and 13×, respectively.

solutions used to prepare grout, and in the same grout that is currently used for hydrofracture waste disposal. The solubility studies use nonradioactive krypton and determine its solubility by pressure-drop measurements. The grout specimen is contained within a standard autoclave equipped with a sealed, magnetically coupled stirrer. The autoclave is capable of 35-MPa (5000-psig) operation although the experimental pressures will be lower. The grout specimens for the diffusion studies will be cast under krypton pressure in this autoclave and then transferred to one of several diffusion apparatuses. Here the krypton release will be monitored by periodic sweeping of the cover gas by helium followed by mass spectrometric determination of the krypton. The specified overpressure of helium will be maintained in the autoclave during the diffusion tests including the sweeping operation. Since it is expected that the diffusion studies will be quite lengthy, a fairly large number of test specimens will be examined in parallel.

Krypton solubility measurements have been completed to a pressure of 0.3 MPa (3 atm). The solubilities in water and simulated waste solution ($\sim 1.5 M \text{ NaNO}_3$) used to prepare the grout mixture also are determined at each pressure. The solubility of krypton in water at 25°C and 0.3 MPa (3 atm) was found to be $0.578 \text{ m}^3(\text{Kr})/\text{m}^3 (\text{H}_2\text{O})\text{-MPa}$ (0.0584 $\text{cm}^3/\text{g-atm}$; literature value,⁴⁰ 0.0535). The solubility in simulated waste solution was $0.322 \text{ m}^3 (\text{Kr})/\text{m}^3 (\text{grout})\text{-MPa}$ (0.00325 $\text{cm}^3/\text{mL-atm}$).

3.9 ASSISTANCE TO OFFICE OF NUCLEAR WASTE ISOLATION

The Geologic Disposal Technology (GDT) Program was established in the Chemical Technology Division on July 1, 1978, when the management responsibility for the overall National Waste Terminal Storage Program passed from the Office of Waste Isolation (OWI), Union Carbide Corporation Nuclear Division, to the Office of Nuclear Waste Isolation (ONWI), Battelle Memorial Institute, Columbus, Ohio. The GDT Program serves as a liaison between ONWI and several programmatic efforts at ORNL in their area of responsibility. The contribution by this Division to the GDT Program is outlined below.

Waste-Rock Interactions

Brine migration in salt. A draft report that reviews and analyzes the available experimental and theoretical information on brine migration in bedded salt was published.⁴¹

A number of licensing topical reports (LTR) for use in the licensing process are being prepared by ONWI based on technical topical reports (TTR) produced by various subcontractors and laboratories. A draft TTR on brine migration in nuclear waste repositories in salt formations was completed and submitted to ONWI for review by a special committee prior to final publication. This report encompasses the known theoretical and experimental data on brine migration under thermal gradients in both bedded and domal salt and develops an overall perspective on brine migration in relation to the design of a nuclear waste repository.

Review of information on the radiation chemistry of materials around waste canisters in salt repositories. The brines, vapors, and salts precipitated from the brines will be exposed to gamma rays and elevated temperatures in the regions close to a waste package in the salt and will be subject to changes in composition brought about by reactions induced by the radiation and heat. The objectives of this work⁴² were to review the status of information on the radiation chemistry of brines, gases, and solids that might be present around a waste package in salt and to assess the need for additional laboratory investigations on the radiation chemistry of these materials.

The basic aspects of the radiation chemistry of water and aqueous solutions, including concentrated salt solutions, were found to be substantially unchanged from those presented in a 1972 review⁴³ of radiolysis and hydrolysis in salt-mine brines.

Effect of gaseous radionuclides in salt repositories. Information relating to gaseous radionuclides present in spent LWR fuel and to their release from canistered spent fuel under plausible storage and disposal conditions was reviewed and analyzed.⁴⁴ Also reviewed and analyzed was information that relates to the integrity of the carbon steel canister in which the spent fuel is to be encapsulated and to the expected rates of transfer of gaseous radionuclides

40. T. J. Morrison and R. B. Johnstone, *J. Chem. Soc.* 101(10), 3441 (1954).

41. G. H. Jenks, *Effects of Temperature Gradients, Stress, and Irradiation on Migration of Brine Inclusions in a Salt Repository*, ORNL-5526 (July 1979).

42. G. H. Jenks, *Review of Information on the Radiation Chemistry of Materials around Waste Containers in Salt and Assessment of the Need for Additional Experimental Information*, ORNL-5607 (March 1980).

43. G. H. Jenks, *Radiolysis and Hydrolysis in Salt-Mine Brines*, ORNL/TM-3717 (March 1972).

44. G. H. Jenks and H. C. Claiborne, *Effects of Gaseous Radioactive Nuclides on the Design and Operation of Repositories for Spent LWR Fuel in Rock Salt*, ORNL-5578 (December 1979).

through crushed-salt backfill within a disposal room in a reference repository in rock salt. The advantages and disadvantages for several different canister-backfill materials were considered, and recommendations were made regarding preferred materials. Other recommendations relate to encapsulation procedures and specifications and to needs for additional experimental studies.

Radiation chemistry of salt-mine brines and hydrates. The work comprises an experimental study of certain aspects of the radiation chemistry of NaCl-saturated $MgCl_2$ solutions and $MgCl_2$ hydrates at temperatures in the range 30 to 180°C. A principal objective of this experimental work was to establish the values for the yields of hydrogen and accompanying oxidants in the gamma-ray radiolysis of concentrated brines that might occur in waste repositories in salt.

It was concluded⁴⁵ that the yield of hydrogen from gamma-irradiated brine solution into a simultaneously irradiated, deaerated atmosphere above the solution is between 0.48 and 0.49 (molecules/100 eV) over most of the range 30 to 143°C.

Additional experimental studies of the radiation chemistry of salt-mine brines are being made. The tentative objectives of these studies are to establish the effects of air on yields of hydrogen and oxygen and to identify the radiolytic oxidant species which may be formed in place of oxygen.

Thermal Analysis

Thermal codes comparison. A direct comparison of transient thermal calculations was made⁴⁶ with the heat transfer codes HEATING5, THAC-SIP-3D, ADINAT, SINDA, TRUMP, and TRANCO for a hypothetical nuclear waste repository. With the exception of TRUMP and SINDA, the codes agreed to within $\pm 5\%$ for the temperature rises as a function of time. The TRUMP results agreed within $\pm 5\%$ up to about 50 years, where the maximum temperature occurs, and then began an oscillatory behavior with up to 25% deviations at longer times. This result could have been caused by time steps that were too large or by some unknown system problems.

Multiple temperature peaking in spent fuel repositories. Calculations for CANDU spent fuel repositories shows a temperature peak at 60 years and a slightly higher one at 13,000 years. Investigation of this behavior using analytical models confirmed the Canadian results and demonstrated that the "double peak" phenomenon is due to the presence of the right mixture of short- and long-lived nuclides in the fuel,

and concluded that the 13,000-year maximum is largely an artifact of the infinite or very large plant source model.⁴⁷

When more realistic repository geometries are used (i.e., disk sources of relatively large finite dimensions and arrays of discrete sources), the second peak disappears for repository sizes less than about 1 km². Over the long term, radial and surface heat transfer causes the thermal history of the disposal region to deviate from that predicted by infinite (or large finite) plant source models by reducing the magnitude of the second peak.

When spent fuel from pressurized-water reactors was examined for multiple temperature maxima, only one peak was found, even for the infinite plane source model.

Expected Repository Environments

Commercial high-level waste and spent fuel. The purpose of this study⁴⁸ was to describe the expected environments associated with high-level waste (HLW) and spent fuel (SF) repositories in salt formations. These environments include the thermal, fluid, pressure, brine chemistry, and radiation fields predicted for the repository conceptual designs.

Initial thermal loadings, distributed over the room and pillar areas, were assumed to be 2.16 kW/canister and 150 kW/acre (37.1 W/m²) for HLW and 0.55 kW/canister and 60 kW/acre (14.8 W/m²) for SF in a base-line repository. Thermal environments were calculated in terms of near-field and far-field models. The salt temperature for HLW peaked at 211°C ~15 years after emplacement of 10-year-old waste. The peak for SF was broader, occurring ~50 years after emplacement at a temperature of 99°C. On the canister surface, the maximum HLW temperature was 308°C and peaked ~10 years after emplacement. For SF, the maximum canister temperature was 114°C and occurred ~25 years after emplacement. The maximum HLW waste centerline temperature of 354°C was reached ~3 years after emplacement. The

45. G. H. Jenks and J. R. Walton, *Radiation Chemistry of Salt-Mine Brines and Hydrates*, ORNL-5726 (July 1981).

46. H. C. Claiborne, R. S. Wagner, and R. A. Just, *A Comparison of the Results of Several Heat Transfer Computer Codes When Applied to a Hypothetical Nuclear Waste Repository*, ORNL/TM-7112 (December 1979).

47. S. W. Beyerlein and H. C. Claiborne, *The Possibility of Multiple Temperature Maxima in Geologic Repositories for Spent Fuel from Nuclear Reactors*, ORNL/TM-7024 (January 1981).

48. H. C. Claiborne, L. D. Rickertsen, and R. F. Graham, *Expected Environments in High-Level Nuclear Waste and Spent Fuel Repositories in Salt*, ORNL/TM-7201 (August 1980).

maximum temperature of the SF pin assembly was 138°C, occurring ~5 years after emplacement.

Sensitivity studies were also made to show the effect of changing the areal heat load, the canister heat load, the barrier material and thickness, and ventilation of the storage room, and of adding a second row to the emplacement configuration.

The total brine inflow to the emplacement hole was estimated at 12 L after 1500 years for the HLW and at 6 L for SF. Assuming a perfectly sealed emplacement hole, peak vapor-space pressures were calculated to be 6.9 and 0.70 MPa for HLW and SF, respectively. The maximum absorbed integrated dose to the salt in 10,000 years was estimated at 1.6×10^{10} and 9.6×10^8 rads for HLW and SF, respectively.

Defense high-level waste. Expected environments for a repository in salt for defense high-level waste (DHLW) from Savannah River were predicted analogously to those described above for spent fuel and reprocessed commercial high-level wastes. The main results of the calculations reported included the following:

1. Rock temperatures, canister wall temperatures, and waste temperatures did not exceed 86, 94, and 101°C, respectively.
2. The total accumulation of brine migrating to the emplacement hole after 1000 years was <0.5 L.
3. Vapor-space gas pressures encountered in a perfectly sealed emplacement hole did not exceed 0.36 MPa.
4. Maximum dose rates in the salt were <1400 rads/h.

Salt Model Pillar Studies

The salt model pillar studies at ORNL address requirements for predicting the behavior of rock salt deposits that may be utilized for the storage or disposal of radioactive wastes. Creep behavior on flow of rock salt in underground workings is an essential element in repository design. Previous work on scale models of mine pillars resulted in the determination of a creep equation that relates temperature, time, and pressure. The current need is to fabricate and test model pillars from salt at potential repository salt deposits in several states including Louisiana, Texas, Mississippi, and Utah. In addition, an analysis of long-term creep data (>10 years) will be made to compare the predicted and actual deformations.

To simulate pillar, roof, and floor conditions that would exist in mined cavities in rock salt, sample

specimens are fabricated to represent scale models of salt pillars and their surrounding rooms. After steel rings are affixed with epoxy around the ends of the samples, effective confining pressure is applied to the roof and floor portions of the loaded models. Constant uniaxial loads are applied to the models by hydraulic compression testers having capacities up to 136,000 kg. Tests are conducted at room temperatures of 22.5, 60, 100, and 200°C for axial loads up to 39 MPa. Tests specimens are fabricated from cores and samples taken at potential repository salt deposits in several states.

A series of samples are now being tested under various temperatures and loads. Deformation curves will be plotted and results compared to calculated curves from empirically developed equations. These data will be used for predictions of the effects of load, temperature, and time on underground openings in rock salt deposits. We also plan to examine the effects of mine flooding in a heated repository utilizing these models.

3.10 TRANSPORTATION TECHNOLOGY PROGRAM

The ORNL transportation effort is mainly in support of the commercial waste program, but also provides important contributions in the spent fuel and defense waste areas. Approximately half of the effort is directed toward detailed logistic assessment and related studies; the balance is for work in a number of areas including development of a legislative data base, improvement of a transportation statistics data bank, criticality and shielding studies, interface criteria work, cask fleet servicing facility studies, and a cask transportation catalog. Recently, special studies have been undertaken for the National Academy of Sciences (NAS).

In the logistic assessment area, an updated version of the Oak Ridge Spent Fuel Logistics Model (SFLM) was developed to evaluate the impact of waste management policy decisions on the transportation requirements for moving spent fuel from the reactors to away-from-reactor (AFR) storage and to geological repositories.⁴⁹ This newer version can run faster but optimizes annually instead of across the entire time horizon. Both models have three basic functions: (1) preparation of a shipment schedule depicting the rate at which the fuel assemblies will enter and leave the transportation system; (2)

49. D. S. Joy and B. D. Holcomb, *Logistics Models for the Transportation of Radioactive Waste and Spent Fuel*, ORNL/TM-6192 (March 1978).

evaluation of appropriate, economical shipment destinations; and (3) calculation and reporting of the transportation and environmental data describing the particular scenario under consideration.

A computerized data base has been developed which contains information for all reactors in the United States which are either operating, under construction, or firmly planned through 1990. The data comprise a summary of historical and projected spent fuel discharges and on-site storage pool capacities. Since detailed reactor information is not available beyond 1990, the model has been designed to automatically schedule and site a series of standard expansion reactors to span the gap between the nuclear data base and the nuclear power capacity projection of interest.

Recently, the logistics models were used to study the regional repository concept being considered in the National Waste Terminal Storage (NWTs) program.^{50,51} Results indicate that the location and capacity of the particular geologic formation being considered will have a large influence on the reactors that can be served and on the size of new adjacent or accompanying temporary storage facilities.

In another study for the NAS, the number of casks and shipments of spent fuel was computed for a 19-year time span. The nuclear power growth curve, as described by the 1980 Official DOE Data Base, reaches almost 160 GW(e) in the year 2000 and indicates few interreactor shipments of spent fuel. Table 3.18 indicates the total number of shipments required by year; Table 3.19 gives the number of casks that would be required if the shipments were made to a facility located west of the Rocky Mountains. Locating the facility east of the Mississippi River would reduce the cask requirements by approximately 30%.

Routing models describing the U.S. highway and railroad systems have become operational during this reporting period. The computerized motor vehicle routing program⁵² originally developed by a private corporation was modified by ORNL for applicability to problems of interest and includes a computerized road atlas containing approximately 12,500 road segments and 9500 nodes. The atlas contains the national system of interstate highways, the U.S. highway system, and all major state highways. Each road segment has been assigned a velocity and distance value, and all toll bridges and toll roads have been specifically identified.

The rail routing program⁵³ uses a minimum-impedance algorithm applied to a modified intercity railroad network coded by the U.S. Federal Railroad

Table 3.18. Annual spent fuel shipments to a single storage facility

Year	Mixed mode		Truck only
	Rail	Truck	
1986	11	188	312
1987	13	575	711
1988	29	288	612
1989	41	1053	1527
1990	44	916	1404
1991	58	635	1281
1992	90	1214	2202
1993	121	1110	2424
1994	166	760	2582
1995	217	1385	3765
1996	248	1593	4275
1997	273	1348	4314
1998	322	1857	5371
1999	396	2030	6322
2000	402	1677	6023
2001	514	2145	7699
2002	502	2262	7652
2003	532	1903	7655
2004	575	2480	8748

Administration (FRA) in 1975 and subsequently corrected and updated by Princeton University⁵⁴ and ORNL. It contains 17,100 links and 14,400 nodes. Ownership and trackage-right information, acquired from FRA and Princeton and corrected at ORNL, permits decomposition of the network. Ninety-three separate railroads are included along with additional categories of other small, intercity railroads and terminal and switching companies. Navigable waterways, which could provide the intermodal link

50. D. S. Joy and B. J. Hudson, *Transportation Analysis for the Concept of Regional Repositories*, ORNL/TM-7170, "TC-0057 (June 1980).

51. D. S. Joy and B. J. Hudson, *Logistics Characterization for Regional Spent Fuel Repositories Concept*, ONWI-124 (November 1980).

52. R. D. Seagren et al., "Motor Carrier Routing Using the COMPU-MAP Program," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, West Germany, Nov. 10-14, 1980.

53. E. L. Hillsman et al., "Predicting Routes of Radioactive Wastes Moved on the U.S. Railroad System," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, West Germany, Nov. 10-14, 1980.

54. Mark A. Hornung and Alain L. Kornhauser, *An Analytic Model for Railroad Network Restructuring*, Princeton University Transportation Program, Report 79-TR-11 (1979).

Table 3.19. Cask fleet requirements for shipping spent fuel to a single western storage facility

Year	Mixed mode		Truck only
	Rail	Truck	
1986	2	6	9
1987	2	17	21
1988	5	9	19
1989	6	31	43
1990	6	27	39
1991	8	19	37
1992	11	36	61
1993	15	33	66
1994	20	23	69
1995	25	40	100
1996	28	45	110
1997	32	39	113
1998	37	52	138
1999	46	56	162
2000	47	47	154
2001	59	59	195
2002	57	63	192
2003	61	52	191
2004	65	69	220

between rail and barge shipments, are also incorporated in the rail data base.

The Nuclear Legislative Data Base,⁵⁵ initiated in 1979, has been modified significantly in structure and format in this reporting period. The program contains comprehensive data bases encompassing legislative and regulatory actions relevant to the transportation of hazardous materials. The data bases are separated according to status level of the legislation, current and historical, and include federal, state, and local legislation regarding the transportation of radioactive materials. Because of their relevance to the transportation issues, actions involving related subject areas such as disposal and storage of radioactive wastes, power plant construction and operation, and remedial action studies are also included in the data bases.

Jointly, the current and historical data bases contain approximately 1500 entries that have been abstracted, grouped into 15 different subject categories, and indexed. This format establishes a system for storing, selectively searching, and documenting specific pieces of legislation.

A study was completed⁵⁶ on fleet servicing facilities (FSF) used for routine servicing, preventive maintenance, and performing requalification license compliance tests and inspections, minor repairs, and decontamination of both the transportation casks

and their associated rail cars or tractor-trailers. It included an evaluation of the specific needs associated only with spent fuel transportation systems. Three concepts were evaluated: an integrated FSF in which the facility is designed as an integral part of the parent plant, a colocated FSF that is built close to an existing parent facility and shares the same services and resources, and an independent FSF that is totally self-supporting and does not depend upon any other facility for support in any area.

The results indicate that, in 1979 dollars, the cost of an independent FSF would be approximately \$26 million; an integrated FSF would add approximately \$13 million to the cost of building a parent facility. The cost of a colocated FSF, while dependent upon the actual site and parent facility, is estimated to cost approximately \$16 million for the specific parent facility considered in the study.

A program to compare the applicability of criticality codes applied to spent fuel shipping casks in a number of countries has been undertaken. Sample criticality problems, based mostly on critical experiments, were supplied to the various participants. One problem was an actual cask design containing fuel that was in a subcritical configuration. Results of these benchmarking problems have been received and are undergoing evaluation. The results are expected to influence international regulations and the way in which each country approves the criticality part of the safety analysis reports on packaging (SARP), which must be approved before casks are licensed.

Shielding calculations are being performed on a cask designed to ship seven spent fuel assemblies from the Clinch River Breeder Reactor. This analysis indicates that a significant amount of neutron shielding will be required in the cask. Once the design becomes relatively firm, interface problems between the cask and the shipping facility will be examined to determine probable dose commitments to personnel responsible for receiving, loading, and shipping the cask.

The Transportation Statistics Data Bank (TSDB) was developed in 1974 to gather, process, and report

55. C. S. Fore and M. M. Heiskell, "Transportation of Radioactive Materials: Legislative and Regulatory Information System," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, West Germany, Nov. 10-14, 1980.

56. C. D. Watson et al., *Fleet Servicing Facilities for Servicing, Maintaining, and Testing Rail and Truck Radioactive Waste Transport Systems*, ORNL/Sub-79/13866/1 (May 1980).

information on the transportation of both radioactive and nonradioactive materials for DOE. The system is now operating although not all DOE sites contribute to or receive reports from it. Recently, the Transportation Technology Center (TTC) requested that ORNL evaluate the TSDB system in order to (1) determine if it could be modified so that information of interest to TTC could be collected (preserving the elements needed by current users), (2) identify what and where additional transportation information was readily available, (3) make recommendations on how to structure a modified system, and (4) evaluate what cost and/or manpower would be required to implement the recommendations. A draft report on this topic is currently undergoing review.

A catalog is being developed to provide authoritative, timely, and accessible transportation data for persons involved in the transport of irradiated reactor fuel. This report will contain concise, easily read information useful in planning shipments and will provide some understanding of the requirements of the federal, state, and local regulatory agencies. The topics to be covered include regulations, spent fuel characteristics, cask characteristics, transportation-facility interface, transportation costs, emergency response, and transportation management.

3.11 FUSRAP STABILIZATION TECHNOLOGY DEVELOPMENT AND APPLICATIONS

This task is a research and development activity to define geologic emplacement barriers for utilization at FUSRAP (Formerly Utilized Site Remedial Action Program) sites to prevent radionuclide migration from the site into the environment. The laboratory work is comprised of three tasks: radionuclide characterization, radionuclide leaching tests, and barrier material evaluation. The St. Louis Airport Storage Site (SLAPSS) will be used to demonstrate the effectiveness of the techniques developed in the laboratory program.

A total of four cores has been received from Weston, Inc. These comprise a complete sequence

from the surface to bed rock (at 14 to 26 m) at three SLAPSS locations. Two of the cores (borings 1A and 1B) have been sectioned in 15-cm (6-in.) lengths and divided longitudinally. One-half of each section has been stored in as-received condition for future leaching or adsorption tests. The other half has been dried and ground to -60 mesh for radionuclide and moisture determination. Gross gamma determinations have been completed on selected core samples from borings 1A and 1B, and ^{226}Ra determinations have been completed on samples of boring 1A. For the radium determination, samples were sealed in counting tubes for greater than 30 d to restore secular equilibrium in the portion of the ^{238}U decay chain from ^{226}Ra through ^{214}Bi . The ^{226}Ra concentration determinations were calculated by integrating the gamma activity of the 0.609-MeV ^{214}Bi peak between 0.55- and 0.67-MeV energy levels collected over 100-min counting periods for three replicate samples. These data, along with moisture content, are shown for selected core samples in Table 3.20.

The uranium adsorption characteristics of clay from various depths of boring 1A are being investigated. Synthetic groundwater solutions were prepared by equilibrating distilled water with either SLAPSS clay or limestone. The solutions were spiked with 10 μg of uranium per milliliter by adding either cationic uranium (UO_2^{2+}) to the clay-equilibrated solution or anionic uranium [$\text{UO}_2(\text{CO}_3)_2^{2-}$] to the limestone-equilibrated solution. SLAPSS samples from the first 6 m adsorbed 80 to 95% of the cationic uranium but only 10 to 30% of the anionic uranium. Samples from 6 to 12 m in depth adsorbed greater than 99% of the cationic uranium, but only 10 to 20% of the anionic uranium. Adsorption of cationic uranium decreased to ~75% with clay at the 12- to 15-m level, and appeared to increase again to the 99% sorption level with clay from the 17.7-m depth. These data are shown graphically in Fig. 3.11. Evidence that natural clay at the SLAPSS may have a high uranium binding capability is a very positive finding.

Table 3.20. Determination of moisture content, total gamma activity, and ^{226}Ra concentration in samples from boring 1A

Sample	Core depth		Weight loss on drying ^a (%)	Total gamma activity (counts/min-g)	^{226}Ra concentration ^b (pCi/g)
	(m)	(ft)			
S1-1A	2.7	9.1	19	195.4 ± 0.7	63.3 ± 1.0
S1-2A	2.9	9.5	21	9.6 ± 0.4	3.1 ± 0.6
S1-3A	3.0	10.0	21	8.1 ± 0.4	2.9 ± 0.6
S2-1A	3.4	11.0	21	39.6 ± 0.4	12.3 ± 0.7
S2-2A	3.5	11.5	22	12.2 ± 0.4	4.1 ± 0.6
S2-3A	3.7	12.3	21	7.9 ± 0.4	2.7 ± 0.6
S3-1A	4.0	13.0	20	25.9 ± 0.4	7.9 ± 0.6
S3-2A	4.1	13.5	19	7.2 ± 0.4	2.5 ± 0.6
S4-1A	4.6	15.0	20	10.2 ± 0.4	3.6 ± 0.6
S5-1A	5.2	17.0	20	10.6 ± 0.4	4.1 ± 0.6
S7-1A	6.4	21.0	19	8.1 ± 0.4	2.3 ± 0.6
S9-1A	7.6	25.0	19	7.8 ± 0.4	2.6 ± 0.6
S11-1A	8.8	29.0	17	7.1 ± 0.4	2.6 ± 0.6
S12-2A	9.6	31.5	18	7.2 ± 0.4	2.3 ± 0.6
S15-1A	11.6	38.0	20	7.6 ± 0.4	2.8 ± 0.6
S10-1A	14.6	48.0	25	10.3 ± 0.4	3.6 ± 0.6
S23-4A	17.4	57.0	22	6.8 ± 0.4	2.5 ± 0.6

^aAt ~100°C.

^bBased on calibration of the gamma counter (coupled to a multichannel analyzer) with a ^{137}Cs standard and multiple counting of an NBS-certified uranium standard (0.10% U and 344 pCi ^{226}Ra /g). The counting efficiency in the integration range was determined to be 20.8%. The ^{226}Ra concentrations were then calculated in the following manner:

$$\frac{\text{counts/min-g}}{0.208(A) \times 0.43(B) \times 2.2(C)} = \text{pCi } ^{226}\text{Ra/g},$$

where (A) is counting efficiency, (B) is 43% ^{214}Bi gamma, and (C) is dis/min-pCi. The arithmetic mean ± standard deviation was determined for three replicate samples and three blanks.

Fig. 3.11. Uranium adsorption characteristics of clays from various depths of core sample B-1A. Solutions: (1) synthetic groundwater prepared by equilibrating 4 L of distilled water with 100 g of clay, spiked with 10 μg U/mL as uranyl sulfate; (2) synthetic groundwater prepared by equilibrating 4 L of distilled water with 100 g of powdered limestone, spiked with 10 mg U/mL as sodium uranyl carbonate.

4. Fossil Energy

Activities in the Chemical Technology Division in support of the ORNL Fossil Energy Program are primarily directed toward conversion of coal to liquid and gaseous fuels and toward direct coal utilization. These activities fall into two major categories: (1) coal conversion process development and (2) engineering evaluation and economic assessments. These activities are discussed in the following sections.

4.1 COAL CONVERSION PROCESS DEVELOPMENT

Short-contact-time stability studies. This is the first report on a new project which was initiated in October 1980. The objective of this research effort is to characterize the stability and reactivity of material produced in the short-contact-time (SCT), low-severity initial step integral to the concept of advanced two-step liquefaction. This concept offers the advantages of decreased hydrogen consumption, reduced light-gas production, smaller reactor size, and wide operating latitude for the production of a broad liquid product slate. A fundamental disadvantage associated with the concept lies with the nature of the material produced in the initial step: the SCT product is only partially reacted, its high preasphaltenene content makes deashing difficult, and the material is thermally sensitive. The behavior of SCT product during downstream processing such as deashing, solids-liquid separation, catalytic upgrading, and product recovery cannot be predicted. It is the aim of this program to develop an index of stability for SCT product in order that performance in downstream unit operations may be characterized.

Present plans allow for the production of SCT material in 19-cm³ shaken tubing bombs in a 300-cm³ autoclave system and a small, semicontinuous flow system that will allow analysis of hot samples. Analysis of samples will include measurement of conversion to pyridine solubles, fractionation (into preasphaltenes, asphaltenes, and oils), and possibly sequential elution solvent chromatography (SESC) analysis, molecular weight determination, and

determination of physical properties such as viscosity and specific gravity. Kentucky No. 9 coal (Fies) and Wilsonville recycle solvent will be used throughout the course of this study.

To provide accurate measurement of the temperature profile during reactions in the shaken tubing bombs, which are heated in a fluidized-bed sandbath, a bomb was modified to permit the insertion of a thermocouple into the vessel through the cap. Continuous monitoring of the temperature of the reacting medium is thus permitted. The vessel contents can be heated from 300 to 700 K in 3.0 to 3.5 min by allowing an initial 100 K overshoot in the sandbath temperature, adding cold sand to the bath, and turning down the sandbath controller set-point when the vessel temperature is 100 K below the target temperature.

It is difficult to arrive at a consistent definition of residence time and reaction temperature for these SCT reactions, because they occur to a significant extent during the initial heat-up phase. A preliminary attempt to characterize SCT material produced in tubing bombs was based on the reaction severity (R_s) parameter developed at Mobil in a similar study:¹

$$R_s = \int_0^t \exp [-E/R T(t)] dt,$$

where t is time, E is the activation energy [a value of 126 kJ/mol (30 kcal/mol) was assumed], R is the gas constant, T is temperature, and dt is time differential. Figure 4.1 shows the relationship between conversion to pyridine solubles and the reaction severity for a 2:1 slurry of Wilsonville recycle solvent and Kentucky No. 9 coal. For the data obtained to date, a fairly smooth increase in conversion with severity has been observed. An attempt will be made to obtain material

---

1. D. D. Whitehurst and L. D. Rudnick, "The Effect of Solvent Composition on the Liquefaction Behavior of Western Subbituminous Coal," presented at the Electric Power Research Institute Contractors' Conference on Coal Liquefaction, Palo Alto, Calif., May 7-8, 1980.

Fig. 4.1. Conversion to pyridine solubles vs reaction severity parameter.

at equal severities under different temperature profiles to explore the effects of maximum temperature on conversion and to determine whether the severity parameter is a unique predictor of overall conversion.

A novel method for fractionation of coal-derived products into preasphaltenes, asphaltenes, oils, and residue is being adapted for use in the analysis of SCT products. This method, which was developed at Air Products and Chemicals, Inc., does not involve the extensive heating required by the conventional soxhlet extraction procedure and is thus better suited to the analysis of the thermally sensitive SCT product. The new procedure allows the complete fractionation to be carried out in 1 man-day; the conventional method required as long as 6 man-days to achieve the same results. An effort is currently in progress to correlate fractionation results from SCT material produced in 20-cm³ tubing bombs to the reaction severity parameter. Results in this area will be reported as soon as the analysis is complete.

A 300-cm³ autoclave system for the production of SCT material is presently in the design phase. The system will incorporate rapid quenching and product removal capabilities to facilitate the analysis of hot products. A pressure injection system for the moisture-free coal will permit preheating of solvent alone to minimize the extent of reaction occurring during

the heat-up period. This system will allow production of larger quantities of material for more rigorous analysis than is possible with the small amounts of product obtained from the tubing bomb experiments. The design will incorporate instrumentation for continuous monitoring of process conditions and could conceivably be programmed for process control based directly on the reaction severity or other suitable stability reactivity parameter.

New liquefaction techniques. The scope of this program encompasses research studies aimed at a better understanding of the chemical processes involved in coal liquefaction, improved methods of classical coal conversion, and entirely new methods for coal conversion. Two novel approaches to coal liquefaction have been studied. One technique utilized a family of new ionic hydrogenation reactions developed at ORNL; the other was an exploration of Heredy-Neuwirth depolymerizations using phenols.

It was demonstrated that partial liquefaction of coal can be achieved by using $\text{BF}_3 \cdot \text{H}_2\text{O}$ in combination with a hydride donor by an ionic hydrogenation mechanism. Initial experiments using isopropanol, ethanol, and methanol as hydride donors were not promising. Although as much as 44% of the carbonaceous material in an Illinois No. 6 coal sample was converted at 300 K, incorporation of the expensive acid catalyst in the products rendered this approach ineffective, and efforts were concentrated on the more promising coal-phenol reactions.

Heredy-Neuwirth depolymerizations of coal using phenol plus Lewis acid catalysts at a low temperature (460 K) required long reaction times (20 h) and resulted in high-molecular-weight products. By increasing the reaction temperature to 700 K (slightly above the critical temperature of phenol), reaction times were reduced to a few minutes, and considerably more low-molecular-weight material was produced. A more significant discovery was also made: acid catalysts are not necessary for the depolymerization reactions of coals using phenols at these elevated temperatures. Conversion of 80% of the carbonaceous material in Wyodak coal was achieved at 730 K without a catalyst or molecular hydrogen.

Initially, a mechanism was proposed that involved thermally induced rupture of covalent bonds in the coal to produce radicals that attack phenol in an aromatic substitution reaction. This mechanism is not currently favored because of the lack of evidence of phenol incorporation into the products. We are now proposing a novel mechanism of hydrogen redistribution within the coal by phenol. The ratio of

atomic hydrogen to carbon (H/C) was shown to increase steadily as conversion increased. At high conversions, the H/C ratio of the product (1.22) is considerably higher than that of the starting coal (0.86), while the H/C ratio of the unconverted residue is reduced to 0.6. It is clear from these data that hydrogen is being moved from one place to another within the coal, and that this shift renders the hydrogen acceptors soluble. Most coals contain a sufficient amount of hydrogen to be in liquid form if the hydrogen were properly distributed. The data obtained here show that it is possible to redistribute the hydrogen in coal in order to produce large amounts of extractable material. Exploitation of this reaction may be an attractive method of obtaining heavy liquid fuels from coals.

One of the main objectives of this project is to exploit new reactions of coal in order to formulate and initiate experimental laboratory evaluation of new process concepts to convert coal to liquid fuels. A three-step process has been proposed based on the phenol-coal reaction. The key to this process is to produce phenols from coal, since about 6% of the phenol is incorporated within the reacted product. It is envisioned that this goal may be accomplished by first oxidizing the coal to a tarry mixture of carboxylic acids, and then catalytically decarboxylating the acids to phenols. This procedure will produce a mixture of multi-ring and multi-hydroxy phenols of unknown reactivity with coal. Thus, the experimental verification of this process involves the following critical steps:

1. Phenol must convert a high percentage of the coal to pyridine-soluble products.
2. Multi-hydroxy phenols must readily convert coal to pyridine-soluble products.
3. Mixtures of carboxylic acids must convert to phenols in high yields and without polymerization or significant loss of OH groups.
4. Coal must oxidize in high yields to a reactive mixture of carboxylic acids.

Tables 4.1 and 4.2 show that both bituminous and subbituminous coals convert to pyridine solubles in high yields. The amounts listed include inconvertible mineral matter and are even higher on a carbon conversion basis.

The initial objective of the coal-polyhydroxybenzene studies is to evaluate the effect of reaction temperature on the extent of coal solubilization, the chemical survival of the polyhydroxybenzenes, and

Table 4.1. Conversion of Wyodak (subbituminous) coal to pyridine solubles

Run	Phenol/coal ratio	Time (min)	Temperature (K)	Pyridine extractability (% of solid product)
10	5	5	700	7
22	15	5	700	39
16	5	15	700	26
25	15	15	700	39
20	10	10	728	59
20-A	10	10	728	61
17	5	5	755	31
21	15	5	755	49
21	5	15	755	37
23	15	15	755	57

Table 4.2. Conversion of Bruceton coal (bituminous) to pyridine solubles by heating with phenol

Phenol/coal ratio	Time (min)	Temperature (K)	Pyridine extractability (% of product)
5.6	5	700	15
5.6	10	700	33
10	10	700	30
1.5	15	733	10
10	15	733	25
15	15	733	59
5	10	755	38
10	15	755	82
15	15	755	66

the degree of incorporation of the polyhydroxybenzenes into the coal-derived products. Preliminary results are now available for hydroquinone (1,4-dihydroxybenzene) from shaken-tubing-bomb experiments run in duplicate. Over 90% of the carbonaceous material was converted to pyridine-soluble material in 15 min at 733 K. The chemical survival and degree of incorporation of the dihydroxybenzene are under investigation.

The prototype catalytic oxidative decarboxylation reaction is the conversion of benzoic acid to phenol in the presence of a soluble copper catalyst, steam, and air, a technology originally developed by the Dow Chemical Co. The reaction is carried out in a benzoic acid melt containing soluble copper salts and various promoters as catalysts. Air and steam at elevated temperatures are sparged into the melt to produce phenol, which is simultaneously stripped from the

system. In a glass reactor, a phenol yield of 83% was achieved compared with 86% reported by Dow.² With this baseline behavior reproduced, the same conditions were applied to terephthalic acid as a representative benzene polycarboxylic acid. No phenolic products have as yet been identified from applying these conditions to terephthalic acid. However, we conclude that the combination of the high melting point of terephthalic acid with its significant vapor pressure did not allow proper mixing of the acid, steam, air, and copper salt catalyst. Higher temperatures are being evaluated, as well as mixtures of acids, to provide a melt at reaction temperature.

Measurement of physical properties of coal liquids. Knowledge of the physical properties (e.g., viscosity, density, thermal conductivity, and heat capacity) of coal liquids and coal-solvent slurries under process conditions is essential for the design of heat transfer equipment, preheaters, reactors, separation units, and process piping systems in liquefaction processes. Physical properties may be strongly influenced by the dissolved gases (e.g., hydrogen) present or by the effects of ongoing reactions. Therefore, flowing stream measurements are essential. In order to determine chemical characteristics, the stream must be quenched and sampled and then analyzed chemically to provide a basis for correlating the chemical composition and physical conditions.

Instruments for measuring the viscosity, density, heat capacity, and thermal conductivity of flowing streams of coal liquids at process conditions are to be

incorporated into the Coal Liquids Flow System (CLFS). The CLFS, shown in Fig. 4.2, is a bench-scale, continuous-flow, high-hydrogen-pressure, high-temperature system that is capable of processing both coal-solvent slurries and solids-free coal-derived liquids at pressures and temperatures up to 31 MPa and 810 K, respectively, and of measuring their physical properties under these processing conditions. The maximum liquid throughput of this system is 4 L/h. The analytical techniques employed for measuring the physical properties are as follows: viscosity—pipeline or capillary tube viscometer; density—gamma-ray absorption; thermal conductivity—transient heated-wire technique; and heat capacity—flow calorimetry.

During this reporting period, operations were conducted using the CLFS to measure rheology and density of several materials: Wilsonville solvent from Kentucky No. 9 coal, 35 wt % Illinois No. 6 coal in Wilsonville solvent, 35 wt % Kentucky No. 9 coal in Wilsonville solvent, and H-Coal samples derived from Illinois No. 6 coal and from Wyodak coal. The gamma-ray slurry densitometer was installed, and the logging of data from the CLFS [temperatures, pipeline viscometer (PLV) pressures, weigh cell readings, heating rate, and gamma densitometer readings] was begun. The significant results obtained

2. W. W. Kaeding, R. O. Lindblom, and R. G. Temple, "Air Oxidation of Aromatic Acids," *Ind. Eng. Chem.* 53(11), 805 (1961).

ORNL-DWG 79-516R

COAL LIQUIDS FLOW SYSTEM

Fig. 4.2. Schematic flow diagram of the Coal Liquids Flow System.

during this reporting period are summarized below. Additional details have been reported elsewhere.³

Rheological characterizations were made using the PLV on a 35 wt % slurry of Illinois No. 6 coal in Wilsonville recycle solvent at an overpressure of 13.9 MPa and temperatures from 400 to 750 K. Data analysis and correlation on the rheological data at 400, 478, 500, 550, and 700 K have been used to derive rheogram plots and correlations, heat transfer data correlations, and flow regime analyses. The rheograms reveal a peak in viscosity between 572 and 644 K with a corresponding departure from Newtonian behavior. The data were fit to a power law model in which the flow curve resulting from a plot of $\ln(\tau_w)$ vs $\ln(8V/D)$ is linear; τ_w is the wall shear stress and $8V/D$ is the Rabinowitsch-Mooney flow parameter with V the slurry velocity and D the pipeline internal diameter. The analysis showed that the flow index (slope of the flow curve) decreased with increasing temperatures from 1.0 (Newtonian) at temperatures below 400 K to 0.3 (pseudoplastic) at 700 K.

Three experimental runs were made at constant mass feed rates of 0.665, 0.793, and 0.855 g/s at 13.9 MPa and at temperatures from 400 to 730 K. Plots of PLV differential pressure (ΔP) vs temperature are shown in Fig. 4.3. The onset of increased ΔP occurred at about 500 K; the peak was at 650 K. At 0.665 g/s, ΔP peaked at 3.8 kPa and dropped to 0.4 kPa at 725 K. Behavior at the other mass feed rates was similar; the gelation phenomenon began at the same temperature, but the ΔP at the viscosity peak was lower (2.4 kPa).

The rheology of Kentucky No. 9 coal in Wilsonville recycle solvent from Kentucky No. 9 coal and solvent alone was also determined. One run was made at 13.9 MPa and a 0.987-g/s mass feed rate using the 35 wt % slurry and varying the temperature. The viscosity peak was at 650 K. The solvent was Newtonian at lower temperatures and had a viscosity of 4 mPa·s at 338 K and 13.9 MPa overpressure. Additional solvent rheology tests with a new batch of solvent were performed at atmospheric pressure and 1.03, 6.89, and 17.24 MPa overpressure. These tests showed a departure from Newtonian behavior as temperature increased above 450 K. In most cases the flow behavior became dilatant (shear thickening) with increasing temperatures (Fig. 4.4).

Densities were also determined for the Illinois No. 6 slurries, Kentucky No. 9 slurries, and Kentucky No. 9 and Illinois No. 6 Wilsonville solvents using the gamma-ray absorption densitometer. Density measurements for the Illinois No. 6 slurries revealed a significant deviation from ideal behavior in the

ORNL DWG 80-1303

35 wt % ILL. NO. 6 (-170 MESH) COAL/IND. NO. 5
WILSONVILLE RECYCLE SOLVENT
PRESSURE = 13.9 MPa (2000 psig)
VISCOMETER DIMENSIONS = 2.77 mm ID x 0.61 m LONG

Fig. 4.3. Viscometer ΔP vs temperature at constant mass flow rate for 35 wt % Illinois No. 6 coal/Indiana No. 5 Wilsonville recycle solvent.

temperature range 500 to 680 K. A decrease was observed at the same temperatures that show a viscosity maximum (the "gel region"), as indicated in Fig. 4.5. No such deviation from expected behavior was evident in the solvent density measurements.

3. L. E. McNease, *Fossil Energy Program Quarterly Progress Report for:*

- Period Ending June 30, 1979, ORNL-5574 (October 1979).
- Period Ending September 30, 1979, ORNL-5612 (January 1980).
- Period Ending December 31, 1979, ORNL-5630 (April 1980).
- Period Ending March 31, 1980, ORNL-5658 (July 1980).
- Period Ending June 30, 1980, ORNL-5671 (October 1980).
- Period Ending September 30, 1980, ORNL-5702 (January 1981).
- Period Ending December 31, 1980, ORNL-5727 (April 1981).
- Period Ending March 31, 1981, ORNL-5773 (June 1981).

Fig. 4.4. Shear stress vs $8V/D$ for Kentucky No. 9 recycle solvent at 17.2 MPa.

Density and rheology measurements were made on H-Coal material collected in sample bombs during operation of the H-Coal Process Development unit (PDU). The samples were of reacted coal collected after it left the reactor. The material was from Illinois No. 6 coal (Run 130-88) and Wyodak coal (Run 130-93). The H-Coal materials were pseudoplastic in rheological behavior with flow behavior indexes in the 0.72 range. They also fit the Bingham plastic flow behavior model almost equally well, and additional shear rate data are needed to determine which model applies. Flow curves for the H-Coal material derived from Wyodak coal are shown in Fig. 4.6. The densities varied from 0.94 g/cm³ for the Illinois No. 6 H-Coal sample at 724 K and 18.2 MPa to a range of 0.84 to 0.98 g/cm³ for the Wyodak H-Coal samples at 719 K and 19.3 MPa.

Fig. 4.5. Density of slurry and recycle solvent as a function of temperature.

The work on the CLFS is continuing; rheology determinations on Kentucky No. 9 coal solvent slurries of 38.5 wt% are currently under way. Future tests include the determination of residence time effects on slurry rheology.

Indirect liquefaction process studies. For the production of transportation fuels from coal, the indirect liquefaction approach, as compared with direct liquefaction processes followed by upgrading of the coal liquid products, should have advantages in the conversion step (considering the severe reaction conditions required for converting coal by direct liquefaction) and in the final product refining step, at least in advanced indirect liquefaction processes such as Mobil's MTG (methanol-to-gasoline) process. However, the one commercially established route to transportation fuels from coal by synthesis gas conversion over Fisher-Tropsch catalysts, as practiced at the Sasol plants, needs improvement in several areas. First, thermal efficiency could be increased if a synthesis gas with a relatively low H₂/CO ratio could be used. Thus, the

Fig. 4.6. Shear stress vs $\delta V/D$ for H-coal PDU reactor effluent samples at 719 K and 19.4 MPa.

product gas from a gasifier could be converted without the additional process step involving reaction with steam. By this shift reaction, a H_2/CO ratio greater than 2 is typically produced in the Sasol process. However, short catalyst life due to carbon deposition could result at lower H_2/CO ratios. The Sasol process could also be improved if a wider product slate could be produced and if selectivities to gasoline and diesel fuels could be increased; the quality of the gasoline fraction, in particular, needs to be improved.

In the RMProcess (Ralph M. Parsons process), for conversion of synthesis gas to methane, steam is added to the feed. Above a certain concentration of steam, the formation of carbon in the catalytic reactor is prevented. As shown by thermodynamic calculations, this steam concentration corresponds to a point which lies in the non-carbon-forming region of a ternary diagram with oxygen, hydrogen, and carbon located at the apexes. The ternary diagram is divided into non-carbon-forming and carbon-forming regions by isotherms, the location of each isotherm being a function of the operating pressure. If the composition of the feed gas to the Sasol entrained-bed reactor is plotted on such a diagram, it

is seen to lie in the non-carbon-forming region. However, a slight decrease from ~ 2.2 in the H_2/CO ratio would move the feed gas composition into the carbon-forming region. Thus, operation with a feed having a H_2/CO ratio less than 1, such as produced in a Texaco gasifier, could not be used directly for the Fischer-Tropsch reaction unless, for example, steam were added to prevent carbon formation.

The Mobil MTG process has a relatively high selectivity to gasoline-range products. Also, the octane rating is higher than that of the Sasol gasoline fraction due to the greater aromatic content. However, after gasification, three process steps are involved by which the raw synthesis gas is shifted, methanol is produced, and then methanol is reacted over a zeolite catalyst to produce gasoline. A one-step process in which the raw synthesis gas is converted with an equivalent selectivity to high-quality fractions should be more thermally efficient, as well as have a lower capital requirement. Mobil has experimented with the direct conversion of synthesis gas over a mixture of Fischer-Tropsch type catalyst with their proprietary zeolite catalyst. This work has been performed in either a fixed-bed or a fluidized-bed reactor. Because of the small catalyst particle size

required to eliminate mass transfer effects, these types of reactors may not be practical on a commercial scale. However, a slurry reactor in which a very finely divided catalyst is intimately mixed with a high-boiling-point liquid would be particularly well suited for the application. Because of the very small particle size, this reactor provides excellent control of the temperature of the catalyst particle.

For synthesis gas conversion studies in areas such as those discussed, a bench-scale unit has been designed and constructed at ORNL. A flowsheet of the unit is shown in Fig. 4.7. The nominal operating conditions are 2.2 MPa (300 psig), 533 K (500°F), and a gas feed rate of 0.28 m³/h (10 scfh). The design is such that operation with either a fixed-bed reactor or a slurry reactor is possible. Start-up conditions are under way in the fixed-bed reactor mode. A commercial ammonia synthesis catalyst is being utilized for converting synthesis gas to hydrocarbons.

After the synthesis gas unit start-up has been completed, a study of catalyst deactivation at low H₂/CO ratios will be carried out. The unit will then be converted to the slurry reactor mode of operation to investigate the effect of mixtures of zeolite and iron catalyst on product selectivity and quality.

Coal slurry mixing. The current designs for direct coal liquefaction call for slurring coal with a process-derived solvent prior to its passing through the preheater into the reactor. Only limited data relating the viscosity of the slurry to factors such as residence time and temperature are available. The coal slurry mixing system at ORNL was designed to study the effects of these variables, as well as the effects of agitator speed, shear rate, and type and size of coal, on apparent viscosity. The system was modeled after the Ft. Lewis, Washington, and Wilsonville, Alabama, pilot plants and utilizes a small-scale mix tank with an agitator and movable baffles, a slurry circulation loop, and an instrument loop. The viscosity is determined by measuring pressure drop through a capillary and then calculating the apparent viscosity from the geometry of the viscometer and the Hagen-Poiseuille Law.

Studies of slurries from Ft. Lewis process solvent and Kentucky No. 9/14 coal (38.5 wt %) have been completed, while the investigation of a Wilsonville process solvent-Kentucky No. 9 slurry (38.5 wt % coal) is continuing. The variation of apparent viscosity with temperature has so far shown three distinct regions for both feed materials. This behavior, shown in Fig. 4.8, is characterized by a decrease of apparent viscosity with temperature from 313 to 445 K (100 to 342°F). An increase in viscosity

has been observed from 445 to 465 K (342 to 379°F), after which viscosity remains essentially constant to 507 K (453°F).

Rheological characterization of both solvents as well as the slurries was performed using the Rabinowitsch-Mooney method. Both process solvents have exhibited essentially Newtonian behavior under all test conditions. Rheograms of slurries, such as Fig. 4.9, exhibit a linear relationship between shear (τ_w) and the flow parameter ($8V/D$). This signifies that a power law model describes the slurries; the slope >1 shows non-Newtonian (dilatant) behavior. The deviation from Newtonian behavior has generally increased with temperature.

Studies will be continued to ascertain the effect of residence time on apparent viscosity. Preliminary data show minimal effect upon viscosity, with the maximum observed rate of change at isothermal conditions of 1.7 mPa·s/h (1.7 cP/h).

Vacuum-still bottoms viscometer. In direct liquefaction processes, various streams are produced which have very high viscosities at the particular operating conditions. Viscosities as high as several thousand centipoises are not unusual. Examples of such streams are VSB (vacuum still bottoms), CSD (critical solvent deashing) first-stage bottoms, LSRC and HSRC (Light and Heavy Solvent Refined Coal) from the CSD unit, and LC-Fining residue. Measurement of the viscosities of these streams is obviously necessary for design purposes. Furthermore, in most cases, it is desirable to continuously monitor the viscosity since changes in operating conditions could significantly affect the downstream processing. For example, removal of essentially all the distillate from VSB could produce such a high viscosity that difficulties in pumping the material to a gasifier or a CSD unit would result.

For the measurement of these highly viscous materials, specifically VSB, a viscometer has been designed and is in the final stages of assembly at ORNL. The viscometer was originally to be installed at a coal liquefaction pilot plant, such as the Ft. Lewis SRC-II plant. The flowsheet of the viscometer system is shown in Fig. 4.10. The basic concept is to measure the pressure drop that results from pumping VSB at a calibrated rate through a length of capillary tubing 3.18 mm (0.125 in.) in diameter. A Bran-Lubbe pump serves as a metering pump, the calibration of which is accomplished by diverting the VSB flow to a sample tank and weighing the VSB collected over a certain period of time. By adjusting the pump stroke, viscosity may be measured at shear rates from 200 to 2000 s⁻¹. Also, a preheater is provided that allows the

Fig. 4.7. Flowsheet for bench-scale indirect liquefaction unit.

Fig. 4.8. Temperature dependence of viscosity for SRC-I slurry.

Fig. 4.9. Rheological characterization of SRC-I slurry.

temperature of the capillary viscometer to be varied from 561 to 672 K (550 to 750°F). A heavy distillate, available from the process, is utilized to flush the system of the VSB. Although not indicated in Fig. 4.10, a process control computer will be supplied to (1) make changes in pump settings, temperature set-points, etc., while recording pressure drop across the capillary as a function of flow rate and temperature; (2) calculate and print out values of viscosity vs shear rate; (3) provide proper sequencing of valve openings and closings in order to flush the system either

routinely or upon operator command; and (4) take appropriate steps in emergency situations.

A metal enclosure houses all equipment and piping that contain VSB. Such equipment includes the VSB and the flush solvent preheaters, the blowdown tank, the capillary viscometer, and the high-temperature VSB ball valves. Because VSB has a relatively high fusion point, the enclosure is insulated and heated to maintain the system at a temperature of approximately 533 K (500°F). Also, a 1.2 × 2.6 m (4 × 8.5 ft) base has been fabricated, upon which the enclosure and the Bran-Lubbe metering pump have been mounted. A rack and panelboard are installed on the base for mounting of the remaining equipment such as pressure gauges, flowmeters, d/p cells, pressure transmitters, and flush solvent ball valves. A cabinet for the process control computer and other electrical components is also installed on the base. Thus, the entire viscometer system will be readily movable as a single unit to any desired location. On site, the only process hookups required are the VSB and the flush solvent supply and return lines. Utilities required are electricity, water, air, and nitrogen.

In order to test the viscometer before transportation to a coal liquefaction process site, a VSB feed system has been designed and fabricated. This system includes a VSB feed tank and a flush solvent feed tank. Vacuum still bottoms will be supplied to the viscometer at conditions that simulate those of a pump-around loop to be installed on the Ft. Lewis vacuum tower.

After completion of the assembly of the viscometer system, startup operations will be conducted utilizing mineral oil. The process control computer and all mechanical and electrical components will be checked, and the capillary viscometer will be calibrated. The system will then be operated with VSB. After successfully demonstrating that VSB can be processed, a program will be undertaken to measure the viscosity of a VSB sample from Ft. Lewis as a function of shear rate and temperature.

4.2 COAL CONVERSION ENGINEERING EVALUATION AND ECONOMIC ASSESSMENTS

Coal Conversion Engineering Evaluations and Analyses

Engineering studies related to coal conversion processes are being conducted for DOE's Office of Fossil Energy (DOE/FE). These studies include technical and economic evaluations of conceptual, commercial-scale conversion plants and processes,

ORNL DRS 80-1480R

Fig. 4.10. Flowchart of the VSB viscometer.

technical reviews of design documents for the demonstration facilities, coordination of direct liquefaction overview reports, and a survey of recent developments in foreign coal liquefaction efforts. In addition, technical support is being provided in the development of process modeling techniques. Process and program analysis studies are also being conducted to provide consistent technical and economic evaluations of the impact of environmental control costs on indirect liquefaction and economic evaluations of in situ coal gasification.

Subprograms included in the studies are the liquefaction technology assessment, technical support to the DOE-ORO offices for DOE project management of the demonstration plants, international energy technology assessment, underground coal gasification, engineering studies related to the environment or health, and process modeling. Certain portions of the liquefaction technology assessment and international energy technology assessment are being performed by industrial firms under subcontract.

Liquefaction Technology Assessment. The objective of the Liquefaction Technology Assessment is to provide technical information, cost information, and economic evaluations needed by DOE to compare selected coal liquefaction processes on a consistent basis. The assessment is being carried out by ORNL in several phases, starting with a review of methanol synthesis technology and a screening study of several liquefaction processes, followed by examination of detailed conceptual designs of selected processes. The conceptual processes start with those employing available technology and progress to those in earlier stages of development.

The principal objective of the methanol synthesis survey was to review and assess the present state of the art of liquid fuels synthesis from coal by the indirect route, with particular emphasis on processes that produce methanol as the primary product.

Available information on processes for the production of methanol and methanol-related fuels from natural gas and coal was reviewed, including existing commercial technology for the production of methanol from synthesis gas by the high-, low-, and intermediate-pressure processes. The technological and economic factors involved in the optimization of a methanol production plant were reviewed. Production of synthesis gas and methanol from coal was reviewed, both from the standpoint of existing technology using Lurgi gasifiers and from that of proposed processing using other gasifiers. An overview of the technology and economics of the

Mobil MTG process for converting methanol to gasoline is presented. A search was made for obsolete or discarded processes that might be useful for the production of low-purity methanol for fuel. It was concluded that none of these older processes offers any advantages over current commercial technology for fuel-grade methanol production.

The screening study, designated Phase 0,⁵ evaluated several liquefaction processes in various states of development. In each case, the core process was integrated with the ancillary processes to form a complete, self-sufficient facility. Where char was produced as an initial product, processes were added to gasify the char and convert it to gaseous or liquid fuels.

In most cases costs estimated by others were used. To re-estimate the costs developed by the process developer would have been beyond the scope of the Phase 0 study. We used W. L. Nelson's refinery inflation index to escalate costs from the original estimates to 1979 values.

Because of the limited scope of the study, it was not possible to make an in-depth assessment of the state of technological readiness of the various processes. Many processes were still at the bench scale, while others were representative of commercial or near-commercial technology. A major conclusion from the screening study is that, when comparing processes, great importance should be attached to their relative status of development, since this factor determines the ability of the process to be deployed on a large scale within the time frame of critical interest.

After the screening evaluations, ORNL began detailed examinations of indirect liquefaction of a western United States subbituminous coal using Lurgi dry-ash gasifiers. Major liquefaction technologies employed in the study were Imperial Chemical Industries (ICI) low-pressure methanol synthesis and Mobil MTG conversion of methanol to gasoline. This processing scheme resembles that of the Mobil-Lurgi study by Schreiner.⁶

4. R. Salmon et al., *Review of Methanol Synthesis Technology: Production of Methanol and Methanol-Related Fuels from Coal*, ORNL-5564 (May 1980).

5. R. Salmon et al., *Screening Evaluations of Selected Coal Liquefaction Processes: Technical and Economic Evaluation of Selected Coal Liquefaction Processes: Phase 0. Preliminary Screening Evaluations*, ORNL/TM-7581 (April 1981).

6. M. Schreiner, *Research Guidance Studies to Assess Gasoline from Coal by Methanol-to-Gasoline and SASOL-Type Fischer-Tropsch Technologies*, FE-2447-13 (February 1978).

Four major cases were studied, representing the following major product slates:

- case B-1, dry methanol (0.1% water) plus substitute natural gas (SNG);
- case B-2, moist methanol (2% water) plus SNG;
- case C-1, maximum gasoline (by conversion of ~90% of the SNG to synthesis gas);
- case C-2, gasoline plus SNG.

Minor products included propane-butane liquefied petroleum gas, crude diesel fuel, phenols, and ammonia.

In each case, the economic study was based on the detailed process design of a conceptual, self-sufficient commercial facility using a coal feed rate to the gasifiers of 14,510 t/d [16,000 tons per stream day (TPSD)] on a moisture- and ash-free basis. This corresponds to a total as-received coal feed rate of ~27,210 t/d (~30,000 TPSD) to the facility. Methanol production rates in cases B-2 and B-1 were about 8.43 dm³/d [53,000 barrels per stream day (BPSD)]. Gasoline production rates in cases C-2 and C-1 were about 3.82 dm³/d (24,000 BPSD) and 6.76 dm³/d (12,500 BPSD), respectively. In all cases, steam and power were generated on site using coal-fired boilers with flue-gas desulfurization. Process designs, equipment summaries, cost estimates, and operating requirements were prepared by Fluor Engineers and Constructors, Houston Division, under a subcontract with ORNL. Fluor's work is summarized in their design report.⁷

Economic calculations to determine product prices under various conditions were made at ORNL using the discounted cash flow method⁸ and Fluor's capital costs and operating requirements. Assuming mid-1979 dollars with no escalation, methanol price was \$0.15/L (\$0.56/gal) in case B-2 and \$0.15/L (\$0.57/gal) in case B-1. Gasoline price was \$0.33/L (\$1.25/gal) in case C-2 and \$0.42/L (\$1.59/gal) in case C-1. Total capital investments varied from \$2.1 billion to \$2.8 billion. In each of the first three cases, SNG accounted for over 50% of the product output on a total heating value basis.

The economic sensitivity studies showed that the two factors having the greatest influence on product price were the method of financing and the inclusion of escalation or inflation. In case C-2, for example, the use of 75/25 debt/equity financing with a 9% annual interest rate on debt reduced the gasoline price from \$0.33/L (\$1.25/gal) to \$0.21/L (\$0.80/gal). With 100% equity financing and 6% escalation of all costs and product prices, the initial gasoline selling price (in 1979 dollars) was \$0.21/L (\$0.78/gal); this price must be escalated at 6% per year to obtain the price in the start-up year, or in any

other year of operation. These and other results of the study are discussed in greater detail in the report.⁹

International Energy Technology Assessment. ORNL is supporting the Lawrence Livermore National Laboratory (LLNL) in a broad program funded by the DOE Office of International Affairs. Primary objectives of the International Energy Technology Assessment (IETA) program are to report on developments in foreign energy technology of current interest and to identify and assess those developments of significance to U.S. programs. During this reporting period ORNL had responsibility for the following areas of work for the IETA program related to fossil energy: (1) coal liquefaction including gasifier development status, (2) materials of construction for coal liquefaction processes, and (3) atmospheric fluidized-bed combustion. The Chemical Technology Division provided technical management support and guidance for the ORNL work primarily in the area of coal liquefaction. Other divisions of the Laboratory carried out work in the second and third areas of interest.

A subcontract was let to Gilbert/Commonwealth (G/C), an engineering and consulting firm, to perform part of the work. Under this arrangement G/C provided a technical review of the status of foreign technology for the liquefaction of coal, including gasifier developments, and of significant developments that are taking place in this area. This review of the state of the art of coal liquefaction was based on literature information and trip reports.

Gilbert/Commonwealth prepared two reports based on the results of their technical review. The first report¹⁰ concentrated on the Sasol facilities in South Africa because of their status as the only commercial-scale coal liquefaction plants in the world. (ORNL prepared an executive summary¹¹ of this report, which is in the process of being reviewed prior to final publication.)

7. Fluor Engineers and Constructors, Inc., *Coal Liquefaction Technology Assessment—Phase 1*, ORNL/Sub-80/24707/1 (April 1980).

8. R. Salmon, *A Revised Version of the Discounted Cash Flow Program PRP with Provisions for Escalation of Uniform Reduction of Debt and Ratio Pricing of Products*, ORNL-5723 (in preparation).

9. R. M. Wham et al., *Indirect Liquefaction of Coal Using Available Technology—Liquefaction Technology Assessment—Phase 1: Indirect Liquefaction of Coal to Methanol and Gasoline Using Available Technology*, ORNL-5664 (February 1981).

10. T. D. Pay, *Foreign Coal Liquefaction Technology Survey and Assessment: Sasol—The Commercial Experience*, ORNL/Sub-79/13837/4 (November 1980).

11. F. M. O'Hara, Jr., *Sasol—The Commercial Experience Executive Summary* (to be published).

The original Sasol plant (Sasol-One), which was placed in operation in 1955, was designed to produce liquid hydrocarbons for motor fuels and chemical feedstocks via the Fischer-Tropsch process.¹²

In 1976, construction was started on Sasol-Two, and commissioning was completed early in 1981. The plant is currently exceeding 80% of its design production and is expected to reach full capacity in the near future.¹³ Sasol-Two is approximately three times as large as Sasol-One (based on the amount of purified synthesis gas produced) and emphasizes the production of motor fuels rather than the vast array of chemicals produced in Sasol-One.

The decision to build Sasol-Three was announced in February 1979.¹⁴ It is intended to be a virtual copy of Sasol-Two, except that motor fuel production will be maximized via hydrocracking of by-products to produce diesel fuels. Start-up is planned for 1982.¹⁵

The second G/C report,¹⁶ which was submitted in draft form, covers direct liquefaction, indirect liquefaction (other than Sasol), gasifier technology, and materials of construction for coal liquefaction processes. (ORNL's Metals and Ceramics Division contributed information on materials of construction for inclusion in this report.) The draft has been reviewed and is currently undergoing revision and updating to incorporate the latest available information. Publication is planned by September 1981.

Work was also initiated on a pictorial report on Sasol by G/C under the subcontract. Facilities will be shown by a collection of approximately 80 photographs and illustrations gathered from open literature sources. The document will also contain brief descriptions of the equipment or features depicted. Publication as an ORNL report is planned by the end of 1981.

Underground coal gasification. The objective of the current underground coal gasification (UCG) project is to assist DOE in evaluating the state of development of various technologies for UCG and the potential offered by these processes by means of technology and economic assessments. This is a continuing project at ORNL, and a number of conversion technologies have been examined in detail at DOE's request. The results are described in an earlier report in this series.¹⁷

We recently completed a preliminary study concerning economies of scale and estimated prices for various products from UCG facilities based on work done previously at ORNL.¹⁸ Results indicate that significant economies of scale are possible over the range of 0.64 to ~6.4 dm³/d (4,000 to 40,000

BPSD) of gasoline-blending methanol production capacity. For example, a reduction of approximately 40% in the price of methanol was calculated based on an increase in plant capacity from 0.64 to 6.0 dm³/d (4,000 to 38,000 BPSD).

Intermediate product prices were also estimated over the range of 0.64 to ~6.4 dm³/d of equivalent methanol production capacity. Ratios of these prices (on a Btu basis) were nearly constant over this range (Table 4.3).

Table 4.3. Intermediate product price ratios of equivalent methanol production capacity

Intermediate product	Intermediate product price ratio ^a
Gasoline-blending methanol	1.00
Clean shifted gas	0.46
Shifted gas	0.43
Scrubbed raw gas	0.36
Departiculated raw gas	0.27

^a Over the range of 0.64 to 6.4 dm³/d (4,000 to 40,000 BPSD).

We are currently conducting a more detailed study of economies of scale and intermediate product prices. For the current study, "appropriate technology" concepts recently of interest are being examined on the basis of results expected from UCG field test programs sponsored by DOE. Results of the study will be used to compare the economic competitiveness of a local, optimally sized UCG plant designed to serve a specific region or group of consumers with that of a much larger plant in a remote location. In

12. J. C. Hoogendoorn, "Gas from Coal for Synthesis of Hydrocarbons," presented at the Ninth Synthetic Pipeline Gas Symposium, Chicago, Nov. 1, 1977.

13. Peter F. Mako, "Coal-Based Synfuels Project Overview South Africa," presented at the Coal Technology Europe '81 Conference, Cologne, Germany, June 9-12, 1981.

14. "Sasol," supplement to the *Financial Mail* (London), Sept. 17, 1979.

15. "Sasol-Two and Sasol-Three Facts," Fluor Corporation, Irvine, Calif., August 1979.

16. T. D. Fay and S. S. Patel, *Foreign Coal Liquefaction Technology Survey and Assessment*, ORNL/Sub-79/13837/6 (to be issued).

17. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1978, ORNL-5383 (August 1978).

18. W. C. Ulrich, M. S. Edwards, and R. Salmon, *Evaluation of an In Situ Coal Gasification Facility for Producing M-Gasoline Via Methanol*, ORNL-5439 (December 1979).

addition to gasoline-blending methanol, the economics of producing various intermediate products are also to be estimated.

A contract was signed with Fluor Engineers and Constructors, Inc., to provide process design and cost estimating services for the evaluation. ORNL will use the information developed by Fluor to perform the desired economic analyses for gasoline-blending methanol and intermediate products. Results of this work will be transmitted to DOE for review before being published.

Engineering Studies Related to Environment and Health

The Chemical Technology Division has carried out several studies that examine the environmental effects of coal liquefaction as well as the impact of various emission control requirements on production costs of synthetic fuels. These studies have been coordinated with other divisions of the Laboratory and have, in some instances, relied on the use of subcontractors. The studies have covered the range of coal liquefaction processes from SRC-I to Lurgi-Mobil MTG.

Economic effects of emission control levels. The first study examined the impact of increasingly stringent emissions control scenarios on the price of producing gasoline from a conceptual indirect coal liquefaction plant processing a generic Wyoming subbituminous coal. In addition, the impact on the gasoline product price produced by reducing the plant size was also examined. The assessment was conducted for the DOE Assistant Secretary of the Environment—Office of Environmental Assessments.

The environmental constraint levels examined in the study ranged from no emission control requirements (except the control of lethal emissions) to stricter-than-current (1979) emission control requirements. Detailed descriptions of the control levels are given in the reports;^{19,20} brief summaries follow:

1. No emission control requirements except the control of emissions detrimental to worker health.
2. Current (1979) emission control requirements for related industries [i.e., atmospheric emissions complying with New Source Pollution Standards (NSPS) for related industries, aqueous discharges with applicable National Pollutant Discharge Elimination System permits, and solid wastes disposal as nonhazardous wastes].
3. Projected stringent emission control requirements (i.e., atmospheric emission requirements more stringent than 1979 NSPS for related industries, zero discharge of priority pollutants in the aqueous emissions, and solid wastes disposed of as hazardous wastes in accordance with Resource Conservation and Recovery Act guidelines).

Because no pollutant discharge regulations presently exist for the coal liquefaction industry, the emission control levels examined in the assessment were developed based on existing federal and/or state regulations for allied industries such as coal-fired power plants, coke ovens, and the petroleum industry. The environmental release levels developed are neither current nor projected future emission regulations for the coal liquefaction industry but were used as a tool to facilitate the assessment.

The coal liquefaction process basically consists of gasifying the coal in Lurgi Mark IV (dry-ash) pressure gasifiers, converting the syngas (after cleanup and shift) to methanol using the ICI low-pressure process, converting the methanol to gasoline and other fuels using the fixed-bed Mobil MTG process, and fractionating and alkylating the products to yield a petroleum-refinery-like slate of liquid and gaseous hydrocarbon fuels.

The conceptual plants were designed as grassroots (i.e., self-sufficient with respect to utilities) facilities capable of processing 21,770 t/d [24,000 TPSD] of as-received coal in the gasifiers. The total facility coal consumption rate is ~27,210 t/d (~30,000 TPSD) for each of the three full-sized cases examined. In addition, to assess the impact of plant size, the study examined plants that were designed to process one-half and one-fourth the above coal feed rate to the gasifiers. Both of the reduced plant sizes were designed to meet the projected stringent environmental emission requirements.

The cost of producing gasoline (one of the products from the plants) was determined using the discounted cash flow method,⁶ which yields the selling price of the product at the plant that will just meet all of the cost obligations of the plant. The selling price

19. P. J. Johnson et al., *The Impact of Environmental Control Costs on Indirect Coal Liquefaction Process*, ORNL-5722 (in press).

20. Fluor Engineers and Constructors, Inc., *Environmental Control Cost Study, Final Report*, ORNL/Sub-80/13838/1 (October 1980).

does not include any additional tax levies on the product or transportation and marketing charges.

The results of the assessment indicate that, based on the premises used in the assessment for the full-sized plant, the impact of designing plants to meet the increasingly stringent environmental control requirement levels stated earlier is relatively small. Design results indicate a slight decrease (~3%) in thermal efficiency when controls are added. Cost estimates indicate a capital cost increase of ~15% to comply with current control requirements; more stringent requirements would add 4% more, for a total increase of 19% above the capital cost without controls. Increases in calculated product prices were not quite as large. Product prices increased 12% in the current requirements case over the case without controls and increased an additional 4% (a total of 16%) when more stringent requirements were imposed.

However, decreasing the plant size to one-half and one-fourth the full-size plant appears to significantly increase the gasoline selling price. This effect is not unexpected due to the economies of scale realized in the full-size plant.

The results reported above apply strictly to the cases examined in the assessment. Other emission control requirements could be postulated that would substantially change the assumed plant designs and, consequently, the calculated gasoline selling price.

Process engineering support for EIS and HEED documents. Process engineering support was provided to other divisions (notably the Energy and the Health and Safety Research divisions) at ORNL upon their request.

The Energy Division was assisted in preparing and subsequently reviewing the process and the effluent control technologies included in the environmental impact statement (EIS) reports on the Solvent Refined Coal (SRC)-I and -II demonstration plants. The EIS reports^{21,22} were issued by DOE in support of two 5442-t/d (6000-TPSD) facilities to demonstrate (on a near-commercial scale) two direct coal liquefaction processes, namely, SRC-I and SRC-II. The SRC-I demonstration facility was to have been located at Newman, Daviess County, Kentucky; the SRC-II facility was to have been located at Fort Martin, Monongalia County, West Virginia.

Support to the Health and Safety Research Division consisted of developing process stream compositions for a generic indirect coal liquefaction process to aid in the preparation of a risk assessment document.

The stream compositions were developed for a conceptual commercial plant capable of processing

25,210 t/d (~27,790 TPSD) of an as-received, generic, low-sulfur Wyoming subbituminous coal into principally ~2,160 m³/d (13,580 BPSD) of gasoline and varying amounts of other liquid and gaseous fuels using the Lurgi dry-ash gasification and the Fischer-Tropsch synthesis processes. The stream compositions were developed for process and environmental release streams from the generic plant and included concentration estimates for components that may be potentially hazardous to the environment.

Process stream compositions were also developed for a conceptual, commercial H-Coal process plant to aid in the preparation of a health and environmental effects document (HEED) on the above direct coal liquefaction technology. The conceptual plant²³ is capable of processing ~13,100 t/d (~14,450 TPSD) of a dry, generic Illinois No. 6 coal into ~2,130 m³/d (13,390 BPSD) of naphtha, ~2,580 m³/d (~16,240 BPSD) of turbine fuel, and varying amounts of other liquid, gaseous, and solid products. As before, the compositions were developed for process and environmental release streams and included concentration estimates for potentially hazardous components.

Technical assessment of environmental controls. A new environmental assessment, Indirect Liquefaction Environmental Control Technology Assessment (ILECTA), began late in the reporting period with the objective of preparing a technical information manual on the pollution abatement aspects of indirect coal liquefaction plants. The manual will present the current state of knowledge on the effluents and on the processing routes that can be used to control the effluents from commercial indirect coal liquefaction plants in an environmentally acceptable manner.

The indirect liquefaction process examined in the assessment consists of syngas production via coal gasification, conversion of the syngas to methanol (using the ICI process), and production of principally gasoline from the methanol (using the Mobil MTG process). The assessment will examine three alterna-

21. U.S. Department of Energy, *Final Environmental Impact Statement, Solvent Refined Coal-II Demonstration Project*, DOE/EIS-0069/V1 and V2 (January 1981).

22. U.S. Department of Energy, *Draft Environmental Impact Statement, Solvent Refined Coal-I Demonstration Project*, DOE/EIS-00/3-D/V1 and V11 (January 1981).

23. Fluor Engineers and Constructors, Inc., *Engineering Evaluation of Conceptual Coal Conversion Plant Using the H-Coal Liquefaction Process*, EPRI AF-1297 (December 1979).

tive gasification systems in this sequence: Lurgi, Texaco, and Koppers-Totzek.

General technical support to major liquefaction projects. The objectives of this task are to perform reviews and evaluations of the R&D proposals and the documented R&D activities for the major liquefaction projects and to carry out intensive studies of limited scope on selected subjects requested and/or authorized by DOE-ORO.

Significant accomplishments during the period were (1) reviews and evaluations of about 80 R&D proposals and plans submitted by contractors to DOE-ORO; (2) completion of a task force report presenting the result of evaluation of the materials of construction and coal liquefaction technologies used in the H-Coal Pilot Plant; and (3) completion of a report resulting from a short-term, intensive study of the SRC-II products hydrotreating data.

Most of the subjects involved in the R&D proposals and plans submitted by International Coal Refining Co. and SRC International, Inc., to DOE-ORO were considered to be relevant to SRC-I and -II demonstration project objectives, although some of these documents are lacking in technical details.

In evaluation of the H-Coal Pilot Plant, the task force found the materials, technology, and equipment used in the H-Coal plant to be adequately selected based on information available at the time when the design of the plant was completed. No insurmountable problem was uncovered; however, a number of potential problems of varying severity were identified, the majority of which were associated with hydrogenation. In addition to discussion of potential problems, the report analyzes the possible consequences of each problem and presents recommendations that may either prevent the problem or mitigate the consequences.

A recently completed study²⁴ dealt with a preliminary evaluation of the hydrotreating data base for upgrading SRC-II syncrude. The study evaluated the accessible data on the hydrotreating of the SRC-II product with emphasis upon the naphtha fraction. Consolidation and analysis of the data resulted in some semiquantitative correlations (trends) between the extent of hydrotreatment and removal of nitrogen, sulfur, heteroatoms, and other materials that would be detrimental to product value. Data that are lacking include, for example, (1) quantitative guidelines for establishing a specific level of on-site hydrotreatment, (2) the extent of stabilization of coal liquids as a function of hydrotreatment severity, and (3) criteria for setting the practical level to which mutagenicity of coal liquids should be reduced.

A study in progress is concerned with coking and coke formation in critical coal liquefaction process equipment including the fired preheater, the dissolver-reactor, the high-pressure separator, and the vacuum column. A dimensional empirical equation has been developed based on the preliminary analysis of the coking-noncoking data for the fired preheater at the Wilsonville plant.

Liquefaction technology overview. The primary objectives of this task are (1) to keep abreast of significant developments in coal liquefaction technology, (2) to evaluate and systematically document technical data of importance to plant design and operation derived from such developments, and (3) to serve as a center for expediting the flow of technical information pertaining to coal liquefaction technology.

The major responsibilities of the Chemical Technology Division under this task include coordination and/or performance of work for the following activities:

1. *The liquefaction technology file* compiles a data base of published and unpublished literature relevant to direct coal liquefaction.
2. *The liquefaction data source book* consolidates pertinent technical information on major coal liquefaction processes in a reference book format.
3. *The liquefaction overview report* deals mainly with review and evaluation of important current developments in four major coal liquefaction processes [SRC-I and -II, Exxon Donor Solvent (EDS), and H-Coal].
4. *In the monitoring of R&D meetings* the staff follows progress at major coal liquefaction facilities by attending R&D review meetings.
5. *In properties data base coordination* the staff compiles and evaluates selected thermophysical, thermochemical, and transport properties of major process streams and products from various sources.
6. *Process data base evaluation* is concerned with evaluation of process design data bases that will have major impact on the design and operation of critical systems in liquefaction plants.

Important accomplishments during the period were (1) establishment of the direct liquefaction technology file system and a system for the data base

24. G. C. Frazier and Ahsan Faruqi, *Review of SRC-II Process Product Hydro-treating Data, for Completeness and Applicability to the Demo Plant*, ORNL/Sub-7685/1 (September 1980).

recording of documents in the ORLOOK computer program, (2) completion of the FY-1979 and -1980 versions of the direct liquefaction source books (drafts), (3) completion of the first issue of the liquefaction technology overview report, (4) attendance at the technical review meetings held at major coal liquefaction pilot plants and process developments units, (5) initiation of work to compile and update thermophysical property data bases, and (6) completion of a nonproprietary report covering the ^{14}C tracer study on the mixed solvent losses in the Kerr-McGee critical solvent deashing processes.

Engineering evaluation support for coal conversion demonstration plants. Technical support was provided to DOE-ORO in carrying out its task of managing the design of direct coal liquefaction demonstration plants. This support has been in the form of reviews of demonstration plant descriptions, drawings, and specifications; analysis and evaluation of corrosion data and process flowsheets in an effort to mitigate corrosion in atmospheric pressure fractionation through process modification; and participation in the evaluation of plans for and data from preheater development tests.

The reviews of design drawings pertained primarily to the SRC-I and -II demonstration plants; a lesser effort was required for review and comment on a conceptual design of a commercial-scale H-Coal process coal liquefaction plant. Reporting on these activities was accomplished by letter to DOE.

Severe corrosion has been observed in atmospheric pressure fractionators at the Wilsonville and Ft. Lewis coal liquefaction pilot plants. Tests performed by others²⁵ have shown that chlorine is essential to the extreme corrosivity of the fractionator fluids, that chlorine is largely eliminated from fractionator liquids during distillation of a relatively narrow boiling-range cut, and that the corrosive chlorine compounds are water soluble. On the basis of these test results, we have proposed process flowsheet modifications to cause a greater fraction of the chlorine to report to a stream that is already being water washed, to reduce the chlorine content of fractionator liquids by withdrawing the liquid downflow to a stripper for removal of chlorine in a small volume of organic liquid, and to improve the effectiveness of chlorine removal from the lower-density fluids by an additional washing stage and by more effective aqueous-organic separators.

Coal Liquefaction Advanced Research Digest. To provide continuing technical assistance to DOE/FE, digest reviews have been written on fundamental subjects related to coal-conversion technology which

are of current or potential interest. These reviews have covered such topics as the chemical reactions of coal liquefaction and the depolymerization of coal. These articles are extensively researched and then thoroughly reviewed both internally by ORNL personnel and externally by researchers with international reputations in the topics treated. Articles on reaction kinetics of coal liquefaction, reaction mechanisms of coal liquefaction, and chemical characterization of coal-derived liquids are currently undergoing external review. A paper on free-radical reactions in coal liquefaction is undergoing internal review, and one on autocatalysis of coal liquefaction is being prepared. These papers will ultimately be grouped by topic and published as the third and fourth issues of the *Coal Liquefaction Advanced Research Digest*.

Miscellaneous studies. Several studies were accomplished by subcontractors on a variety of topics related to coal conversion and utilization. One such study²⁶ examined the cost of production of medium-Btu gas via the Battelle Agglomerating Ash Burner Process (BAABP), assuming this process to be functional. The assumed process has a high thermal efficiency and relatively low capital cost per unit of production. These factors stem primarily from multistage operation, which permits the use of air instead of relatively pure oxygen for combustion of carbon to generate heat and which isolates the products of combustion from the fuel gas. Although process evaluations and comparisons are recognized to be inexact, the BAABP appears to have the potential for high thermal efficiency and low unit production cost.

Another study²⁷ evaluated the Texaco synthesis gas generation process for the production of hydrogen from SRC-II vacuum bottoms residue. Based on gasification tests carried out by Texaco, the operability and efficiency of the gasifier have been considered. Preliminary process designs for a Texaco gasification facility for a commercial-scale coal liquefaction plant were prepared. A number of

25. J. R. Keiser et al., "Corrosion of Solvent Refined Coal Pilot Fractionation Columns," presented at the National Association of Corrosion Engineers, Toronto, Ontario, Canada Apr. 6-10, 1981.

26. T. Y. Chang and A. S. West, *Evaluation of the Battelle Agglomerating Ash Burner Process for the Production of Medium Btu Gas*, ORNL/Sub-7240/4 (June 1979).

27. T. Y. Chang and A. S. West, *Evaluation of the Texaco Synthesis Gas Generation Process for the Production of Hydrogen from SRC-II Residue*, ORNL/Sub-7240/6 (December 1979).

economic studies were performed to establish a near-optimal operating pressure and a method of acid-gas removal.

The report concludes that the Texaco gasifier is well suited for the efficient production of hydrogen from SRC-II residue and that only minimal developmental work is needed prior to commercialization. However, because of the short duration of the test runs, refractory and burner lives are a point of concern. Results indicate that the gasifier should be designed to operate at ~ 5.6 MPa (800 psig), based on the current state of oxygen compression technology.

A preliminary process design and a cost estimate²⁸ were developed for the addition of a new coal extraction system to the Cresap, West Virginia, pilot plant. The new facilities being considered would provide for direct contact of the coal slurry with a recirculating stream of hydrogen-rich gas at pressures in the range of 9.4 to 17.3 MPa (1350 to 2500 psig). Preliminary process flowsheets and planning drawings are included.

Also examined in this study are the possibilities for continued component testing in the existing Cresap pilot plant.

Process Modeling

The objective of this project is to assist DOE/FE in its plan for computer analysis and computer support for coal conversion studies. Past work at ORNL included assistance to Purdue and Lehigh universities in the development of computer programs for this plan. Physical property data were collected and computerized primarily by Purdue and will be used in support of future process modeling efforts. Purdue's general design program was aimed at material and energy balances, equipment sizing and costing, and general economics. Lehigh's dynamic simulation programs addressed plant design primarily from the standpoint of process performance during transient operations, but can also be used for steady-state conditions. Past work included development of a computer program to model the HYGAS pilot plant. Our current work includes process modeling and systems engineering support to Morgantown Energy Technology Center (METC) and installation and use of the Advanced System for Process Engineering (ASPEN) process simulation on the ORNL computer system.

Support to DOE/METC. A computerized steady-state process design and modeling system was developed at Purdue University for DOE during 1976-79. During the same period, Lehigh University

developed an unsteady-state process modeling system based on the numerical solution of large sets of differential equations. These systems were directed toward the design and analysis of large-scale facilities for the production of synthetic fuels from coal or oil shale. With ORNL assistance, portions of both modeling systems were modified for use on IBM equipment and installed on the computing facilities at METC. Most of the ORNL work in process modeling over the past two years has been devoted to the implementation of the programs developed by Purdue and Lehigh. In some cases, as in the case of the Purdue physical properties program, substantial changes have been made to increase the versatility of the system. The work has been performed under the direction of METC in support of their engineering analysis effort in energy systems. Some of the specific tasks accomplished under this program are (1) publication of an interim report giving a general overview of the Purdue and Lehigh programs,²⁹ (2) preparation of a draft report on the current status of implementation and testing of the Purdue programs, (3) preparation of a draft report on the testing and evaluation of the Purdue physical properties program (PPROP), (4) modification of PPROP to allow the handling of process streams containing solids, (5) implementation and testing of the Purdue oil hydrotreating program, and (6) implementation and testing of the Purdue cost estimating and financial analysis program (PCOST).

A major portion of the work performed at ORNL was devoted to the modification of PPROP to permit the handling of solids. A report on this task is in preparation.³⁰ Two new direct access data files were added to the program, one containing the properties of various solids and the other a library of standard particle-size distributions. Solids for which data have been entered include coals of various types, char, ash, limestone, and dolomite.

Other work currently in progress includes the implementation and testing of the Purdue programs

28. Martin M. Beskind and R. C. Hammersley, *Phase A Report on Converting the Cresap Test Facility to a Two-Stage Coal Hydroliquefaction Process*, ORNL/Sub-7240-5 (May 1979).

29. D. M. Lister, *Review of Department of Energy Sponsored Codes and Documentation Available from Purdue and Lehigh Universities' Process Modeling Contracts*, K/CSD/TM-35 (April 1981).

30. R. Salmon et al., *Modification of the Purdue University Physical Properties Package PPROP to Allow the Handling of Streams Containing Solids*, ORNL/TM-7844 (in preparation).

BED (a generalized simulation of fluidized beds),³¹ PCOST (a process cost estimation package),³² and SSPP (a steady-state pyrolysis program).³³ All of these programs require changes to achieve compatibility with IBM systems.

Mathematical model of the HYGAS pilot plant reactor. A mathematical model of the HYGAS pilot plant reactor was presented in early process modeling work.³⁴ The model is based on subdivision of the gasification process into the independent, sequential steps of devolatilization, volatile cracking, rapid methane formation, and slow hydrogasification. Models for each step have been obtained from the literature. Where necessary, separate algorithms were used for Montana lignite and Illinois No. 6 coals.

Results show that, for a specific coal type, the product gas composition is essentially constant over the range of operating conditions reported by the Institute of Gas Technology (IGT). This effect is due, in part, to the high steam-to-oxygen ratio required to maintain bed fluidization. The large fraction of steam keeps the operating temperature within a narrow range. Because water-gas shift equilibrium is assumed and temperature is essentially constant, little variation in product composition is expected for a specific coal type. This conclusion is supported by experimental evidence.

The model predicts the composition of the product gas fairly well. It predicts higher temperatures than

those reported by IGT and gives mixed results for char conversion. Discrepancies probably result from inadequacies in model formulation, the assumption of adiabatic behavior, and uncertainties in published data.

ASPEN process simulator. Under terms of a contract negotiated with the Massachusetts Institute of Technology (MIT), the ASPEN process simulator was acquired. ASPEN is a computer-based process modeling system for performing detailed material and energy balances, equipment sizing, and costing calculations for all types of chemical processes, including fossil energy conversion processes. The ASPEN code has been installed on the ORNL computer system, and members of the process modeling group have attended training courses at MIT.

31. B. W. Overturf and G. V. Reklaitis, *BED—A Generalized Model of a Fluidized Bed Reactor*, Purdue University, Lafayette, Ind., 1980.

32. Y. Soni et al., *PCOST Costing Program*, Purdue University, Lafayette, Ind., 1979.

33. F. Kayihan and G. V. Reklaitis, *Steady-State Pyrolysis Program SS/PP User's Manual*, Purdue University, Lafayette, Ind., 1980.

34. J. P. Meyer et al., *Mathematical Model of the HYGAS Pilot Plant Reactor*, ORNL-5475 (April 1979).

5. Basic Science and Technology

5.1 SEPARATIONS SCIENCE

New Separations Agents

Continued need exists for new separations agents with improved selectivity, stability, and physical properties for applications in hydrometallurgy, fuel reprocessing, waste-stream treatment, and resource recovery.

Work on a series of carbamoylmethylphosphonates, bidentate extractants effective in extracting trivalent lanthanides and actinides from nitric acid solutions,¹ has been completed and reported in a paper submitted to *Radiochimica Acta*, a presentation at Actinide Workshop IV, Los Alamos, N.M., in May 1980, and a report to be issued as ORNL/TM-7494. The respective abstracts follow:

"Extraction of Trivalent Actinides and Lanthanides by Carbamoylmethylphosphonates—The Effects of Size and Structure of the Extractant Molecule," by R. R. Shoun and W. J. McDowell. *Abstract:* Seven carbamoylmethylphosphonates (CMP's), $(RO)_2P(O)CH_2C(O)NR_2$, have been studied under identical experimental conditions to determine the relative effects of size and structure of the extractant molecule on the extraction of americium from nitric acid. Those compounds with unbranched alkyl chains (R and R') appear to be superior extractants; however, they generally have higher aqueous phase distribution, which may make them less useful in actual application. Nitric acid extraction, europium loading, and the dependence of americium extraction on aqueous acid concentration and on extractant concentration are discussed for a selected CMP.

"The Investigation of Lanthanide-Carbamoylmethylphosphonate Complexes by Extraction Equilibria and NMR," by R. R. Shoun. *Abstract:* Earlier investigations of the extraction behavior of the carbamoylmethylphosphonates (CMP) basically assumed bidentate coordination between the phosphoryl and carbonyl oxygens of the CMP and the trivalent actinide or lanthanide and thus neutral species extraction.

Recent equilibrium solvent extraction data and NMR studies suggest a different mechanism or additional mechanisms involved in such complex formation. The dependence of americium extraction on aqueous acid concentration, with a constant ionic strength of six, indicates a possible cation exchange mechanism, while NMR studies in progress indicate a possible variation of the number of protons present in the CMP-lanthanum complex. Protonation of the nitrogen may explain some of the observed behavior.

Effects of Radiation, Acid, and Base on the Extractant Dihexyl-[(diethylcarbamoyl)methyl]phosphonate, by C. T. Bahner, R. R. Shoun, and W. J. McDowell. *Abstract:* The effects of exposure to gamma radiation (^{60}Co) and of contact with acidic and basic aqueous solutions on dihexyl[(diethylcarbamoyl)methyl]phosphonate (DHDECMP) were studied. Gamma radiation decomposes DHDECMP into a variety of products. The most troublesome of those are the acidic compounds that cause problems in stripping the actinides and lanthanides from the extractant at low acid concentrations. The rate of degradation of DHDECMP by radiation is about the same or only slightly higher than that of tri-*n*-butyl phosphate (TBP). It is relatively easy to remove the radiation-produced impurities by equilibration (scrubbing) with sodium carbonate or sodium hydroxide or by column chromatographic methods.

The hydrolysis of DHDECMP in contact with aqueous solutions containing less than 3 M HNO₃ is not more severe than that of TBP under the same conditions but is significant at higher acid concentrations. Hydrolysis of DHDECMP in contact with aqueous sodium hydroxide solution does occur, but it should not pose an important problem with the short contact times such as those anticipated for the removal of the radiation-induced degradation products by caustic scrubbing. The results of various chromatographic tests to characterize the degradation products of DHDECMP are also given.

A new experimental supply of bis(2-ethylhexyl)sulfoxide was determined by infrared spectrophotometry and high-performance liquid chromatography (HPLC) to be 97% pure, markedly better than previous² supplies. The impurity, separated by HPLC, appeared to be the disulfide. Extraction behaviors of the ~100% and the 97% materials were essentially identical. These extractions show the expected analogy to TBP, while permitting nitric acid concentrations to be lower by a factor of ~3.

An alkyl-substituted crown ether, di-*t*-butyl-dicyclohexo-18-crown-6, suffers less loss from organic to aqueous phase than do simple crown ethers (see Table 5.2), which is attributed to both lower aqueous solubility and higher organic solubility.

1. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5383, pp. 33, 36.

2. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542, p. 44.

Descriptive and Systems Chemistry

Alcohol extraction. The comparison of various classes of organic compounds as potential extractants for ethanol from dilute aqueous solution³ was completed and published.⁴ No distribution coefficient D^E_{EtOH} was found as high as 1, and in general the separation factor $SF^E_{\text{EtOH}} = D^E_{\text{EtOH}}/D^E_{\text{H}_2\text{O}}$ was high only when D^E_{EtOH} was lower. For the classes of compounds studied, the order of ethanol extractability was hydrocarbon $\approx$ halocarbon $<$ ether $<$ ketone $<$ amine $<$ ester $<$ alcohol $\approx$ phosphate. The highest D^E_{EtOH} found from 1 M ethanol solution to undiluted solvent was 0.7 with 2-ethyl-1-butanol, $SF^E_{\text{EtOH}} = 30$; the highest SF^E_{EtOH} found was 300 with cyclohexane, $D^E_{\text{EtOH}} = 0.007$. Tributyl phosphate gave $D^E_{\text{EtOH}} = 0.5$ and $SF^E_{\text{EtOH}} = 8$.

Crown ethers. Work with mixtures of crown ethers and cation exchange extractants⁵ continued to expand the scope and significance of the size-selective synergistic extraction. A report was presented at the International Solvent Extraction Conference (ISEC 80), Liege, Belgium, in September 1980. The abstract follows:

"Size-Selective Synergism by Crown Ethers in the Extraction of Alkali Metals by Di(2-ethylhexyl) Phosphoric Acid," by W. J. McDowell, W. F. Kinard, and R. R. Shoun. *Abstract:* Although the macrocyclic polyethers, known as crown ethers, complex metal ions and do so preferentially according to the size correspondence between the ion and the crown ether cavity, their usefulness as liquid-liquid extraction reagents has been limited by the necessity of solubilizing the anion in the organic phase. The common mineral acid anions are difficult to transfer to the organic phase and organophilic anions are expensive or impractical. A method is described that avoids this problem by combining organic-soluble cation exchangers with the crown ethers in the organic phase. The resulting mixtures show synergistic extraction for cations, and for the alkali metal ions the synergistic effect is size selective. The size dependence of the synergistic extraction in the system di(2-ethylhexyl) phosphoric acid/crown ethers parallels the extraction of picrate salts of the alkali metals and of the complex formation of the alkali picrates with crown ethers. A preliminary evaluation of concentration dependencies in the extraction of potassium by di(2-ethylhexyl) phosphoric acid-dicyclohexo-18-crown-6 mixtures in benzene suggests an organic phase complex containing two alkyl phosphoric acid groups and one crown ether per potassium.

The initial work with di(2-ethylhexyl) phosphoric acid (HDEHP) has been extended to other cation exchangers, both weaker (carboxylic) and stronger (sulfonic) acids. Tests with didodecyl-naphthalenesulfonic acid (HDDNS), Table 5.1, confirmed that both the synergistic enhancement and the size selectivity occur at high loadings as well as at the near-tracer levels used in most of this study. (The magnitude of the extraction coefficients in Table 5.1 is very low

Table 5.1. Simultaneous alkali extractions at high loading from 2.5 M nitrate solution (LiNO_3 , NaNO_3 , KNO_3 , RbNO_3 , CsNO_3 , each at 0.5 M) by 0.1 M crown ether + 0.1 M didodecyl-naphthalenesulfonic acid

Crown ether	Extraction coefficient, $D^E \times 10^3$				
	Li	Na	K	Rb	Cs
	17	90	40	27	17
	3	5	100	20	8
	11	10	45	45	32

because of the high loading.) Tests started with transition metal ions showed synergistic extraction of Mn^{2+} by HDDNS mixed with cyclohexo-15-crown-5 (C15C5); however, low extraction of Cr^{3+} and Fe^{3+} by HDDNS was made still lower (antagonism) by addition of C15C5.

Fundamental studies in the system KNO_3 - HNO_3 -water-HDDNS-DC18C6-toluene (see below) indicate that each extracted potassium ion is complexed with one DDNS⁻ ion and one DC18C6 molecule.

All of the foregoing work has been hindered by the excessive water solubility of crown ethers that are readily available at present. Some typical losses from organic to aqueous phase are shown in Table 5.2. (Inquiries from several other laboratories about the loss-to-aqueous data being developed here indicate a growing awareness of how important such losses can be in liquid-liquid extraction and in phase-transfer catalysis.) The special alkylated crown ether (fourth entry in Table 5.2) shows notably lower loss, and other alkylated crown ethers are being obtained through a university subcontract.

Pathways of radionuclides in uranium recovery. Of the important decay products in the ^{238}U chain, ^{210}Po has been the most difficult to analyze and hence the least well documented as to pathway and final fate in uranium ore processing. With a new highly sensitive and accurate assay, ^{210}Po was determined in

3. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542, p. 43.

4. J. W. Roddy, "Distribution of Ethanol-Water Mixtures to Organic Liquids," *Ind. Eng. Chem. Process Des. Dev.* 20, 104-8 (1981).

5. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542, p. 42.

Table 5.2. Loss of crown ethers from solutions in toluene to various aqueous solutions

0.1 M crown ethers in toluene	Loss to aqueous (% at equal volumes)				
	Water	1 M NaNO ₃	4 M NaNO ₃	1 M BaCl ₂	1 M MgSO ₄
	90	75	85		
	30	60	70		
	15	12	20	70	2.5
					<0.4
	7	7	5		
	6	5	3		

process samples taken essentially simultaneously throughout an acid mill (sulfuric acid leach-amine solvent extraction), a carbonate mill (sodium carbonate leach-precipitation), and a fertilizer plant recovering uranium from the intermediate wet-process phosphoric acid. In each case, essentially all of the polonium reported to the solid leach residue.

The prerequisite to this study was the development of an assay method capable of total collection of the polonium and determination of a low alpha count in the presence of a very high beta-gamma background. The abstract of a paper in preparation follows:

"An Improved Sensitive Assay for Polonium-210 Using a Background-Rejecting Extractive Liquid Scintillation Method," by G. N. Case and W. J. McDowell. *Abstract:* A procedure is described for the determination of polonium-210 in various types of materials including ores, mill tailings, and environmental samples by a combined solvent extraction-liquid scintillation spectrometry method. Concentration of polonium-210 and separation from interfering elements (such as iron) are accomplished by extraction from a solution $\sim 7\text{ M H}_3\text{PO}_4$ - 0.01 M HCl with 0.20 M trioctylphosphine oxide (TOPO) combined with a scintillator in toluene. The polonium-210 is determined by counting the 5.3 MeV alpha with a photon-electron rejecting alpha-liquid scintillation (PERALS) spectrometer. Extraction coefficients of over 1000 for polonium assure quantitative recovery, while all other alpha emitters in the decay chains of uranium-238, uranium-235, and thorium-232 are rejected by the extraction procedure. Calculations based on several samples show the standard deviation about the mean to be $\sim 1.2\%$. A lower limit of detection of 0.0038 pCi is

proposed based on a counting time of 1000 min and an easily obtainable background of 0.01 cpm under the alpha peak.

(See also Fig. 5.5.)

Tertiary amine extraction phase behavior. A study of tertiary amine extraction has been started, addressed to problems of slow phase disengagement, emulsions, and interfacial crud formation in uranium mills. A portion of the work now completed was presented at the Second Symposium on Separation Science and Technology for Energy Applications in May 1981; the abstract follows:

"Factors Influencing Phase Disengagement Rates in Solvent Extraction Systems Employing Tertiary Amine Extractants," by B. A. Moyer and W. J. McDowell. *Abstract:* Phase disengagement rate is a critical property in determining the usefulness of a particular solvent extraction system in hydrometallurgy. A survey of a number of commercial tertiary amine extractants of the type used in uranium extraction hydrometallurgy has been carried out to suggest whether structural factors influence phase disengagement behavior and to provide a useful comparison of different amines with regard to phase disengagement and uranium extraction. The amines $((\text{C}_n\text{H}_{2n+1})_3\text{N})$ were chosen to cover a range of alkyl chain lengths including straight-chain and branched-chain compositions, and the chemical makeup of the liquid-liquid systems closely paralleled that of the systems used in the Amex uranium extraction process. Batch phase disengagement tests showed significant trends with respect to amine structure and composition using acid sulfate solutions with or without added colloidal silica and actual ore leach solutions as the aqueous phase. In general, organic-continuous (OC) phase disengagement became

slower with increasing n (number of carbons per chain) whether branched or linear chain, but for any given n the branched-chain amines had much faster OC phase disengagement than the linear-chain amines. A key structural factor affecting OC phase disengagement was found to be the backbone chain length (longest chain in each alkyl group) since the OC phase disengagement measurements could be correlated vs backbone chain length on a single curve regardless of whether the amine was branched or linear. Aqueous-continuous (AC) phase disengagement rate was rapid for the acid sulfate solution but decreased greatly with decreasing n when colloidal silica was added or when leach solution was used. With both leach and colloidal silica solutions, AC phase disengagement was correlated with wetting behavior of the amine systems on a glass (silicate) surface. A model based on silica attachment to the liquid/liquid interface was suggested to explain the stabilization of AC dispersions by silica and the related problem of interfacial crud formation. In addition to faster AC phase disengagement and less emulsion (crud) stabilization, the larger-molecular-weight amines ($n \geq 10$) were found to have higher uranium extraction coefficients and lower tendencies to form third phases. Presumably, solubility losses to the aqueous phase are also lower. The results suggest that the performance of some Amex systems may be improved by using branched-chain tertiary amine extractants of higher molecular weight than are now normally used.

Both laboratory-grade amines and a range of hydrometallurgical-grade commercial amines were used (Table 5.3). Break times after aqueous-continuous dispersion both in actual leach liquors and in sodium sulfate solutions containing added colloidal silica showed good correlation (Fig. 5.1) with liquid-liquid-glass contact angles that had been measured in silica-free solutions. The effects of amine size and shape (i.e., straight or branched alkyl

Fig. 5.1. Half-volume break times of amines dispersed in Na_2SO_4 solution (pH 1) containing colloidal silica and in actual leach liquor.

groups) on phase-disengagement time proved to be different for aqueous-continuous (AC) and for organic-continuous (OC) dispersions. In AC mixing, disengagement rate is impaired most for the amines with straight, relatively short alkyls. Those with longer straight alkyls are impaired less, and those with branching, still less. In OC mixing, break time increases with increasing number of carbon atoms in the "backbone" chains, but does not increase when carbon atoms are added as branches without increasing the backbone length (Fig. 5.2).

Table 5.3. Commercial and laboratory tertiary amines examined for phase disengagement behavior

		Number of carbons per alkyl group		
		Total (range)	Total (average)	"Backbone" (average)
Straight	Trioctylamine	8	8	8
	Alamine 336	8-10	9.0	8.9
	Adogen 364	8-10	9.0	8.9
	AZamine T810	8-10	9.4	8.8
	Adogen 368	8-13	9.9	9.8
	Trilaurylamine	12	12	14
Branched	AZamine T8B	~8	8.1	~6
	Adogen 381	~8	8.4	~6
	AZamine T10B	~10	10.2	~7
	Adogen 382	~10	10.3	~7
	Adogen 383	~13	13.2	~9
	Tri(2-ethylhexyl)amine	8	8	6

Fig. 5.2. Break times of amines dispersed in pH 1 Na_2SO_4 solution.

Fundamental Chemistry

The extraction of iron from sulfate solutions by a primary amine⁶ was completed and published.⁷

The determination of distribution equilibria between aqueous ethanol solutions and a series of normal alkanes was completed and submitted for publication in *Industrial and Engineering Chemistry, Fundamentals*. Determination of distribution equilibria in the quaternary system EtOH-HOH-TBP-*n*-octane, together with delineation of the quaternary phase diagram (Fig. 5.3) and an infrared spectrophotometric investigation of the species involved,

6. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542, p. 41.

7. F. G. Seeley and W. J. McDowell, "Fe(III) Extraction Equilibrium in the System: $\text{Fe}_2(\text{SO}_4)_3$ -(NH_4)₂ SO_4 vs Primene JM-T Sulfate-Toluene," *J. Inorg. Nucl. Chem.* 43, 375-78 (1981).

Fig. 5.3. One-phase and two-phase regions in the quaternary system EtOH-HOH-TBP-*n*-octane. Each ternary face of the tetrahedral diagram is shown undistorted, with three typical tie lines included in each ternary two-phase region. The pseudoternary cross section EtOH-HOH-1 M TBP is also shown almost undistorted in view B.

was written for submission to the *Journal of Physical Chemistry*. The respective abstracts follow:

"Distribution of Ethanol-Water Mixtures to Several Normal Alkanes from C_4 to C_{16} ," by J. W. Roddy and C. F. Coleman. **Abstract:** Distribution measurements for ethanol ($D_{E_{H_2O}}$) and water (D_{H_2O}) from aqueous ethanol solutions (0.02 to 10 M) to several normal alkanes (C_4 to C_{16}) were made at 25°C by a tracer counting technique. The coefficients together with infrared spectral measurements in the frequency range of OH stretching mode were analyzed in an attempt to elucidate the bonding present in these systems. The $D_{E_{H_2O}}$ were all low (≤ 0.02). They were essentially constant for each alkane over a wide concentration range (0.02 to $\sim 5 M$), then rose sharply at 7 and 10 M . The D_{H_2O} s were much lower, but increased with increasing ethanol concentration, so that the ethanol:water separation factor dropped from ~ 4500 at 0.1 M to 20 at 10 M ethanol. Results of computer analysis of the solution data can be interpreted in terms of monomeric anhydrous ethanol and the formation of a monohydrate $EtOH \cdot HOH$, and suggest the additional hydrate species $(EtOH)_2 \cdot HOH$.

"Distributions and Miscibility Limits in the System Ethanol-Water-Tri-*n*-butyl Phosphate Diluent," by J. W. Roddy and C. F. Coleman. **Abstract:** Tracer counting techniques have been used to measure the distribution coefficients of ethanol ($D_{E_{H_2O}}$) and water (D_{H_2O}) from aqueous solutions to undiluted TBP and its solutions in *n*-octane at 25°C. $D_{E_{H_2O}}$ is near unity when the TBP is undiluted and the aqueous ethanol concentration is greater than 5 M ; it decreases with dilution in either phase, to about 0.005 at 0.03 M TBP and 0.01 M aqueous ethanol. The corresponding D_{H_2O} decreases from about 0.1 to 0.00003, so that the separation factor $D_{H_2O}/D_{E_{H_2O}}$ increases from about 10 to over 130. To expedite use of these data, the apparent formation quotients of putative types of species were evaluated by computer fitting. The distribution measurements together with stepwise tracing of phase boundaries were used to delineate three ternary phase diagrams (the fourth ternary, $EtOH$ -TBP-octane, has no miscibility gap) and the pseudoternary $EtOH$ - HOH -1 M TBP. Infrared spectral data in the frequency range of the hydroxyl and phosphoryl stretching modes were analyzed to assess the shifting nature of the intermolecular bonding, but they were not sufficient to identify specific species.

In the size-selective synergistic extraction of potassium ion from aqueous potassium nitrate solution by mixtures of didodecyl-naphthalenesulfonic acid (HDDNS) and dicyclohexo-18-crown-6 (DC18C6), a continuous-variations analysis (analogous to Job's Method⁸) and log-log slope analysis of the extraction (Fig. 5.4) combine to indicate that each extracted potassium ion is complexed with one DC18C6 molecule and one DDNS⁻ anion. In contrast, previous study of extractions using di(2-ethylhexyl) phosphoric acid (HDEHP) indicated that each potassium ion is complexed with one DC18C6 molecule, one DEHP⁻ ion, and one HDEHP molecule. This is consistent with the tendency of HDEHP to form both dimers and dimer ions $H(DEHP)_2$, whereas the stronger acid HDDNS presumably has less tendency to dimerize.

ORNL DWG 81-831

Fig. 5.4. Log-log slope analysis and continuous variations analysis of composition of extracted K^+ -DDNS-DC18C6 complex.

Ash Removal from Solvent Refined Coal

Continued work on the removal of residual mineral particulates ("ash") from the unfiltered oil produced in the Solvent Refined Coal (SRC) process by contact with an inorganic melt included comparison of different melts that remove the minerals by physical interaction or by chemical reaction. The responses of SRC oils prepared under different (pilot plant) conditions were also compared. These included SRC oil deliberately prepared so as to contain readily precipitable asphaltenes, which

carry down most of the particulates, and it was found that in the presence of a dc voltage gradient, such asphaltenes settle more quickly and form a thinner, denser, and more sharply demarked layer from which the deashed oil can be readily decanted.

PERALS Spectrometry

Photon-electron rejecting alpha liquid scintillation spectrometry continues to be a tool of prime importance in our own laboratory and of increasing outside interest.^{9,10} The rejection of beta and gamma background counts was considerably improved during the past year, as illustrated in Fig. 5.5.

Computer-Searchable Separations Systems Data Base

The Separations Systems Data Base (SEPSYS)¹¹ is available in the ORLOOK retrieval system of the computer time-sharing option (TSO). During the past year it has also been placed as a private file in the DOE/RECON (Department of Energy/Remote Console) system to evaluate the compatibility and work out details of management in that system. The results have been favorable, and steps are now under way to make the DOE/RECON version of SEPSYS publicly available. This system has much wider availability than does the TSO-ORLOOK system.

5.2 FUEL CYCLE CHEMISTRY

The Fuel Cycle Chemistry program has continued to investigate and define the fundamental chemistry that occurs in the Purex process. Results from this program have already increased the understanding of separation schemes, explained separation phenomena, offered alternative separation techniques, and defined some postseparation chemistry that affects partitioned products. The total effort of this program maintains a focus on the fundamental chemistry of separations processes in nuclear fuel reprocessing. Spectroscopy investigations are currently investigating the photochemistry of actinides and fission products and actinide metal-metal association in hydrolysis products. Studies of fission product chemistry are defining the solvent extraction of ruthenium, technetium, and rhenium with justifiable attention to the mechanism of extracting the anion forms TcO_4^- and ReO_4^- with metal cations. Waste stream process studies have identified several molybdenum oxides and several unusual molybdate and zirconate precipitates that contained uranium, plutonium, and zirconium cations. The acid and

temperature conditions have been defined for formation of the precipitates with varying degrees of hydration.

Spectrophotometry of Alpha-Active Materials

The several areas that were investigated during the past year include photochemical reactions of selected actinides and fission products and Raman studies of hydrous polymer species of some actinides. The photochemical effort has produced results that offer alternate means for separating selected actinides and/or fission products in fuel reprocessing. Much of the photochemistry of these elements remains uncertain in spite of the vast amount of other information that has been accumulated over the past several decades. With recent advances in laser photochemistry, several impressive proposals have arisen for controlling some troublesome problems in reprocessing schemes. A thorough understanding of the fundamental photochemical processes must be available in order to evaluate the merit of such claims.

Raman studies of hydrous actinide polymers were initiated to determine the structural and association characteristics of both individual and mixed actinide systems. Some applied programmatic work [Consolidated Fuel Reprocessing Program (CFRP)] previously observed that uranium as a uranyl species was entrained with the plutonium polymer. That observation spawned the Raman studies to determine how the actinide metals are associated in the structural network of hydrous polymers.

Neptunium photolysis. During the past year the photochemistry of neptunium was investigated with neptunium at low concentrations like those in reprocessing schemes. A paper describing these results has been published,¹² and an addition to the existing patent disclosure has been filed. Interest in

9. W. J. McDowell, "Alpha Liquid Scintillation Counting: Past, Present, and Future," pp. 315-32 in *Liquid Scintillation Counting, Recent Applications and Development, Volume 1, Physical Aspects*, C.-T. Peng, D. L. Horrocks, and E. L. Alpen, eds., Academic Press, New York, 1980.

10. W. J. McDowell and G. N. Case, "New Advances in Alpha Spectrometry by Liquid Scintillation Methods," pp. 111-20 in *American Nuclear Society Topical Conference on Measurement Technology for Safeguards and Material Control*, T. R. Canada and B. S. Carpenter, eds., National Bureau of Standards Publication No. 582 (1980).

11. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542, p. 45.

12. H. A. Friedman and L. M. Toth, "Photochemically Induced Reduction of Trace Np(VI) in U(VI)-HNO₃ Solutions," *J. Inorg. Nucl. Chem.* (in press).

ORNL-DWG 80-20601R

BUG= 1.0 CNT= 0
 [47] 1.0: 256.0 INT= 26483 N

A 1-mL scintillation sample containing ^{210}Po at $\sim 5 \times 10^{-11}$ Ci (~ 0.015 Bq, ~ 1 α decomposition/min) and $^{152-154}\text{Eu}$ γ ~ 3300 β - γ counts/min, counted for 8 min. All the counts visibly registered are β or γ (plus cosmic-ray secondaries, etc.). The arrow points to where the few α counts are presumably buried.

BUG= 1.0 CNT= 0
 [47] 1.0: 256.0 INT= 6 N

Same sample, same scale of plot, same 8-min counting time, same conditions except that β and γ (etc.) pulses have been rejected by pulse-shape discrimination. A few counts at the ^{210}Po α energy are barely visible.

BUG= 1.0 CNT= 0
 [47] 1.0: 256.0 INT= 5312 N

Counting time increased from 8 min to 88 h. The ~ 5000 α decompositions give a clear peak at the correct ^{210}Po energy. The background is visible but not very important (500 counts outside of the α peak, and estimated 85 counts under it). Result: 0.90 ^{210}Po α decomposition/min-mL (4.0×10^{-11} Ci/mL; 0.015 Bq/mL).

Fig. 5.5. Precise, sensitive trace alpha analysis: high background rejection by pulse-shape discrimination.

photochemistry has grown as a result of these findings to such an extent that the development of photochemical alternatives in fuel reprocessing is currently under consideration at the Savannah River Laboratory.

Dilute Np(VI) can be reduced to Np(V) in the presence of large amounts of $\text{UO}_2(\text{NO}_3)_2$ by a photochemical process that first involves the photoreduction of NO_3^- to NO_2^- . Although UO_2^{2+} competes strongly for photons, the accompanying stabilization of Np(V) by UO_2^{2+} tends to compensate for the UO_2^{2+} screening effect. Figure 5.6 compares the amount of Np(V) formed in the presence of large amounts of UO_2^{2+} with that formed in the absence of added solutes when photolyzed with 254-nm radiation. The concentrations of the Np(V) for solutions containing no added $\text{UO}_2(\text{NO}_3)_2$ (dashed lines) have been normalized with respect to the amount of light absorbed by NO_3^- in the corresponding solutions containing 1.0 M $\text{UO}_2(\text{NO}_3)_2$ (solid lines).

Fig. 5.6. Production of Np(V) as a function of 254-nm photolysis time where the concentrations for solutions containing no added $\text{UO}_2(\text{NO}_3)_2$ (dashed lines) have been normalized with respect to the amount of light absorbed by NO_3^- in the corresponding solutions containing 1.0 M $\text{UO}_2(\text{NO}_3)_2$ (solid lines). Nitric acid concentrations were A and A', 0.1 M; B and B', 1.0 M.

The stabilization of Np(V) by U(VI) has been recently identified as occurring through the formation of a novel $\text{NpO}_2^+-\text{UO}_2^{2+}$ complex. However, the structure of the complex has not been identified. Figure 5.7 shows a spectrum of the photolyzed solution in the region where Np(V) absorbs. Both the characteristic band of the bridged complex at 995 nm and that of unassociated NpO_2^+ at 982 nm are evident, thus establishing the validity of this interpretation. Although the bridged complex of neptunium has been a topic of recent interest with other investigators, these photochemical effects are the first direct chemical consequences of that association.

Experiments on neptunium in HNO_3 have been performed using 254- and 300-nm radiation on 0.1 and 1.0 M HNO_3 solutions containing 1 M $\text{UO}_2(\text{NO}_3)_2$ and either 0.01 or 0.001 M NpO_2^{2+} . Because the primary photochemical reaction involves photoreduction of NO_3^- to NO_2^- , still lower

Fig. 5.7. Spectrum of a solution containing Np(V) produced by photochemical reduction using 254-nm light. Initial concentrations were 0.1 M HNO_3 , 0.01 M NpO_2^{2+} , and 1.0 M UO_2^{2+} .

concentrations of Np(VI) are expected to be reducible by this process.

Plutonium photolysis. The photochemistry of plutonium in nitric acid was examined because previous investigations^{13,14} were confined to perchloric acid solutions. The interfering light absorption by nitric acid and its subsequent photolysis seen in the neptunium studies prompted a return to the plutonium system to evaluate the possibility of similar effects on the plutonium chemistry.

The photochemical reduction of Pu(IV) in nitric acid solutions containing hydrazine has been shown to occur with the formation of a Pu(IV) peroxy complex intermediate. This complex is responsible for the enhanced rates of Pu(IV) reduction in dark periods following the photolysis. The photolysis of HNO_3 in the presence of N_2H_4 demonstrates some of the complex chemistry associated with N_2H_4 solutions. In this instance, it results in a potentially practical situation because the peroxy complex of Pu(IV) is reduced at a faster rate with N_2H_4 than is the uncomplexed Pu^{4+} ion.

Literature surveys. Literature surveys of the photochemistry of americium and technetium have been made and published as ORNL technical memoranda^{15,16} prior to the initiation of laboratory experiments. It was concluded that the redox chemistry of both of these elements should be affected by ultraviolet (uv) light, but the americium would require uv wavelengths of 210 nm or less. Because such a light source was not yet available, studies of technetium were initiated. Soluble technetium species are also of interest because there are claims in the literature that some are subject to ligand substitution (nonredox) photochemical reactions; these mechanisms offer yet another means of controlling the chemistry of the ions in solution.

Raman studies. These structural studies have been most recently directed at the nature of the bonding between dissimilar actinide ions which was indicated in the course of CFRP development studies. The association of the uranyl ion with Pu(IV) hydrous polymers retarded the rate of polymer growth, but the nature of the bonding is such a novel phenomenon that no precedent information was available in the open literature.

Raman spectroscopy appeared to be an ideal means of studying this problem because the fundamental vibrational frequencies of the uranyl ion have been well characterized. Since handling problems associated with plutonium added to the complexity of the research, the association of UO_2^{2+} with Th(IV) hydrous polymers was selected first before proceeding to Pu(IV) polymers. In order to establish the

nature of the bonding that occurs when the uranyl ion associates with other species during a hydrolysis reaction, the hydrolysis and self-association of uranyl ion were examined because the hydrolysis chemistry of uranyl is well understood. The Raman study of the pure uranyl system study has been completed and published.¹⁷ Some of these results are described below.

The Raman spectrum of aqueous uranyl ion has been measured as a function of pH and uranyl ion concentration. The symmetrical stretching vibration has been found to consist of three bands at 869, 851, and 836 cm^{-1} , which are identified as belonging to the UO_2^{2+} , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and $(\text{UO}_2)_3(\text{OH})_3^+$ ions, respectively. The Raman spectral measurements correlate with equilibrium thermodynamic measurements as shown in Fig. 5.8, where the concentrations of the uranyl ion and its hydrolysis products are plotted as a function of pH at an ionic strength of 0.3. The notation is 1.0 = UO_2^{2+} ; 2.2 = $(\text{UO}_2)_2(\text{OH})_2^{2+}$; and 3.5 = $(\text{UO}_2)_3(\text{OH})_3^+$. The positions marked A-F correspond to the pH values at which the similarly identified curves of Fig. 5.9 were obtained. It is evident then that the Raman method allows a determination of both the nature of the bonding and the approximate concentration of the uranyl species. The shift in the frequency of the ν_1 vibrations as shown in Fig. 5.9 (as the uranyl ion is bridged by an increasing number of hydroxyl linkages) is attributed largely to overlap of the nonbonding ϕ_u and δ_u uranium orbitals with ligand orbitals, resulting in a considerable ligand-metal electron density shift accompanied by weakening of the actinyl bonds.

The above results demonstrate that there is considerable promise in using the Raman method to characterize the nature of the bonding in the mixed actinide systems (i.e., where uranyl ion is believed to bridge to thorium or plutonium hydrous polymer networks). Experiments to examine the degree of this

13. J. T. Bell and H. A. Friedman, "Photochemical Reactions of Aqueous Plutonium Systems," *J. Inorg. Nucl. Chem.* **38**, 831 (1976).

14. H. A. Friedman, L. M. Toth, and J. T. Bell, "Photochemical Reactions of Aqueous Plutonium Systems-II," *J. Inorg. Nucl. Chem.* **39**, 123 (1977).

15. H. A. Friedman, *Feasibility Study for the Oxidation of Americium(III) by Photolysis*, ORNL TM-7359 (December 1980).

16. H. A. Friedman, *Literature Survey of the Aqueous Chemistry of Technetium Related to Photolysis*, ORNL TM-7525 (July 1981).

17. L. M. Toth and G. E. Begun, "The Raman Spectra of Uranyl Ion and Its Hydrolysis Products in Aqueous HNO_3 ," *J. Phys. Chem.* **85**, 547 (1981).

Fig. 5.8. Equilibrium distribution of the uranyl ion and its hydrolysis products as a function of pH for 0.1 M $\text{UO}_2(\text{NO}_3)_2$ (ionic strength = 0.3) with 1.0 = UO_2^{2+} ; 2.2 = $(\text{UO}_2)_2(\text{OH})_2^{2+}$; and 3.5 = $(\text{UO}_2)_3(\text{OH})_4^+$. Positions marked A-F correspond to pH values at which similarly identified curves of Fig. 5.9 were obtained.

type of bonding were undertaken during the past summer with the assistance of a summer student employee. By following the shift in position of the Raman active symmetric stretching mode of the UO_2^{2+} ion, evidence of UO_2^{2+} attachment of hydroxy-bridged Th(IV) polymers was found when mixtures of these actinides were allowed to hydrolyze and aggregate. On heating these uranyl-containing Th(IV) polymers to 70°C, shifts in the Raman spectra of the uranyl ion occurred and were interpreted as being due to the conversion of the hydroxy-bridged polymer aggregates to oxygen-bridged aggregates. These experiments are still in progress.

Chemistry of Selected Fission Products

The many gaseous and solid fission products produced in nuclear power reactors present numerous problems in all stages of the nuclear fuel cycle due to their intense radioactivity and/or complicated chemical behavior. Despite many man-years of effort, the chemistry of some of these elements as it relates to nuclear fuel processing is still poorly understood.

Solvent extraction behavior of ruthenium. Historically, one of the most intractable fission products has been ruthenium. With its 1-y half-life and energetic β -

Fig. 5.9. Raman spectra of the uranyl symmetric stretching vibration for aqueous 0.1 M $\text{UO}_2(\text{NO}_3)_2$ at pH = (A) 1.3, (B) 3.07, (C) 3.45, (D) 3.55, (E) 3.88, and (F) 4.02 corresponding to equilibrium shift from unhydrolyzed mononuclear species with ν_1 at 869 cm^{-1} to hydrolyzed dinuclear and trinuclear species with ν_1 at 851 and 836 cm^{-1} , respectively. Excitation, either 514.5- or 633.1-nm radiation and slits, 7 cm^{-1} .

and γ -ray emissions, ^{106}Ru typically accounts for 5 to 10% of the total gamma activity in dissolver solutions prepared from short- and intermediate-cooled fuels. Further, its variety of oxidation states and coordination complexes, each with different solvent extraction properties, produces a series of difficulties in the chemical treatment of nuclear fuels.

A study designed to further quantify and explain the solvent extraction behavior of ruthenium in the Purex process was published¹⁸ during FY 1980. The distribution behavior of equilibrium mixtures of ruthenium(III) nitrosyl complexes between aqueous nitric acid solutions and tributyl phosphate in *n*-dodecane diluent (TBP-NDD) was studied. The influence of nitric acid concentration and of various small anions in the aqueous phase was determined. As shown in Fig. 5.10, the distribution coefficient for ruthenium ($D_{Ru} = [Ru]_{organic} / [Ru]_{aqueous}$) reaches a maximum near 1.0 *M* nitric acid. The equilibrium value of D_{Ru} is approached very slowly, requiring 4–6 h even in a completely emulsified system. Figure 5.11 shows the way in which a neutral nitrate salt ($NaNO_3$)

Fig. 5.10. Ruthenium distribution coefficients as a function of nitric acid concentration at various stirring times.

Fig. 5.11. Ruthenium distribution coefficients as a function of sodium nitrate concentration at various stirring times.

increases D_{Ru} by increasing the concentrations of the more extractable trinitrato and tetranitrato ruthenium nitrosyl complexes. Figure 5.12 shows the second-order dependence of D_{Ru} in the concentration of free (uncomplexed) TBP in the organic phase. Aqueous bisulfite, chloride, and fluoride ions have little effect on D_{Ru} in this system, but oxalate substantially reduces the extraction of ruthenium. Dibutyl phosphate (DBP) exhibits a synergistic effect in combination with TBP that enhances D_{Ru} considerably.

Solvent extraction behavior of technetium. A second troublesome fission product is ^{99}Tc , which occurs as a high-yield (6.06%), long-lived ($T_{1/2} = 2.12 \times 10^5$ y) fission product of ^{235}U . Its chemistry in HNO_3 -TBP-NDD systems, where it occurs mainly as the pertechnetate anion (TcO_4^-), is much less complicated than that of ruthenium, but has some unique problems of its own. Typical distribution behavior for technetium in this system and in the analogous hydrochloric acid system at 25°C is shown in Figs. 5.13 and 5.14, respectively. Analysis of

18. D. J. Pruett, "The Solvent Extraction Chemistry of Ruthenium, Part I," *Radiochim. Acta* 27, 115 (1980).

Fig. 5.12. Ruthenium distribution coefficients as a function of free TBP concentration.

this data suggests the following stoichiometry for the extraction reaction:

The concentration equilibrium constant for this reaction is 0.97, 0.29, and 0.08 at 25, 40, and 60°C respectively.

It has been observed that reprocessed uranium may be contaminated with substantial amounts of technetium. A possible source for this problem is found in the data presented in Fig. 5.15. The addition of 0.1 M uranyl nitrate to an aqueous solution of pertechnetate can increase D_{Tc} as much as 10,000

Fig. 5.13. Technetium distribution coefficient as a function of nitric acid concentration at various TBP concentrations.

times. Apparently, a uranyl-pertechnetate complex is formed that is much more extractable than pertechnic acid. This phenomenon is currently being studied in more detail.

Solvent extraction behavior of rhenium. Since technetium has no stable isotopes and is available from only a few specialized sources, the solvent extraction behavior of perrhenate was studied as a possible substitute for technetium to be used in cold testing experiments. The behavior of rhenium was shown to be identical to that of technetium on a

Fig. 5.14. Technetium distribution coefficients as a function of hydrochloric acid concentration at various TBP concentrations.

qualitative basis, and the relationship $D_{U_1} = 2.5 D_{U_2}$ was found to apply over a wide range of conditions.

Waste Stream Processing Studies

Fuel cycle history includes several incidents where precipitation of solid materials has caused

Fig. 5.15. Effect of uranyl nitrate on technetium distribution coefficients.

serious consequences in fuel reprocessing. In this Basic Energy Sciences (BES) Fuel Cycle Chemistry Program, the Waste Stream Studies group is investigating the potential for precipitation during fuel reprocessing and in management of high-level waste. Investigations include observations of precipitates and the subsequent identification and characterization of the precipitates. X-ray diffraction is used to identify the precipitates; the precipitate composition is determined by conventional chemistry. Most of these precipitation reactions are slow with unusually long induction periods. This induction period may be the most important characteristic of these precipitations.

The initial waste stream studies focused on the use of synthetic high-level waste solutions to identify potential precipitates. Those studies identified molybdenum-containing precipitates, particularly zirconium molybdate, and zirconium oxide as the most

susceptible to formation.¹⁹ This finding was simultaneously confirmed by hot-cell tests.²⁰

Nineteen precipitates have been identified in these BES studies (Table 5.4). Zirconium molybdate is the most likely precipitate from waste solutions whose nitric acid concentration ranges from 0.4 to 3 M. Zirconium molybdate precipitates can carry up to 16% thorium(IV), nearly as much plutonium(IV), but little uranium(VI). Tellurium can precipitate with zirconium molybdate in very substantial quantities, easily substituting for the molybdenum in the crystal lattice. Zirconium tellurate and plutonium, thorium, and uranium molybdates can all precipitate under certain conditions. In the presence of zirconium and at acid concentrations greater than 10 M, hydrated molybdenum oxides preferentially precipitate in all known cases. Following molybdate precipitation, any excess zirconium can precipitate as zirconium oxide.

The concentration of molybdenum in 3.7 M HNO₃ at 70°C as a function of time is shown in Fig. 5.16. The solution appeared stable for about 35 h (i.e., the induction period). Precipitation then began and

continued for the next 100 or more hours. The induction period is a function of acid concentration and of temperature, and a log plot of induction time versus acid concentration for precipitation of MoO₃ from nitric acid solutions at 50°C is shown in Fig. 5.17. The maximum induction time near 4 M HNO₃ is related to the precipitation of different hydrates of the oxide at the lower acid and at the higher acid concentrations.

More than 19 different materials have been identified as precipitates from simulated acidic high-level waste solutions. Twelve of these have not been previously identified. All precipitations were preceded with induction periods depending on acid concentration, temperature, and the degree of supersaturation.

19. M. H. Lloyd, "Instabilities in Solid-Phase Formation in LWR Reprocessing Solutions," *Trans. Am. Nucl. Soc.* 24, 233 (1976).

20. D. O. Campbell and S. R. Buxton, "Hot Cell Studies of Light Water Reactor Fuel Reprocessing," *Trans. Am. Nucl. Soc.* 24, 232 (1976).

Table 5.4. Molybdenum- and zirconium-containing precipitates that can form in high-level waste and fuel reprocessing solutions

Generic formula	Actual formula	Crystal system
Zr(MoO ₄) ₂ ·xH ₂ O	ZrMo ₂ O ₇ (OH)·2H ₂ O	Tetragonal
Zr(MoO ₄) ₂ ·xH ₂ O ^a		<i>h</i>
Zr(MoO ₄) ₂ ·xH ₂ O·y(Pu, UO ₂ or Th) ^b	<i>c</i>	Tetragonal
Zr(MoO ₄) ₂ (TeO ₄)·xH ₂ O	<i>d</i>	Tetragonal
Zr(TeO ₄) ₂ ·xH ₂ O ^c		<i>h</i>
Pu(MoO ₄) ₂ ·xH ₂ O ^c	Pu(MoO ₄) ₂ ·2H ₂ O	Orthorhombic
Th(MoO ₄) ₂ ·xH ₂ O ^c	Th(MoO ₄) ₂ ·5H ₂ O	<i>h</i>
UO ₂ MoO ₄ ·xH ₂ O	UO ₂ (Mo ₂ O ₇)(H ₂ O)·H ₂ O	Monoclinic
UO ₂ MoO ₄ ·xH ₂ O ^c		<i>h</i>
MoO ₃	MoO ₃	Orthorhombic
MoO ₃ ·y(Ru) ^e	<i>e</i>	Orthorhombic
MoO ₃ ·xH ₂ O ^c	α-MoO ₃ · ¹ / ₂ H ₂ O	Monoclinic
MoO ₃ ·xH ₂ O ^c	β-MoO ₃ · ¹ / ₂ H ₂ O	<i>h</i>
MoO ₃ ·xH ₂ O	MoO ₃ ·H ₂ O	Monoclinic
MoO ₃ ·xH ₂ O	MoO ₃ ·H ₂ O	Triclinic
MoO ₃ ·xH ₂ O	MoO ₃ ·2H ₂ O	Monoclinic
MoO ₃ ·xH ₂ O ^c	4MoO ₃ ·3H ₂ O	<i>h</i>
ZrO ₂	ZrO ₂	Monoclinic
ZrO ₂ ^a		<i>h</i>

^aUnique precipitates which have been discovered during this study.

^bNot yet identified.

^cPu⁴⁺, UO₂²⁺, or Th⁴⁺ carrying by ZrMo₂O₇(OH)·2H₂O.

^dTe solubility in ZrMo₂O₇(OH)·2H₂O.

^eRu carrying by MoO₃.

Fig. 5.16. The precipitation of molybdenum(VI) oxide from 3.7 M HNO₃ at 72°C.

Fig. 5.17. The induction period before observed precipitation of molybdenum(VI) oxide from nitric acid solutions at 50°C.

5.3 CHEMICAL ENGINEERING RESEARCH

Chemical engineering research includes a variety of fundamental research studies which contribute to the successful completion of mission-oriented devel-

opment programs at ORNL and elsewhere. Of particular interest is the investigation of new engineering concepts in the separation and material science areas which relate to the utilization of advanced energy sources, the conservation of energy, or the recovery of important resources.

A rotating annular chromatograph is being developed to separate several components continuously with a relatively high throughput. The pressurized chromatograph is capable of either isocratic or gradient elution operation. Scale-up parameters are being demonstrated with a commercial ore liquor containing copper, nickel, and cobalt. Granular electrofiltration is being investigated as an innovative technique for removing submicron particles from fluids. By passing a dilute suspension through a packed bed either normal or parallel to an electric field, filtration can be achieved with a minimal pressure drop. The operating characteristics of high-temperature slagging processes are being studied for potential improvements in the recycle of scrap metals. An energy-efficient gas absorption-fractionation technique for the separation of hydrogen-carbon monoxide-methane mixtures is being studied using a process-derived solvent at high pressure. The sedimentation characteristics of different particles are being investigated to enhance solid-liquid and solid-solid separation techniques.

Continuous Chromatography

Multicomponent liquid chromatographic separations have been achieved by using a slowly rotating annular bed of sorbent material. By continuously introducing the feed material to be separated at a stationary point at the top of the bed and eluent everywhere else around the annulus, elution chromatography occurs. The rotation of the sorbent bed causes the separated components to appear as helical bands, each of which has a characteristic, stationary exit point; hence, the separation process is truly continuous.

Investigation of the concept has proceeded in several areas. The design and construction of a new, stainless steel, continuous annular chromatograph (CAC-III) now gives us three units with different geometries to study. The two plastic chromatographs, CAC-ME and CAC-II, have lengths of 0.58 m with annulus widths of 6.4 and 12.7 mm and annulus diameters of 89 and 280 mm, respectively, whereas the CAC-III has a length of 1.1 m, an annulus width of 32 mm, and an annulus diameter of 445 mm. Figure 5.18 is a photograph of the CAC-III during construction. It has since been operated

Fig. 5.18. New, stainless steel, 445-mm-diam continuous annular chromatograph.

successfully at the design pressure of 1.1 MPa (150 psig). In addition to varying the overall outer dimensions of a continuous annular chromatograph, smaller inner cylinders have been fabricated for both of the plastic units. The resulting increase in cross-sectional area allows a directly related increase in

feed throughput to the CAC. Initial results using the CAC-ME indicate that the annulus width can be at least doubled with no loss of separation efficiency.

Three metal recovery systems, all using cation exchange resin in the CAC units, have been explored: separation of iron and aluminum in ammonium

sulfate-sulfuric acid solutions;²¹ separation of hafnium from zirconium in sulfuric acid solutions;²² and separation of copper, nickel, and cobalt in ammonium carbonate solutions.²³ This last system simulates the leach liquor of the Caron process for recovering nickel and cobalt from laterite ores. It has been studied, using similar conditions, on each of the chromatographs. Comparison on the basis of feed-to-eluent flow rate ratios shows that all three units perform similarly, giving us considerable faith in our scale-up technique.

The separation of hafnium from zirconium is important to the nuclear industry where pure zirconium, containing <100 ppm hafnium, is used as fuel cladding in nuclear reactors. The effects of feed rate and zirconium concentration on the separation of zirconium and hafnium in the CAC-II are shown in Fig. 19. A resolution value of unity indicates no dead volume between the two species but virtually no overlapping either. Resolution values of less than 1 mean that overlapping of the two main peaks has occurred. Under constant eluent conditions, the resolution between zirconium and hafnium decreases as the feed rate is increased and also as the feed concentration is increased. Eluent and feed conditions are currently being sought which will produce resolution values greater than unity at significantly greater feed throughput rates. At the present time, using the optimum conditions shown in Fig. 5.19 (four nozzles feeding 2 mL/min of 36.5 g Zr/L each), the CAC-II could produce over 150 kg of pure

zirconium per year. The larger CAC-III, operating at 1.1 MPa, would increase this production rate to 2000 kg of zirconium per year. Even larger production rates will be possible if the annulus width can be increased without loss of separation efficiency as is indicated by tests in the CAC-ME unit.

Modeling of the CAC has continued. Plate theory²⁴ can be used to predict accurately the effect of rotation rate upon separation,²⁵ but requires knowledge of the distribution coefficients and the number of plates. Alternatively, an idealized analytical model adapted to the CAC,²⁶ requiring only the distribution coefficients, incorporates the nonlinear competitive solute-resin binding isotherms common in many separations and allows prediction of the effects of high feed concentration and bed loading on solute peak positions in the column effluent. Dispersion effects are not presently considered in the model, but work is under way to include them in an improved version.

In addition to its obvious applicability for hydrometallurgical separations, the CAC should also find uses in organic, chemical, biochemical, and pharmaceutical separations and purifications. A number of inquiries have been received from several industrial firms concerning commercial use of the continuous chromatography concept. We are actively pursuing this transfer of information and have achieved strong links with industry.

Granular Electrofiltration

Granular electrofiltration has been shown to be effective in removing small particles (0.05 to 1.0 μ m

Fig. 5.19. Effects of feed rate and concentration on resolution in the zirconium-hafnium system using the 280-mm-diam CAC-II.

21. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542, p. 47.

22. J. M. Begovich and W. G. Sisson, "Continuous Ion Exchange Separation of Zirconium and Hafnium," presented at the 110th AIME Annual Meeting, Chicago, Ill., Feb. 22-26, 1981; to be published in the *Transactions*.

23. R. M. Canon, J. M. Begovich, and W. G. Sisson, "Pressurized Continuous Chromatography," *Sep. Sci. Technol.* 15(3), 655 (1980).

24. C. D. Scott, R. D. Spence, and W. G. Sisson, "Pressurized, Annular Chromatograph for Continuous Separations," *J. Chromatogr.* 126, 381 (1976).

25. R. J. Torres, C. S. Chang, and H. A. Epstein, *Fundamental Studies in Continuous Annular Chromatography*, ORNL-MIT-329 (1981).

26. R. L. Bratzler and J. M. Begovich, *A Mathematical Model for Multicomponent Separations on the Continuous Annular Chromatograph*, ORNL TM-6706 (December 1980).

diam) from dilute suspensions in organic liquids.²⁷ Work during this reporting period has followed three parallel paths: (1) laboratory studies using synthetic suspensions and carefully controlled conditions, (2) filtration of coal liquefaction product in a high-pressure, high-temperature granular electrofilter, and (3) theoretical and computer modeling of granular electrofiltration. Since granular filtration is restricted to dilute suspensions, its most likely use is in conjunction with an inexpensive, less efficient solid-liquid separation pretreatment process, such as settling or centrifugation.

The laboratory studies have continued using synthetic suspensions of TiO_2 , BaSO_4 , and carbon black particles suspended in cyclohexane. Deep bed and shallow (differential) bed runs have been made covering a wide range of operating conditions. Results from the laboratory studies show that granular electrofiltration is very effective for the clarification of dilute suspensions in liquids of low electrical conductivity.

A second granular electrofiltration apparatus has been designed and built for use with actual coal liquefaction product at 100°C and 0.7 MPa (100 psi). A schematic of this system is shown in Fig. 5.20. The filter is a 2-in.-diam (nominal) stainless steel pipe, 0.6 m (24 in.) long, with the high-voltage electrode running the length of the pipe through its center. Figure 5.21 shows the results of one filtration run using Solvent Refined Coal (SRC) product materials obtained from the Pittsburgh and Midway Mining Co. pilot plant at Wilkersonville, Alabama. The SRC raw product was diluted with SRC recycle solvent to simulate a pretreated feed for granular electrofiltration. As seen in Fig. 5.21, the ash content (reflecting

Fig. 5.20. Schematic of the experimental apparatus for the filtration of SRC materials.

Fig. 5.21. Results of one SRC filtration run.

the solids content) of the effluent is acceptably low for approximately the first 30 min of the run. These results demonstrate the potential of granular electrofiltration for use in difficult solid-liquid separations found in fuel conversion processes. The current between the electrodes increased steadily over the length of the run, due to the accumulation of electrically conductive ash particles.

The theoretical and computer modeling has supported the experimental efforts. This effort has produced a theoretical, predictive model as well as an empirical model for scale-up purposes. The theoretical model is derived from first principles and contains no empirical parameters. It is an excellent qualitative representation of granular electrofiltration behavior, though it systematically overpredicts filter performance. The empirical model is well founded in theory and is useful in scaling up data from small filters.

Future work on granular electrofiltration will focus on the removal of particles from gas streams.

High-Temperature Slagging Studies

Most important metallurgical extraction processes depend on reactions involving slag-gas-metal systems. The thermodynamics of these reactions are often well established; however, the kinetics of these systems have received less attention. This study

27. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542, pp. 49-51.

includes the development of improved slag-metal contacting equipment and the use of slagging processes in selected applications. The applications of current interest include the removal of copper from scrap iron and undesirable impurities from recycled aluminum.

Gas lances can be used to agitate and promote mass transfer in a metallurgical furnace, where a layer of slag floats on a molten metal phase and extracts a component from the molten metal solution. A potential high-temperature slagging process was simulated using a gas-sparged, mercury-water contactor. A polarographic technique was used to measure aqueous-film mass transfer coefficients determined from the diffusion-limited, electrically driven reduction of quinone to hydroquinone at the solution-mercury surface. The effects of gas rate, vessel size, and aqueous phase viscosity (addition of sucrose) were investigated. The mass transfer data are represented well by the following correlation for the Sherwood number (see Fig. 5.22):

$$N_{Sh} = 1.33 N_{Re}^{0.70} N_{Sc}^{1.3}$$

This expression has a familiar form, and the exponents on Reynolds and Schmidt numbers are of the magnitude generally observed for fluids flowing across flat plates and through tubes.

The extraction of copper (1 wt %) from iron-base scrap metals using sodium sulfide as the light phase appears to be a potentially attractive high-temperature slagging application. Scouting experiments were performed in 3.5-cm-ID, unagitated alumina crucibles (99 g Fe, 1 g Cu, and 20 g Na₂S). After 4 h at 1550°C, chemical analyses indicated a 40 wt % extraction of copper by the light phase;

Fig. 5.22. Correlation of mass-transfer data for bubble-agitated liquid-liquid system.

however, the sodium sulfide also removed a significant amount of the iron (~20 wt %).

Advanced Concepts for Methane Purification

Advanced coal gasification processes now under development will require unique gas cleanup and separation processing. Examples are the catalytic gasifier under development at Exxon and the "flash hydrolysis" gasifier under development at Rockwell International. The "advanced" feature of these gasification schemes is that the methane is produced in the gasification reactor instead of in a downstream methanator, therefore eliminating a large amount of gas processing (water-gas shift, methanation, etc.). A price must be paid for this convenience; these processes require the separation of hydrogen and carbon monoxide (for recycle to the gasifier) from the methane product. Conventional technology for this separation is cryogenic distillation of the hydrogen-carbon monoxide-methane mixture. Because of the low temperature (~180°C) and low pressure [0.2 MPa (2 atm)] required for cryogenic distillation, its users must pay a high energy cost for refrigeration and product recompression. A more energy-efficient gas absorption-fractionation technique for separation of hydrogen-carbon monoxide-methane mixtures has been conceived. This technique would use a process-derived solvent (liquid CO₂ is the leading candidate, but liquid NH₃ and H₂S have some attractive features) at high pressure and is based on the fact that methane is more soluble in the solvent than hydrogen or carbon monoxide. A schematic of the process is shown in Fig. 5.23.

Computer simulation of this process predicts that the gas separation requirements for pipeline gas production can be met. The product methane can be

Fig. 5.23. Schematic of absorption-fractionation process for CH₄ purification using liquid CO₂ as the solvent.

produced at pipeline gas pressure without further compression, and the H_2 -CO recycle stream will require only a small recompression to make up for the pressure drop of the gas processing equipment. Additional savings are realized by reducing refrigeration requirements since the minimum processing temperature is about -20°C .

This process appears very promising, but some more basic data must be obtained. These data needs include vapor-liquid equilibria of the multi-component mixtures and information on the chemistry of liquid CO_2 - H_2S mixtures.

Sedimentation Studies

The objective of this study is to develop the means for predicting the sedimentation characteristics of a mixture of particles of different sizes. Methods are available for predicting the settling rate of a suspension of uniform particles. The project entails both experimental work and the development of a computer simulation program.

For over half a century, thickeners have been designed by the Coe and Clevenger method.²⁸ In this method it is assumed that four zones usually form: from the top, zone A—clear liquid, zone B—initial concentration, zone C—graded concentration, and zone D—sediment. Dixon²⁹ has recently argued that zone C cannot exist, causing much controversy in the field and casting doubt on the soundness of the Coe and Clevenger method. Theoretical treatments of the settling process always begin with the assumption that the particles are uniform in size, shape, and density. This assumption may well be the primary cause of differences between theoretical models and real operating systems.

Experimentation. Traditional design of thickeners is based on data from batch sedimentation tests, in which a test suspension is allowed to settle out in a glass cylinder. The data taken are positions of the clear interface versus time. No method for measuring solids concentration versus height, which would answer questions about zone C, is ever used. Often, very little is done to characterize particle size or size distribution.

We have designed and built an experimental apparatus which will provide solids concentration profiles during batch settling tests. A schematic drawing of this apparatus is shown in Fig. 5.24. The equipment consists of a 5.0-cm-ID glass column, 75 cm long. The settling solids are tagged with ^{59}Fe tracer. The concentration of the particles is measured by counting gamma emissions from the ^{59}Fe with a

Fig. 5.24. Apparatus for batch sedimentation studies.

NaI detector behind a collimating slit with lead shielding. Signals from the NaI detector are processed through a multichannel analyzer, yielding a signal proportional to solids concentration. The detector can be positioned at any location along the axis of the glass column.

Initial experiments have measured settling rates of 53- to 63- μm -diam ion exchange beads in water. The purpose of these experiments was to establish the capabilities of the experimental technique and to test the equipment design. No ^{59}Fe tracer was used in the initial tests. In typical results from a batch settling test (Fig. 5.25), the clear liquid-settling solids interface drops linearly with time; similarly, the sediment level rises linearly with time. One would predict these results based upon classical theory for a uniformly mixed slurry containing particles of a single size.

Settling tests will be performed with slurries in which the particles loaded with ^{59}Fe tracer are all approximately the same size. Subsequent tests will be performed in which up to three distinct particle sizes are used, each tagged with a different tracer. These experiments will provide the data to verify or disprove the Coe and Clevenger method and data to test a computer simulation now under development.

Computer simulation. Numerous experimental studies have been made with slurries of particles assumed to be the same size, shape, and density. These studies have shown that the downward velocity

28. H. S. Coe and G. H. Clevenger, *Trans. AIME* 55, 356 (1916).

29. D. C. Dixon, "Momentum-Balance Aspects of Free-Settling Theory. I. Batch Thickening," *Sep. Sci.* 12, 193 (1977).

Fig. 5.25. Batch sedimentation test results.

of the solids can be correlated with the Stokes velocity of the particle and the solids concentration in the slurry. Utilizing relationships of this type, a computer program is under development to simulate batch sedimentation tests. A finite-difference procedure is used, in which the cylinder containing initially a uniform suspension is divided into a number of height increments. The mass of particles in each increment is initially assumed to be located in a plane at the mid-height of the increment. Time is also incremented, and the velocity and location of each group of particles are calculated for each time increment using the void fraction of the height increment in which it is located. The simulator is designed so that a system with up to three different particle sizes can be tested.

5.4 FUNDAMENTAL PROCESSES IN ADSORPTION PUMPING AND TRANSFER OPERATIONS USING DEEP BEDS OF ADSORBENTS

At least three energy-related areas can be identified in which deep beds of sorbents are used to transport (or pump) and store gases or volatile material: (1) vacuum pumping, (2) hydrogen storage, and (3) tritium or hydrogen purification. Representative systems from each of these three deep-bed sorption processes are being studied to determine the relative importance of transport and equilibrium processes. Physical properties (thermal conductivities, diffusivities, equilibrium adsorption isotherms, reaction rate constants, etc.) will be derived from the literature, where possible, or determined in separate experiments. The properties will then be used in mathemat-

cal models being developed to predict the performance of these systems.

The first phase of this work involved modeling iron-titanium hydrogen storage beds. In earlier work it was found that an equilibrium model in which heat transfer controlled bed performance predicted many of the rather unusual aspects of the experimental temperature and pressure curves quite well; however, events such as maximum temperature were predicted to occur at the wrong times. The model was then modified by adding the effects of chemical kinetics. Eight different rate expressions, which included both pressure- and composition-dependent forms, were added to the model for comparison with the data. An expression which has the form $dC/dt = kC_s(C^* - C)/(C_s - C^*)$ predicted the data most accurately. In this expression, C is the composition of the storage medium at a specific node, C^* is the equilibrium composition at the temperature and pressure of the node, and C_s is the saturation composition of the material. It has been found that $C_s \sim 0.75$, which means that only about 75% of the material in the bed is available for hydrogen storage.

Construction of the experimental apparatus for the vacuum pumping phase of this work has been completed. The apparatus consists of a 1.73-cm-diam by 30-cm-long cylinder bed, which is cooled by immersion in an appropriate coolant (e.g., liquid nitrogen). Various adsorbents, depth of adsorbent, adsorbates, and temperatures will be explored. The apparatus is fitted with constant feed rate valves, which are calibrated for several gases. The inlet pressure and differential pressure across the bed will be measured as a function of feed rate and time.

5.5 RESOURCE RECOVERY

Combustion of pulverized coal in power plants for the generation of electricity forms about 60 to 70 million tons of fly ash annually in the United States. About one-fifth of this ash is currently utilized in pozzolanic cements and other, smaller markets with the remainder being discarded, primarily by landfill or wet ponding techniques. We have had an active program for the last few years to investigate methods of recovering valuable materials from fly ash.³⁰⁻³²

30. F. G. Seeley and W. J. McDowell, "Process for Recovery of Metal Values from Fly Ash," U.S. Patent 4,252,777 (Feb. 24, 1981).

31. F. G. Seeley and W. J. McDowell, "Salt-Soda-Sinter Process for Recovery of Metal Values from Fly Ash," U.S. Patent 4,254,088 (Mar. 3, 1981).

32. R. M. Canon, A. D. Kelmers, W. J. McDowell, F. G. Seeley, and J. S. Watson, "Metal Removal from Coal Ashes and Wastes," pp. 120-34 in *Solid Waste Research and Development Needs for Emerging Coal Technologies*, American Society of Civil Engineering, San Diego, 1979.

Much of the experimental work has centered on alumina since fly ash could supply an appreciable portion of the U.S. aluminum demand, which is now obtained primarily from foreign bauxite deposits. Fly ashes from power plants located throughout the United States were characterized with regard to both chemical and physical properties. Various methods of solubilizing aluminum were evaluated. These included acidic and basic leach methods as well as sinter-leach and pressure digestion-leach techniques. The solubilization of aluminum and other metals from various fly ashes was correlated with the chemical and physical properties of the respective ashes. The recovery and purification of alumina from both sulfuric acid and hydrochloric acid leach solutions were investigated. Iron and some other contaminants were removed from the leach solution by solvent extraction or ion exchange techniques. Further purification of aluminum from sulfate solutions was achieved by ammonium alum precipitation, while hydrogen chloride gas sparging was used to precipitate purified aluminum chloride from chloride solutions. Alumina was obtained from some of these precipitates by calcination and was compared with typical Bayer plant alumina specifications.

Dissolution Chemistry of Fly Ash

The chemistry of the dissolution of aluminum from fly ashes by the direct acid leach method was investigated.³³ Significant results may be summarized as follows:

1. Fly ashes are complex, nonequilibrium mixtures of crystalline, glassy amorphous, and irregular, spongy amorphous phases. Aluminum may be present in any or all of these phases.
2. The content of basic elements of the fly ash, primarily calcium, plays a significant role in the aluminum distribution among these fly-ash phases. High-base-content ashes contain little or no crystalline aluminum compounds and may have much of the aluminum in the irregular amorphous phase, whereas a significant fraction of the aluminum in low-base ashes is found in the crystalline mullite phase.
3. Aluminum solubilization behavior in hydrochloric acid leaching is controlled by the properties of the three solid phases and may vary dramatically for different ashes. Western ashes show rapid and major aluminum solubilization at ambient temperature and short times, whereas eastern ashes

give substantially lower aluminum solubilization even at high temperatures and extended times.

4. The explanation of fly ash dissolution behavior based on these considerations is qualitative, and caution should be exercised in generalizing direct acid leach process behavior based on information from a single ash.
5. Since dissolution behavior is related to the original mineral composition of the coal, the same coal used in different power plants would be expected to yield fly ashes of similar aluminum solubilization behavior. Conversely, a given power plant using coal from different sources could produce fly ashes of widely different properties with concomitantly different leaching behavior.

Hydrochloric acid leach kinetic tests for several fly ashes were carried out at three temperatures and the data plotted (Fig. 5.26) as the fraction of aluminum

33. A. D. Kelmets, B. Z. Egan, F. G. Seeley, and G. D. Campbell, "Direct Acid Dissolution of Aluminum and Other Metals from Fly Ash," presented at the 110th AIME Meeting, Chicago, Feb. 22-26, 1981, and published as TMS Paper A81-24, The Metallurgical Society of AIME, Warrendale, Pa., 1981.

Fig. 5.26. Rate of aluminum solubilization from three fly ashes at 25°C, 50°C, and reflux temperature. Leach conditions: ~8 N HCl, 10% pulp density.

solubilized vs log time. Solubilization of aluminum from the South Dakota ash appeared to be almost independent of temperature after 1 h. Solubilization from the Oklahoma and Tennessee ashes was similar at reflux temperature, although these ashes were quite different with regard to base content and crystalline phases present. Dissolution behavior of these ashes was different at 50°C. These differences in leach kinetics are believed to reflect differences in the distribution of aluminum between the crystalline, glassy, and amorphous phases present in the fly ashes.

In the Calsinter method for the recovery of aluminum and other metals (Fig. 5.27), fly ash is sintered with a source of CaO such as flue-gas desulfurization scrubber sludge or limestone at 1000–1200°C, and the sinter product is ground and leached with dilute H_2SO_4 .^{34–36} The leach step parameters have been optimized following the sintering of ash and limestone mixtures of ten fly ashes. Batch leach rate studies with Tennessee ash have shown that >90% aluminum solubilization from the sinter residue was achieved in 1 h at ambient

temperature with 4 N H_2SO_4 at up to 20% pulp density. A three-stage, batch-countercurrent leach system was operated under steady-state conditions; 8.4 moles of H_2SO_4 were required per mole of Al_2O_3 solubilized from Tennessee ash sinter residue. In this countercurrent test, solubilization of aluminum (97%), iron (97%), titanium (82%), and a number of trace metals was also obtained. Solvent extraction employing a primary amine (Primene JM-T in toluene) removed 100% of the iron and 95% of several other metals in the countercurrent leach solution and rejected >90% of the aluminum to the raffinate.^{37,38} A cursory examination of the crystallization of ammonium alum from the solvent extraction raffinate by saturation with ammonium sulfate showed excellent decontamination (Table 5.5) with respect to Fe_2O_3 , K_2O , MnO_2 , and P_2O_5 . Concentrations of CaO and MgO, however, were above commercial specification limits for Bayer process alumina. Tests are under way to investigate the additional purification obtained by redissolution of the ammonium alum in saturated ammonium sulfate and reprecipitation as hydrated alumina by ammonia gas sparging. The hydrated alumina would then be sintered to yield alumina or subsequent reduction to aluminum metal.

In the pressure digestion-acid leach (PDAL) technique (Fig. 5.28), mullite is reacted with sodium hydroxide. This digestion step produces Na-Si-metal compounds that are generally soluble in mineral acid. The process is less energy intensive than the sinter-leach techniques, but reagent consumption is high. Optimization studies are continuing on the digestion

Fig. 5.27. Generalized flowsheet for the Calsinter method.

34. L. K. Felker and F. G. Seeley, "Chemical Development of the Calsinter Process for Recovering Resource Materials from Fly Ash," presented at the 178th National ACS Meeting, Washington, D.C., Sept. 10–15, 1979.

35. B. Z. Egan, F. G. Seeley, and A. D. Kelmers, "Chemistry of the Calsinter Process for Recovery of Aluminum from Fly Ash," presented at the 109th AIME Annual Meeting, Las Vegas, Nev., Feb. 24–28, 1980, and published as SME Paper 80-47, The Metallurgical Society of AIME, Warrendale, Pa., 1980.

36. F. G. Seeley, L. K. Felker, and A. D. Kelmers, "Dissolution and Recovery of Aluminum and Other Metals from Calsinter Process Sinter Product," presented at the 110th AIME Annual Meeting, Chicago, Feb. 22–26, 1981, and published as TMS Paper A81-22, The Metallurgical Society of AIME, Warrendale, Pa., 1981.

37. F. G. Seeley and W. J. McDowell, "Fe(III) Extraction Equilibria in the System $Fe_2(SO_4)_3-(NH_4)_2SO_4$ vs Primene JM-T Sulfate-Toluene," *J. Inorg. Nucl. Chem.* **43**, 375–78 (1981).

38. F. G. Seeley, W. J. McDowell, L. K. Felker, A. D. Kelmers, and B. Z. Egan, "Determination of Extraction Equilibria for Several Metals in the Development of a Process Designed to Recover Aluminum and Other Metals from Coal Combustion Ash," *Hydromet.* **6**, 277–90 (1981).

Table 5.5. Alum comparisons with Bayer alumina specifications

Element	Metal oxide based on Al_2O_3 content (%)		
	Ammonium alum	Bayer plant A	Bayer plant B
CaO	1.1	0.06	0.030
Cr ₂ O ₃	0.11	0.001	0.0003
Fe ₂ O ₃	0.0001	0.03	0.02
K ₂ O	<0.0001	0.005	0.005
MgO	0.52	0.001	0.004
MnO	0.0022	0.001	0.0015
P ₂ O ₅	<0.0001	0.005	0.01
TiO	0.013	0.005	0.002

ORNL DWG 80-1411

Fig. 5.28. Generalized flowsheet for the pressure digestion-acid leach (PDAL) method.

step of this approach, but suitable conditions have been found to be 4 h at 200°C (1.7 MPa). An HCl leach of the solids from pressure digestion yields extraction values for Al, Fe, and Ti of 90, 48, and 54%, respectively. Iron extraction is low because a significant fraction is removed during digestion. This leach can be carried out at ambient temperature in approximately 2 h.

Chloride leach liquors resulting from PDAL and from direct acid leach (DAL) are similar, and both approaches utilize the same subsequent separations methods. Proper adjustment of the free acid content (to ~12%) causes the formation of a negatively

charged iron complex. This iron can then be removed by anion exchange without affecting the aluminum in solution. Other impurities can be removed by multiple crystallization of aluminum chloride with HCl sparging. This produces high-purity crystals of $AlCl_3 \cdot 6H_2O$, which can be calcined to metallurgical-grade Al_2O_3 . Iron is stripped from the resin by dilute acid and eventually calcined to Fe_2O_3 .

Experimental investigations on the DAL approach focused on extraction; scouting studies were performed on the downstream separation of metals. Leaches of an East Tennessee fly ash^{39,44} have been performed using three common acids: HCl, H_2SO_4 , and HNO_3 . All of these acids are ineffective at ambient temperature, but at reflux temperatures (105–110°C) HCl is the most effective, and good metal removal can be achieved. Suitable HCl leach conditions were determined to be 2 to 3 h at reflux temperature using stoichiometric amounts of acid (Fig. 5.29). Essentially all metals in the amorphous phase which may be available for release to the environment after disposal are removed in the leach step. Extraction values for the three major metals (Al, Fe, and Ti) are 48, 78, and 32%, respectively.

Fig. 5.29. Relationship between aluminum extraction and leach time for an 8 N HCl leach at 17% initial pulp density.

Extraction of metals from the residues of coal gasification has also been studied.⁴⁵ Initial tests indicate that the lower burner temperatures typical of these systems will not result in formation of acid-insoluble mineral forms. High metal recoveries (>90%) can be obtained for several metals using direct acid leach.

39. J. M. Gilliam and R. M. Canon, "Removal of Metals from Coal Ash," presented at the 15th Intersociety Energy Conversion Engineering Conference, Seattle, Aug. 18–22, 1980.

Preliminary Process Economics

The techniques described previously have been combined into two processes and studied in sufficient detail to permit an economic analysis. This work was performed under contract with the Electric Power Research Institute. Three simple criteria were used in selecting the processes: (1) the process must not be dependent on site-specific markets for products (such as cement, silica, or sand), (2) it must be capable of removing all metals that are available for release to the environment after disposal, and (3) the operations in the various steps should not increase environmental concerns. The selected processes represent two general approaches to the problem. Hydrochloric acid DAL is a minimum-treatment method for removing primarily those metals available for environmental release. (This process is essentially the PDAL method without a pressure digestion step.) Pressure digestion-acid leach is a maximum-recovery process that chemically alters the insoluble mullite phase to form acid-soluble compounds, permitting essentially complete metal recovery.

Economic analyses of both processes indicate that processing 1 million tons (dry basis) of ash annually requires capital investments of \$42.5 million for DAL and \$55 million for PDAL. Yearly income is \$15 million for DAL and -\$22 million for PDAL. The operating loss for PDAL is due principally to the acid lost in neutralizing the alkali additive (NaOH), a problem common to all maximum-recovery processes. The profitability of the DAL process makes it the most attractive recovery stream to date, and efforts are continuing on its development.

5.6 ACTINIDE OXIDES, CARBIDES, AND NITRIDES

High-Temperature Equilibrium Between Thorium Dioxide, Thorium Dicarbide, and Carbon

Measurements of CO pressure over the thorium dioxide, thorium dicarbide, carbon phase region were made in the range 1328 to 1976 K.⁴⁰ These along with other consistent measurements were used to determine the 298 K second-law heat of formation and entropy values for thorium dicarbide to be 129 ± 6 kJ/mol and 67.0 ± 3 J·mol⁻¹·K⁻¹, respectively, and the third-law heat of formation value to be -122 ± 9 kJ/mol.

Chemical Compatibility of Uranium Carbides with Cr-Fe-Ni Alloys

At 1273 K, the principal products in the reaction of uranium carbides with Cr-Fe-Ni alloys are UNiC₂ and the Laves phase U(Fe,Ni,Cr)₂.⁴¹ At 973 K, the principal products are UNi₃ and (Cr,Fe)₇C₃. At the lower temperature, reaction with uranium monocarbide is limited by the rate of formation of UNi₃. Liquid formation was observed in the UC-type 316 stainless system at 1292 ± 8 K and at 1351 ± 12 K in the UC-Inconel 718 system.

Thermodynamic Studies of Thorium Carbide Fuel Preparation and Fuel/Clad Compatibility

The carbothermic reduction of thorium and uranium-thorium dioxide to monocarbide has been assessed.⁴² Equilibrium calculations have yielded Th-C-O and U-Th-C-O phase equilibria and CO pressures generated during reduction. The CO pressures were found to be at least five orders of magnitude greater than any of the other 15 gaseous species considered. This confirms that the monocarbide can be successfully prepared by carbothermic reduction. The chemical compatibility of thorium carbides with the Cr-Fe-Ni content of clad alloys has been thermodynamically evaluated. Solid solutions of (ThNi₃) and of (Cr₇C₃) and (Fe₇C₃) were the principal reaction products. The Cr-Fe-Ni content of 316 stainless steel showed much less reaction product than that of any of the other six alloys considered.

5.7 FUSION ENERGY STUDIES

Fusion energy studies in the Chemical Technology Division are concerned with the processing of tritium fuel for fusion reactors and the containment of tritium in fusion power plants. The current experimental program is investigating tritium recovery

40. T. M. Besmann and T. B. Lindemer, "High-Temperature Equilibrium Between Thorium Dioxide, Thorium Dicarbide, and Carbon," *J. Inorg. Nucl. Chem.* **43**, 981 (1981).

41. E. C. Beahm and C. A. Culpepper, "Chemical Compatibility of Uranium Carbides with Cr-Fe-Ni Alloys," to be published August 1981 in *Nuclear Technology*.

42. T. M. Besmann and E. C. Beahm, "Thermodynamic Studies of Thorium Carbide Fuel Preparation and Fuel/Clad Compatibility," pp. 277-95 in vol. 1 of *International Symposium on Thermodynamic of Nuclear Materials, 1979, Proceedings of a Symposium*, International Atomic Energy Agency, Vienna, 1980.

from liquid lithium, the most promising tritium-breeding material. Another effort is being directed toward quantifying potential tritium releases from proposed fusion power reactor designs.

Tritium Separation Technology

This program studies fundamentals of tritium separation processes needed for fusion and fission reactor systems. The major current effort is directed at methods for removing tritium from molten lithium, the most promising breeding material for fusion reactor blankets, but solid blanket materials are also considered. The tritium recovery method must be particularly efficient to maintain a sufficiently low concentration (possibly less than 10 ppm) and correspondingly low inventory of tritium in the blanket. This program has produced results which show that yttrium sorbents can remove tritium from lithium effectively.

Several forms of yttrium sorbers have been tested with a wide range of physical properties and some variation in purity. Table 5.6 summarizes these results. Yttrium from Lot 536 is very pure, relatively ductile, and similar in appearance to stainless steel. Lot 464 contains more oxygen than 536 and is more brittle, but still has the appearance of stainless steel. Yttrium sponge has the appearance of a slightly porous metallic stone. Pelletized powder is made from very pure commercially available powder. The powder is pressed into 0.635-cm (0.25-in.)-diam by 0.635-cm-long pellets at 52 MPa (7500 psi) and sintered in vacuum at 1100°C for 10 min. The resulting product is quite porous and sturdy. Lot 286 is very impure and brittle and has a highly porous and somewhat flaky laminated structure.

These materials were contacted with a batch of molten lithium containing approximately 1 ppm tritium. Results of 11 different series of runs at two different temperatures are summarized in Table 5.6.

Data have been analyzed using a model for material uptake from a limited volume of well-stirred solution. Some runs were made with, and some without, shaking of the contacting chamber to confirm that mass transfer was controlled by diffusion in the solid phase. The apparent diffusivities of the yttrium sorbents range from that reported for pure yttrium metal for Lot 536 to almost 100 times that of the pure metal for Lot 286. It appears that the diffusivities of these materials can be estimated by assuming that the pores in the yttrium sorber are filled with liquid lithium, which has a much higher tritium diffusivity than the yttrium metal.

A new, smaller effort is directed toward equilibrium and transport properties of hydrogen isotopes in adsorbents at low temperatures. Low-temperature adsorption can be used for separation and purification of hydrogen isotopes from gas streams. A cryostat has been constructed which is capable of operating at temperatures between 77 and 4.2 K, and it is currently being tested for thermal stability.

Magnetic Fusion Energy Environmental Studies

The Chemical Technology Division has contributed to a Laboratory-wide study of environmental aspects of fusion energy by providing an assessment of source terms for pollutants, waste management operations, and fuel and construction materials availability. The studies addressed a range of potential reactor design options, but quantitative estimates (except for materials) were made only for a water-cooled reactor design (STARFIRE) prepared by Argonne National Laboratory and a helium-cooled reactor with blankets much like an ORNL-Westinghouse design. The studies incorporated the best information available from similar operating systems as well as the details available from fusion reactor design studies.

Table 5.6. Summary of yttrium sorber data

Sample	Surface area (m ² /g)	Density area Density of yttrium	Diffusivity in sorber	
			Diffusivity in metal	
			300°C	400°C
Lot 536	0.0051	0.982	2.0	0.80
Lot 64	0.034	0.968	8.3	
Sponge	0.055	0.867	31	
Pelletized powder	0.090	0.505	51	
Lot 286	0.368	0.503	96	17

5.8 URANIUM RECOVERY FROM LOW-LEVEL AQUEOUS SOURCES

A literature review and technology assessment was undertaken to evaluate low-level aqueous sources as potential unconventional uranium resources for the future. Known reserves of terrestrial uranium ores are limited and may constrain nuclear power expansion at some future date, depending upon the assumed scenario and mix of burner and breeder reactors. Both freshwater and seawater sources of uranium were considered. An ORNL TM report was prepared,⁴³ the abstract of which follows:

The aqueous sources of soluble uranium were surveyed and evaluated in terms of the uranium geochemical cycle in an effort to identify potential unexploited resources. Freshwater sources appeared to be too low in uranium content to merit consideration, while seawater, although very dilute (~ 3.3 ppb), contains $\sim 4 \times 10^9$ metric tons of uranium in all the world's oceans. A literature review of recent publications and patents concerning uranium recovery from seawater was conducted. Considerable experimental work is currently under way in Japan; less is being done in the European countries. An assessment of the current state of technology is presented in this report. Repeated screening programs have identified hydrous titanium oxide as the most promising candidate adsorbent. However, some of its properties such as distribution coefficient, selectivity, loading, and possibly stability appear to render its use inadequate in a practical recovery system. Also, various assessments of the energy efficiency of pumped or tidal power schemes for contacting the sorbent and seawater are in

major disagreement. Needed future research and development tasks are discussed. A fundamental sorbent development program to greatly improve sorbent properties would be required to permit practical recovery of uranium from seawater. Major unresolved engineering aspects of such recovery systems are also identified and discussed.

5.9 CHEMICAL THERMODYNAMIC ASSESSMENTS FOR FLUIDIZED-BED COAL COMBUSTORS

An assessment of the chemical equilibria expected between coal ash and CaO in an atmospheric, fluidized-bed combustor was performed.⁴⁴ It was concluded that, as coal ash approaches equilibrium with limestone, (1) temperatures above 1150–1250 K preclude CaSO_4 formation and (2) under conditions in which CaSO_4 is an equilibrium phase, the ash decreases the CaSO_4 stability, significantly raising SO_2 pressures.

43. A. D. Kelmers and H. E. Goeller, *Uranium Recovery from Low-Level Aqueous Sources*, ORNL TM-7652 (March 1981).

44. T. M. Besmann, T. B. Lindemer, and C. Ling, "Thermodynamic Calculations on Coal Ash and CaO Interactions," *Ceramic Bull.* 59(4), 484 (1980).

6. Biotechnology and Environmental Programs

This section reviews research and development in the following areas: (1) chemical processes that utilize living microorganisms or active fractions from living organisms, (2) advanced automated analytical instrumentation and techniques for application to analyses of physiologic fluids and to chemical process control, (3) monitoring of fossil energy process facilities to determine environmental suitability, and (4) chemical processes for pollution abatement.

6.1 BIOPROCESS RESEARCH AND DEVELOPMENT

Research and development work in bioprocesses has emphasized the production of fuels and chemicals from biomass and the development of new generic technology. Recent activities have been in five major areas: (1) assessments, (2) photosynthetic water splitting, (3) cellulase kinetics and stabilization, (4) fixed-film bioreactors, and (5) ethanol recovery. Other bioprocess work on the biosorption of heavy metals is described in Sect. 3.4.

An overview paper entitled *The Outlook for Biofuels* was prepared for the ORNL National Energy Perspective (ORNL PPA-81 6). The overview addresses technical, environmental, economic, and social issues. The most attractive approach for mid- and long-term biomass energy production appears to be an integrated biomass energy facility that would grow woody biomass in an intensive manner, harvest and convert it to a useful form (fuels or chemicals), and use the waste products as nutrients to grow more biomass. Recommendations for research and development include new plant species, genetic engineering, new cultivation and harvest methods, and improved rates, yields, and energy efficiency in biomass conversion and separation processes.

An assessment of the potential for nonfuel chemicals from biomass is under way. Major issues are being identified through extensive contact with

recognized biomass authorities. A linear programming algorithm is being used to optimize the projected use of various biomass resources for the production of various chemicals by various processing routes.

Photosynthetic hydrogen production has been studied *in vitro* and *in vivo*. Simultaneous photoproduction of hydrogen and oxygen has been measured for the first time by the *in vitro* chloroplast-ferredoxin-hydrogenase (CFH) system. This result provides direct demonstration of true photosynthetic water splitting by the CFH system. Data are indicated in Fig. 6.1. The turnover kinetics were studied using single-turnover flashes of light, and the results are shown in Fig. 6.2. Decreased yields per flash at higher frequencies are interpreted to indicate kinetic saturation of the CFH system. The intrinsic rate capability of the CFH system is quite rapid and exhibits turnover rates for both hydrogen and oxygen in the millisecond time scale. The measured turnover kinetics are comparable to the maximum rate of excitation computed for photosynthetic reaction centers in full sunlight. Since normal

Fig. 6.1. First demonstration of simultaneous photoproduction of hydrogen and oxygen in cell-free chloroplast-ferredoxin-hydrogenase system.

Fig. 6.2. Hydrogen and oxygen yields per flash vs frequency.

photosynthesis occurs at rates less than this maximum, these results indicate that in vitro hydrogen production can utilize higher light intensities than normal photosynthesis can utilize. Hence more efficient use of light energy at higher intensities can be obtained.

In vivo studies have been performed with microscopic and macroscopic marine algae. These organisms offer routes for the production of hydrogen and oxygen from seawater, a virtually inexhaustible resource currently subject to no agricultural or human consumption demand. Several species have been shown to be capable of simultaneous photoproduction of hydrogen and oxygen,¹ as shown in Table 6.1.

The stoichiometric ratio of hydrogen to oxygen is very close to 2:1 in some cases, which suggests true photosynthetic water splitting.

Table 6.1. Summary of results on simultaneous photoproduction of hydrogen and oxygen in selected marine green algae

Alga	Strain	H ₂	O ₂
<i>Chlamydomonas</i>	11-35	+	+
<i>Chlamydomonas</i>	D	+	+
<i>Chlamydomonas</i>	0-5	+	+
<i>Chlamydomonas</i>	f-9	+	+
<i>Chlamydomonas</i>	f-17	+	+
<i>Chlamydomonas</i>	C'P	+	+
<i>Chlorella</i>	580	Trace	+
<i>Chlorella</i> sp.	0-17	-	+
<i>Haematococcus</i>	Fla-9	+	+

In other experiments with macroscopic algae,² oxygen production was observed with no simultaneous production of hydrogen. The identity of the molecular species being reduced is not known. Further study on this problem will be necessary to assess potential applications.

Studies on the cellulase enzymes are aimed at improved kinetic rates and improved stability for use in cellulose bioconversion processes. The most abundant biomaterial on earth is cellulose, the major component of woody biomass. It is a potentially important precursor for fuels and chemicals. The enzyme cellulase catalyzes the hydrolysis of cellulose to glucose, which can be fermented to produce fuels and many chemicals.

An important component of the cellulase enzyme system is β -glucosidase, which catalyzes the hydrolysis of cellobiose (a glucose dimer) to glucose. This enzyme is subject to product inhibition that can reduce the efficiency of cellulase action. The inhibition of β -glucosidase in *Trichoderma reesei* C30 cellulase by D-glucose, its isomers, and derivatives was studied using cellobiose and *p*-nitrophenyl- β -glucoside (PNPG) as substrates for determining enzyme activity. The enzymatic hydrolysis of both substrates was inhibited competitively by glucose with approximate K_i values of 0.5 mM and 8.7 mM for cellobiose and PNPG as substrate, respectively. This inhibition by glucose was maximal at pH 4.8, and no inhibition was observed at pH 6.5 and above. The α -anomer of glucose inhibited β -glucosidase to a greater extent than did the β -form. Compared to D-glucose, L-glucose, D-glucose-6-phosphate and D-glucose-1-phosphate inhibited the enzyme to a much lesser extent, unlike D-glucose-1-cysteine which was almost as inhibitory as glucose itself when cellobiose was used as substrate (Table 6.2). Fructose (2 to 100 mM) was found to be a poor inhibitor of the enzyme. It is suggested that high rates of cellobiose hydrolysis catalyzed by β -glucosidase may be prolonged by converting the reaction product glucose to fructose, using a suitable preparation of glucose isomerase.

Several chemical modifying agents have been applied to *T. reesei* C30 cellulase in efforts to increase enzyme stability. Methylacetimidate, dimethyladipimidate, dimethylpicolimidate, dimethylsuberimidate, and *O*-methylisourea have

1. Research performed in collaboration with Dr. R. R. L. Guillard of the Woods Hole Oceanographic Institution.

2. Research performed in collaboration with Professor J. Ramus of the Duke University Marine Laboratory.

Table 6.2. Comparison of various glucose derivatives and isomers as inhibitors of β -glucosidase^a

Glucose derivative or isomer	Cellobiose		PNPG	
	ν	ζ Inhibition	ν	ζ Inhibition
None	51.3	0	124.0	0
D-glucose	12.6	75	50.7	59
D-glucose-6-phosphate	32.0	38	62.7	49
D-glucose-1-phosphate	36.0	30	90.7	27
D-fructose	43.3	16	106.7	14
D-glucose-1-cysteine	14.7	71	90.7	27
L-glucose	35.6	31	93.3	25

^aEach reaction mixture contained: cellobiose, 2 mM; enzyme, 5 mg mL⁻¹; inhibitor, 5 mM or PNPG, 2 mM; enzyme, 2.5 mg mL⁻¹; inhibitor, 10 mM. Values are nmol glucose or PNP min⁻¹ mL⁻¹ (v).

been used. The first four agents caused significant loss in activity compared to the native enzyme, although the loss in activity did not seem to correlate with the extent of modification of free amino groups. The addition of *O*-methylisourea did not cause a loss in activity, and the modified enzyme appears to have higher thermal stability and improved pH-activity function. One hypothesis is that the conversion of the amino acid lysine in cellulase to homoarginine improves the thermal stability.

Fixed-film bioreactors have been employed for continuous production of ethanol from glucose by *Zymomonas mobilis* and for phenol oxidation in simulated coal conversion wastewater by a mixed bacterial fungal culture. Bioreactors employing cells of *Z. mobilis* attached to glass fiber pads were operated continuously for as long as 28 days. Ethanol production, which is related to bed-associated cell concentration, was found to occur in three distinct phases: an exponential phase, a linear phase, and a "steady-state" phase (Fig. 6.3). After prolonged operation, a bacterial floc developed in the reactor. The maximum effluent ethanol concentration and the maximum volumetric productivity were 6.4% and 152 g L⁻¹ h, respectively, and both were attained at a liquid residence time of from 10 to 15 min. Both maxima occurred after the development of the bacterial floc. The flocculant bacterium has been isolated and tentatively identified as a flocculant strain of *Z. mobilis*. The high reactor productivities observed in this system previously have been seen only in much more complex reactor systems with cell recycle and vacuum stripping.

Studies on phenol oxidation in fixed-film bioreactors indicate that the highest rates of phenol removal occur with low cell concentrations on the coal

Fig. 6.3. Ethanol production vs time in an immobilized *Z. mobilis* reactor. Arrows indicate days where changes in operating parameters were made.

support particles. Several potential explanations for this observation are being investigated, and reactor systems are being designed for continuous operation. In addition, the attachment of microbial cells to the coal particles is being studied.

A critical issue in the production of gasohol is the energy required to produce ethanol, the gasoline extender. A major portion of this energy currently is required for separation of the ethanol from a dilute aqueous phase by distillation. Nondistillation methods offer possibilities for considerable energy savings. Extraction of ethanol from an aqueous phase was studied experimentally using several six- to nine-carbon alcohol solvents and two solid sorbents, a divinyl benzene cross-linked polystyrene and an experimental proprietary molecular sieve. In each case the ethanol was recovered from the solvent or solid sorbent by vapor stripping with nitrogen or argon. All of these systems exhibited sufficiently attractive distribution coefficients and separation factors to warrant further investigation and conceptual process designs. There appears to be potential for significant energy savings compared to distillation, with similar capital costs.

6.2 MONITORING AND MEASUREMENT RESEARCH AND DEVELOPMENT

The efforts in this area have been concentrated in three general categories: (1) environmental monitoring with emphasis on characterizing effluents from advanced energy conversion processes and the development and field testing of new monitoring instrumentation; (2) personnel monitoring in which advanced measurement techniques are being developed to monitor personnel operating energy conversion processes for their exposure to toxic products or by-products; and (3) development of sophisticated instrumentation to monitor advanced fossil energy conversion processes or to measure physical properties of fluids within these processes under extreme reaction conditions.

Environmental Monitoring

One of the major objectives of this effort has been the development of instrumental technology for the monitoring of surface contamination by polycyclic aromatic hydrocarbons (PAHs) in fossil energy conversion facilities. Field tests of a recently developed instrument, the portable fluorescence "spill" spotter¹ in coal conversion pilot plants will be discussed. Ongoing efforts in the monitoring and characterization of effluents from coal conversion processes will be reviewed.

Monitoring Surface Fluorescence in Coal Conversion Pilot Plants. Development of the portable fluorescence "spill" spotter has continued, and advanced prototypes have been fabricated (see

Fig. 6.4) and field tested at pilot conversion facilities in three locations: the Solvent Refined Coal (SRC) pilot plant at Fort Lewis, Washington; the gasifier of the University of Minnesota at Duluth (UMD); and the H-Coal liquefaction pilot plant at Catlettsburg, Kentucky. The instrumental development received an IR-100 Award during 1980 as one of the 100 most significant technical products of the year.

The portable fluorescence spotter, shown in Fig. 6.4, may be powered either from a 120-V ac line or, by replacing the top of the electronics package, from an integral rechargeable battery pack, providing 60 to 90 min of continuous operation. The instrument has operated reliably during four field testing visits (two visits made to the H-Coal pilot plant), with the only operational problem being failure of a digital voltmeter. This problem occurred during the visit to the UMD gasifier when the lamp was ignited near the electrostatic precipitator.

The instrument was calibrated (at the bench and in the field) by (1) placing a disc (16-mm-diam by 3.2-mm-thick optical cement) containing known amounts of product oils or pure compounds [such as benzo(a)pyrene] in the beam, and (2) adjusting the built-in digital voltmeter to a fixed value at a set instrumental gain. Most field measurements were performed with an excitation filter centered around 360 nm (310 to 390 nm at one-half peak height, Schott UG-1) and an emission cut-on filter (cut-on at 430 nm, 50% T at 456 nm, Schott KV-450). These wavelength ranges are optimal for PAHs such as benzo(a)pyrene.

Measurements were performed in "clean" areas of the pilot plants, such as lunchrooms and offices, and in shops and operating sections of the facilities. On some occasions, tools that were being returned to tool stores after use on in-plant repair jobs were found to be heavily contaminated with PAH-containing oils that could be readily transferred to skin and other surfaces. In general, measurements in lunchroom areas indicated only low-level contamination that was usually in the form of dried spots that were not transferable. A typical set of measurements from one of the facilities is shown in Table 6.3, with contamination reported in terms of $\mu\text{g cm}^{-2}$ of a heavy distillate product. Operating areas within the older pilot plants are generally heavily contaminated with dried material that has a fluorescent emission

3. D. D. Schuresko, "Portable Fluorometric Monitor for Detection of Surface Contamination by Polynuclear Aromatic Compounds," *Anal. Chem.* 52, 13 (1980).

Fig. 6.4. Advanced prototype fluorescence "spill" spotter showing battery charger and replaceable battery pack at left of the electron module

Table 6.3. Area measurements of surface fluorescence

Measurement	Location	Distillate equiv. ^a ($\mu\text{g cm}^2$)	Comments
1	LR ^b floor	<1.3-4.4	Dried spots; not transferable
2	LR chair	2.9	Dried spots; not transferable
3	LR table	<1.3	Dried spots; not transferable
4	LR wall	<1.3	Dried spots; not transferable
5	LR wall moulding	5.4	Dried spots; not transferable
6	LR carpet	3.8	Dried spots; not transferable
7	MS ^c floor (spot)	82.5	Moist contamination
8	MS wrench No. 1	<1.3-6.0	Moist contamination
9	MS wrench No. 2	2.5->1100	Moist contamination
10	CR ^d helmet No. 1	222->1100	Contaminated with light oil
11	CR trousers	8.3	Inside pants pocket; difference between visually clean and soiled areas
12	CR trousers	<1.3	Outside of work trousers near back pocket
13	CR trousers	3.2	Spot on trousers
14	CR shirt	3.2	New shirt, worn first time; spot inside cuff, but no other contamination
15	CR boots	3.2-8.3	Difference between heel and clean (raised) portion of insole; dried material on boot not detectable without solvent (not used)
16	CR helmet No. 2	2.5-46.3	Fluorescence visible in beam

^aDetermined by referring signal to a standard curve prepared from measured amounts of heavy distillate deposited on aluminum-foil-backed paper and normalized to weight per unit surface area by dividing by the focused beam area (3.15 cm²).

^bLR = lunch room.

^cMS = machine shop.

^dCR = clothing change room.

that is concentration-quenched. When dispersed by wetting with a cleaning solvent, the fluorescence usually increases manyfold. Contamination on metal surfaces can be removed using solvents; however, contamination on bare concrete floors is difficult (and in some cases, impossible) to remove because of its porosity.

Chemical Characterization of Complex Organic Materials Resulting from Coal Conversion Processes. Chemical characterization of organics in coal-conversion-related materials is centrally important to making progress in many areas of coal conversion research. Specifically, the areas of process control technology, waste management, and evaluations of health and environmental impacts depend on analyses of a wide array of complex materials. To this end, representative samples from operating facilities need to be characterized, which involves sample preparation (preconcentration, etc.), fractionation, and molecular identification.

The work in this area is divided into two subtasks. The major effort involves a base program on characterization and identification of organics in coal liquid samples (product and waste streams). The second subtask is oriented toward site-specific efforts in the Gasifiers-in-Industry (GII) Program with primary emphasis on the characterization of aqueous waste streams. In each subtask, both process development and environmental control are benefited by identifying compounds that are refractory to, removed by, or produced in the various coal conversion technologies. Experimental studies that support the development of improved cleanup procedures for aqueous effluents from the treatment of wastes from coal conversion processes will be summarized. A brief presentation will be made on the results of a study which compared the relative adsorption properties of a novel adsorbent (open-pore polyurethane foam) and three common commercial adsorbents.

Characterization of coal-conversion process waste-treatment effluents. The sampling and chromatographic analysis of profile samples of effluents from coal conversion processes serve a twofold purpose: (1) the results provide process development feedback; (2) they help to identify compounds that are refractory, removed, or are produced during the course of specific wastewater treatments. In order to accomplish these goals in a reasonable turnaround time, a commercial high-performance liquid chromatography (HPLC) system was modified. This system has allowed us to separate a synthetic aqueous coal waste in ~15 min as compared to 18 h on an ion exchange system.⁴

A series of samples from a coal tar chemical plant waste treatment facility illustrates the high resolution that can be achieved with current HPLC techniques (Fig. 6.5). These 30-min runs previously required a minimum of 17 h.⁵⁻⁷ Multiple detectors, including uv-absorbance and fluorometry, greatly aid in compound detection and identification. As can be seen from Fig. 6.5, wastewater treatment for this particular coal tar chemical plant is extremely effective in removing organic compounds.

The efficacies of a number of cleanup procedures for aqueous coal conversion wastes have been evaluated. Comparisons of the various treated wastes have been accomplished using HPLC. A single test liquid, the aqueous waste from the ORNL Bench-Scale Hydrocarbonization Experiment (BSHE) coal liquefaction process (run HC-25), was used throughout these studies. Figure 6.6 illustrates the response of a fluorescence detector following chromatographic separation of HC-25 scrubber waste before and after a lignite adsorption cleanup. Responses recorded by an ultraviolet detector were virtually identical, whereas the fluorescence monitor (Fig. 6.6) indicated that considerable removal of fluorescing products had occurred in the wavelength ranges usually representative of PAHs. These results were confirmed by other analytical data for the two samples shown below:

	Total organic carbon (ppm)	Phenol (ppm)
Before cleanup	107	4
After cleanup	100	3.7

These values represent a material decrease of <7%, where a total fluorescence decrease of 40% was noted. This study indicates the utility of multiple detectors and the effectiveness of this particular adsorption method in selectively removing certain fluorescing materials. An alternative procedure using activated sludge was found to be even more effective by the

4. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for the Period Ending December 31, 1978*, ORNL-5520 (April 1979).

5. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for the Period Ending March 31, 1978*, ORNL-5421 (July 1978).

6. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for the Period Ending June 30, 1978*, ORNL-5444 (November 1978).

7. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for the Period Ending Sept. 30, 1978*, ORNL-5487 (January 1979).

Fig. 6.5. Chromatographic profiles of aqueous effluents from a three-stage waste treatment facility.

Fig. 6.6. Reverse-phase chromatograms of HC-25 wastewater before and after lignite adsorption using fluorescence detection.

same monitoring procedure because it completely removed the fluorescing compounds along with 80 to 90% of the uv-absorbing components.

This cleanup methodology has been developed further by subsequently treating the biotreated (activated sludge) wastes with activated charcoal and ozonation. Studies involved utilizing these methods in series and varying the order of treatment. To evaluate the effectiveness of these tertiary treatments, the aqueous products were chromatographed. Results indicated that the order of treatment was extremely significant, with the most effective treatment being ozonation followed by charcoal adsorption. It was speculated that ozonation degrades the existing organic compounds (hydroquinones, trimethylpyridines, etc.) into smaller species or, at least, into those with a greater affinity for the adsorption media. Further studies, quantitative as well as qualitative, are being carried out on ozonated HC-25 waste to determine the mechanism of this phenomenon. The knowledge gained from these studies should prove useful in designing the aqueous waste treatment facility for H-Coal in Catlettsburg, Kentucky. Detailed results of these aqueous waste treatment effluent studies have been reported.⁸

Adsorption studies in tertiary wastewater cleanup. A comparative study was carried out to determine the efficiencies of a variety of novel and commercial adsorbents for coal waste cleanup. One such adsorbent is open-pore polyurethane (OPP) foam—a material produced by reacting a polyaryl-polyalkylene-polyisocyanate with a polyol in the presence of a catalyst:

The polymer structure is a very uniform agglomeration of spherical particles, with uniform diameters of 1 to 10 μm ; the latter is influenced by reaction time and temperature. Optimum reaction conditions for polymerization were determined by electron microscopy and flow-rate studies. Using optimized conditions, large 1- by 12-in. OPP columns were prepared and compared with the use of a four-column bench-scale adsorption apparatus, having the same type columns filled with three common commercial adsorbents (XAD-2, Columbia activated charcoal, and Ambersorb XE-348). Breakthrough curves for total organic carbon (TOC), total phenol, etc., on a synthetic and an actual coal conversion wastewater were then obtained for each of these columns.^{9,10}

Extensive work had been done in the past on the characterization and identification of components in coal conversion wastewaters; hence the general classes of compounds present were known. With this in mind, a synthetic feed was prepared with representative compounds from a number of these classes, including the following: aniline (primary amine), 2,4,6-trimethylpyridine (simple nitrogen ring compound), 2,6-dimethylquinoline (nitrogen heterocyclic), phenol (parent of phenolic class), 3,4-xyleneol (dimethyl phenol), and indole (nitrogen heterocyclic). In addition, the scrubber water from a bench-scale carbonizer (representing an actual conversion wastewater) was used as a feed in these studies. Figure 6.7 illustrates the breakthrough curves for TOC obtained for each of these columns using

Fig. 6.7. Total organic carbon breakthrough curves for synthetic feed on 1- by 12-in. columns of the bench-scale adsorption apparatus. C/C_0 = concentration (i.e., TOC in ppm) of effluent divided by concentration of feed. One aliquot = 34 mL (i.e., 10 min at 3.4 mL/min).

8. M. S. Denton and S. R. Dinsmore, "Characterization and Identification of Organics in Coal-Conversion Process Aqueous Waste-Treatment Effluents," presented at the Thirty-first Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, New Jersey, Mar. 10-14, 1980.

9. M. S. Denton, S. R. Dinsmore, J. I. Brand, J. Beams, and F. L. Ball, "Open-Pore Polyurethane as a Medium for Coal Conversion Process Aqueous Effluent Cleanup," *First Symposium on Separation Science and Technology for Energy Applications*, ed. by A. P. Malinauskas, *Sep. Sci. Technol.* 15(3), 587-613 (1980).

10. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for the Period Ending Dec. 31, 1979*, ORNL-5630 (April 1980).

synthetic feed. It is apparent from these data that XAD-2, a styrene divinylbenzene copolymer, exhibited little capacity for the constituents of this feed; however, the two commercial carbonaceous materials (Columbia activated charcoal and Amborsorb XE-348) exhibited a relatively high capacity for all components. A detailed description of this work appears in the literature^{9,10} and indicates that the nitrogen-containing compounds (a primary amine and pyridine) broke through rapidly on XAD-2 and the open-pore polyurethane, while the latter exhibited a good capacity for phenol. With such class and individual compound breakthrough data, a tertiary cleanup stage can be designed to fit individual process requirements.

Additional work has also been performed which employs other types of adsorption media on an analytical scale, using 10- by 0.4-cm-ID columns.¹¹ With such columns, a greater variety of experimental variables can be conveniently investigated. Effluents from these columns during breakthrough studies can be easily collected and, after extracting them into a suitable organic solvent (e.g., methylene chloride), can be analyzed by glass capillary gas chromatography. This method enables the investigation of the breakthrough behavior of individual components of very complex solutions (e.g., *o*-, *m*-, and *p*-cresol and 3,4-, 2,3-, 3,5-, 2,4-, and 2,6-xylenol), thus providing valuable information concerning the manner in which compounds in aqueous wastes are removed, degraded, or made refractory to various cleanup processes. Scale-up studies are under way relating analytical- to bench-scale operations. Additional coal conversion wastewater streams are also being examined. A summary of the adsorbent comparison work presented in ref. 11 is given for a number of common adsorbents in Table 6.4.

Personnel Monitoring

The efforts in this area have been oriented toward development of measurement technology or instrumentation to monitor personnel exposure to toxic products of energy conversion processes. Measurement of physiological changes that have been induced as a result of exposure to PAHs is one avenue being pursued. In addition, measurements of skin contamination by carcinogenic liquid coal products are being performed using the fluorescence "spill" spotter, with the ultimate goal of this work being the development of a dose-response relationship using animal models for these important products that have a strong potential for inducing skin carcinogenesis. In keeping with the previous analytical

biomedical expertise that has been developed in the division, CTD personnel have been involved in the development of a new, centralized clinical laboratory facility in the Health Division at ORNL, and its formation and initial operation will be described briefly. Such involvements are extremely useful since they interface the development scientist with the medical community and provide the potential for early application of new instruments and methodologies in the real world.

Development of Monitoring Techniques for Exposure of Operating Personnel to Polycyclic Aromatic Hydrocarbons. The purpose of this program is to develop rapid, sensitive methods by which personnel in the energy conversion industry can be monitored for their exposure and physiological response to potentially carcinogenic PAHs and related chemicals.

Multi-ring aromatics such as 1,2-benzo(*a*)pyrene (BaP) are abundant in synthetic liquid and solid fuels produced from coal, and a large percentage of these PAHs have been found to yield compounds of strong carcinogenic and/or mutagenic potential after undergoing activation by mammalian enzyme systems. Many PAHs are metabolized to produce reactive intermediates that are thought to interact with susceptible sites in the genetic material. This metabolic activation is achieved by a complex of enzymes known as the cytochrome P-450 mixed-function oxidase (MFO) system, which is genetically microheterogeneous and is differentially induced (i.e., its activity is enhanced) by prior exposure to PAHs. Thus determination of MFO activity and inducibility may serve as a means for estimating the extent of human exposure to PAHs, for early diagnosis of overexposure and/or precancerous physiological changes, and for screening hypersusceptible personnel all of which are clearly required components of the health protection practices of the developing synthetic fossil fuel industry.

The subset of cytochrome P-450 mediated MFO preferentially induced by exposure to PAH-type inducers [e.g., 3-methylcholanthrene (3-MC), benz(*a*)anthracene (BA), and BaP] has been referred to as "aryl hydrocarbon hydroxylase" or cytochrome P-448 MFO. This MFO activity is associated with the endoplasmic reticulum of many

11. M. S. Denton and S. R. Dinsmore, "A Comparison of Synthetic Process Aqueous Effluent Cleanup," presented at the American Chemical Society National Meeting, Las Vegas, Aug. 24-29, 1980.

Table 6.4. Adsorbent optimization summary table: number of micro grams of each compound passed through each column prior to breakthrough ($C/C_0 \geq 0.3$)^a

Compound	Column						
	XAD-2	XAD-4	XAD-7	XAD-8	ACC	UC	XE-348
Phenol	249	996	498	996	4831 (0.0000)	1992	1494
2,4,6-Trimethylpyridine	54	270	1079	1079	5233 (0.0000)	2698	2698
<i>o</i> -Cresol	407	2172	1086	1086	5267 (0.0000)	3258	1629
<i>p</i> -Cresol	384	2046	1023	1023	4962 (0.0000)	3069	2046
2,6-Xylenol	760	3039	1013	1013	4913 (0.0000)	4305	2533
2,4-Xylenol	886	4052	1013	1013	4913 (0.0000)	4305	3039
3,5-Xylenol	887	4056	1014	1014	4918 (0.0000)	4310	3042
2,3-Xylenol	624	2994	998	998	4840 (0.0000)	4242	2495
3,4-Xylenol	626	3003	1001	1001	4855 (0.0000)	4254	3003
Indole	880	4024	2012	2012	4879 (0.0000)	4779 (0.0646)	4527
Biphenyl	753 (0.0860)	2580 (0.0120)	1927 (0.0590)	1566 (0.0300)	587 (0.0000)	575 (0.0000)	572 (0.0000)
2,6-Dimethylquinoline	4684 (0.1890)	12,876 (0.0740)	2004	3106	4860 (0.0000)	4760 (0.0000)	4734 (0.0000)
β -Naphthylamine	3045	10,658	2030	3147	4923 (0.0000)	4821 (0.0000)	4796 (0.0000)
2-Aminobiphenyl	5343 (0.1200)	16,250 (0.0460)	7588	9864 (0.2137)	2407 (0.0000)	2357 (0.0000)	2345 (0.0000)
Phenanthrene	431 (0.1680)	1311 (0.3000)	980 (0.0000)	796 (0.0000)	550 (0.0000)	539 (0.0000)	536 (0.0000)

^aIn cases where the defined breakthrough point was never reached during the run, the actual final C/C_0 value is given in parentheses.

mammalian cells and has been studied in liver microsomes, skin tissue, lymphocytes and monocytes,^{12,14} and in lung cells (such as pulmonary macrophages).¹⁴ The latter cell types (lymphocytes, monocytes, and pulmonary macrophages) represent samples that potentially may be collected from plant personnel in order to monitor P-448 MFO activities.

In our initial efforts,¹⁵ we used as an animal model fibroblasts from the 15-day-old fetuses of Syrian hamsters that had been isolated by successive tissue subculturing. In the final culturing, the cells were grown in a medium containing varying amounts of a standard inducer, BA, or a coal-derived tar or liquid. Enzyme induction was assessed by the subsequent rate of metabolism employing BaP as substrate, using the measurement procedure developed by Nebert and Gelboin.¹⁶ We found that typically the maximal

MFO activity was eightfold inducible at a 1.4-ppm (6- μ M) concentration of BaP in the growth medium.

12. J. B. Vaught et al., "Comparison of Benzo(a)pyrene Metabolism by Human Peripheral Blood Lymphocytes and Monocytes," *Can. Let.* 5(5), 261-68 (November 1978).

13. T. L. McLemore et al., "Analysis of Arylhydrocarbon Hydroxylase Activity in Human Lung Tissue, Pulmonary Macrophages, and Blood Lymphocytes," *Cancer (Philadelphia)* 41(16), 2292-2300 (1978).

14. H. W. Tyrer, E. T. Cantrell, and A. G. Swan, "Automated Single-Cell Analysis of Arylhydrocarbon Hydroxylase in Human Lymphocytes," *Life Sci.* 20(10), 1723-28 (1977).

15. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542 (November 1979).

16. D. W. Nebert and H. V. Gelboin, "Substrate-Inducible Microsomal Arylhydroxylase in Mammalian Cell Cultures. I. Assay and Properties of the Induced Enzyme," *J. Biol. Chem.* 243, 6242 (1968).

In some experiments, we used a "direct" assay, monitoring the decrease of BaP substrate by the decrease with time in its fluorescence ($\lambda_{EX} = 303$ nm, $\lambda_{EM} = 404$ nm). By using this procedure, we demonstrated that a sample of UMD gasifier tar produced a maximal fourfold induction of MFO activity at a concentration of only 0.05 ppm in the growth medium (Fig. 6.8); thus the UMD tar is a significantly more potent MFO inducer (on a weight basis) than is BaP. However, the measurement of a

Fig. 6.8. Induction of P-450 mixed-function oxidase enzyme by a coal tar.

small decrease in substrate fluorescence with a substantial nonspecific fluorescence background makes this procedure again relatively difficult to automate.

The assay procedure of Nebert and Gelboin, although highly sensitive, is rather tedious (multiple extractions are required) and restrictive (only a fraction of the total metabolites formed are actually measured), and it is not well-suited for automation.

Evidence indicates that the metabolism of the synthetic substrate 7-ethoxyresorufin (7-ER) is under the same genetic control as the metabolism of BaP via the cytochrome P-448 MFO complex,^{17,18} and its activity may specifically reflect this P-448-associated

activity. The substrate is not thought to be carcinogenic and yields a single highly fluorescent metabolite, resorufin. No extraction steps are required, and the direct enzymatic assay is easily automated. We have adapted the assay to the centrifugal analyzer system, with its computer system and ancillary automated rotor loading equipment, thus permitting high sample throughput (up to 15 samples per assay, plus an onboard fluorescence standard). In our more recent work, we have used 7-ER substrate to study the dose-response relationship of this enzyme induction for a number of xenobiotics, using mouse liver microsomes (high MFO content) as the cell model. The test compounds were dissolved in corn oil, and a single injection was made intraperitoneally into C57 B6 mice 48 h prior to their sacrifice and the subsequent preparation of microsomal protein pellets for analysis. For the PAH compound 3-methylcholanthrene, we noted a significant cytochrome P-448 MFO induction at a dose of only 5 mg/kg, with maximal induction at doses in excess of 25 mg/kg. Some compounds other than PAHs, notably planar polychlorinated aromatic hydrocarbons,^{19,20} also induce cytochrome P-448 MFO activity, and there is reportedly a correlation between this enzyme induction and the various toxic responses to this class of compounds. In Fig. 6.9 we examine the effect of varying dosages of polychlorinated biphenyls (PCBs) on the induction of P-448 MFO activity in these same mice. Also illustrated is the dose-response for the oxidation product of this mixture prepared by accelerated degradation (heating at 300°C for one week) in an oxygen atmosphere. Morita et al.²¹ treated Aroclor 1254 in a similar manner and afterwards found that the highly toxic compounds, polychlori-

17. M. D. Burke and R. T. Mayer, "Ethoxyresorufin: Direct Fluorometric Assay of a Microsomal O-alkylation Which Is Preferentially Inducible by 3-Methylcholanthrene," *Drug Metab. Dispos.* 2, 583 (1974).

18. M. D. Burke, R. T. Mayer, and R. E. Kouri, "3-Methylcholanthrene-Induced Monooxygenase (O-Deethylation) Activity of Human Lymphocytes," *Cancer Res.* 37, 460 (1977).

19. J. A. Bradlaw and J. L. Casterline, Jr., "Induction of Enzyme Activity in Cell Culture: A Rapid Screen for Detection of Planar Polychlorinated Organic Compounds," *J. Assoc. Off. Anal. Chem.* 62, 904 (1979).

20. A. Parkinson, L. W. Robertson, and S. Safe, "Reconstituted Human Breast Milk, PCBs as Potent Inducers of Arylhydrocarbon Hydroxylase," *Biochem. Biophys. Res. Commun.* 96, 882 (1980).

21. M. Morita, J. Nakagawa, and C. Rappe, "Polychlorinated Dibenzofuran (PCDF) Formation from PCB Mixture by Heat and Oxygen," *Bull. Environ. Contam. Toxicol.* 19, 665 (1978).

Fig. 6.9. The PCH Aroclor 1260 subjected to high-temperature oxidation: a more potent inducer of the P-448 MFO enzyme system than the original mixture.

nated dibenzofurans, were formed in significant yield (up to 1000 ppm). This class of compounds has also been found as trace impurities in some batches of industrial-grade PCBs.²² The comparative data shown in Fig. 6.9 indicate that the "cooked" material is many times more potent an inducer of MFO activity than is the original material. This simple bioassay was able to provide a quick comparison of toxicological risk in these complex, uncharacterized mixtures. We hope to extend these bulk measurements to measurements of enzyme induction in single cells from easily obtained physiologic samples.

Monitoring skin contamination by PAH. During the field tests of the fluorescence "spill" spotter at the pilot plant coal conversion facilities, the instrument was utilized to measure the amount of fluorescent contamination transferred to the skin of operating personnel during the course of normal work exposure. Measurements were performed on the hands, palms, and neck of each volunteer. Office personnel as well as operating personnel were measured. Interpretation of the resulting data was compromised by the lack of an appropriate calibration curve in which known amounts of coal liquids or PAH compounds were spotted and measured on human skin, and it was not feasible or medically acceptable to obtain such a curve. Thus results were merely recorded as fluorescent signal levels for the three measurements and are presented as incidence vs

signal level, where the signal level is roughly correlated with a quantitation in terms of $\mu\text{g cm}^{-2}$ of a heavy distillate (see Fig. 6.10). The difference here is the solubility of the product in skin lipids and its resulting fluorescence as opposed to a standard curve prepared by spotting the heavy distillate on aluminum-foil-backed filter paper. Normal background probably ranges between 0.10 and 0.15 relative fluorescence in the figure, and most measurements exceeding this level were for the palms of the hands. One individual, working in an extremely contaminated area of the pilot plant, had all three measurements elevated and was the most severely contaminated of any person monitored.

Fig. 6.10. Skin contamination of pilot plant personnel: number of occurrences vs relative fluorescence.

As the above study indicates, it is an extremely difficult task to relate topical exposure of living skin to coal liquids and to determine the potential of the various coal liquids for inducing skin carcinogenesis. Dr. J. M. Holland and his group in the Biology Division are attacking the problem by means of long-term skin "painting" experiments using hairless mice. Three distillation products obtained from each of two operating modes (fuel oil and syncrude) of an H-Coal process development unit (PDU) were studied by Dr. Holland and his group. The mice (25 male and 25 female) were exposed three times per week to 50- μL applications of 100, 50, and 25 w/v % concentrations of the six products for periods of time ranging up to 30 weeks. The animals were examined

22. J. G. Vos, J. H. Koehman, H. L. Van der Maas, M. C. de Braak, and R. H. de Vos, "Identification and Toxicological Evaluation of Chlorinated Dibenzofuran and Chlorinated Naphthalene in Two Commercial Polychlorinated Biphenyls," *Ed. Cosmet. Toxicol.* 8, 625 (1970).

daily for evidence of the formation of carcinogenic skin lesions; the number of skin tumors, days to tumor development, and deaths were tabulated over the period of the study. These data were utilized to compute a "carcinogenicity index," a relative comparison of five of these products (insufficient material for one of the products to complete its study) on the basis of their ability to cause skin tumors. Table 6.5 describes the distinguishing features of each of the products tested and their effects on the mice. Note that the relative carcinogenicities of these liquids are in rough proportion to their content of BaP. The "spill" spotter is capable of quantifying surface fluorescence on many different types of surfaces, including living skin. To ascertain its utility as a sensitive monitor of contamination on living skin, experiments were performed in which known amounts of actual coal liquids were spotted on living, hairless mice, and the fluorescence followed as a function of time by means of the "spill" spotter.

Five of the six products shown in Table 6.5 (insufficient amount of the atmospheric overhead, No. 1308, sample) were diluted with acetone to 50, 10, 1, 0.1, and 0.01 (v/v). These five dilutions of the five distillation products were applied as duplicate 2- μ L spots on each thigh of 25 hairless mice, and the fluorescence (360 nm excitation wavelength, >430 nm emission) was monitored at regular intervals over the following 72 h using the fluorescence "spill" spotter. The most potent inducers of skin tumors (sample Nos. 1314, 1309, and 1310 in Table 6.5 containing 144 to 456 μ g of BaP per g of coal liquid), at dilutions of 1:1 and 1:10 in acetone, were detectable above background for ~48 h after the 2- μ L applications. The 1:100 dilutions of the two liquids containing the highest concentrations of BaP (Nos. 1310 and 1314) were detectable for 2 to ~6 h after application, while the 1:1000 dilutions for these same three liquids were detectable only immediately after application (at ~10 min), but not after 1 h. The

Table 6.5. Results* from "skin painting" experiments on hairless mice using distillation products from two operating modes of an H-Coal process development unit

Run mode	Material (ORNL No.)	Boiling point range ^b (°C)	BaP content ^c (μ g/g)	Concentration ^d (w/v %)	Death	Carcinogenicity index
Fuel oil	Atmospheric overheads (1312)	131-270	1.5	100	0	0
				50	0	
				25	0	
	Atmospheric bottoms (1313)	179-425	43	100	0	8
				50	0	
				25	0	
	Vacuum overheads (1314)	168-438	296	100 ^e	5	83
				50	1	
				25	0	
Syncrude	Atmospheric overheads ^f (1308)	134-305	0.19	100	0	r
				50	0	
				25	0	
	Atmospheric bottoms (1309)	185-433	144	100	5	51
				50	0	
				25	0	
	Vacuum overheads (1310)	186-458	456	100 ^e	8	96
				50	8	
				25	2	
	Acetone			100	0	

*Personal communication, Dr. J. M. Holland (Biological Division), January 1981.

^bPerformed by Analytical Chemistry Division.

^cIn acetone.

^dExposure discontinued at 6 weeks due to acute skin irritation.

^eExposure discontinued at 16 weeks due to insufficient material.

atmospheric bottoms sample containing less BaP (43 $\mu\text{g g}$, No. 1313) was detectable for ~ 24 h at a 1:1 dilution; however, at a 1:10 dilution it was detectable only initially (~ 20 min after application) and returned to background within 1 h. The product containing the lowest concentration of BaP (1.5 $\mu\text{g g}$, No. 1312) was within the $\pm 2\sigma$ (95%) range of the controls for all measurements and all dilutions under the conditions of this experiment. Self-absorption or concentration quenching of the fluorescence from applications of 1:1 dilutions of the most potent oils was quite apparent; measurements at 1 h were generally much higher than the initial measurements, after the oils had solubilized in the skin lipids and diffused outward from the point of application.

For these coal liquids, our initial experiments indicate that the "spill" spotter has adequate sensitivity for meaningful skin measurements. The response and the duration of response after application appear to be related quantitatively to the BaP content of the product and to their relative potency as inducers of skin carcinogens on hairless mice.

Implementation and Operation of a Centralized Clinical Laboratory. Since 1970, personnel of the Chemical Technology Division have been involved in the implementation, routine operation, and maintenance of centrifugal analyzers in the clinical laboratory of the ORNL Health Division. These machines, which were invented and developed at ORNL, have been used to provide chemistry values for employees as they are scheduled and processed for their periodic physicals. Initially a 15-cuvette GeMSAEC centrifugal analyzer²³ was used; however, in 1973 it was replaced with a miniature centrifugal system²⁴ that had been developed using funds provided by both the Atomic Energy Commission and the National Aeronautics and Space Administration.

With an increasing repair rate, it became apparent early in 1980 that the miniature centrifugal analyzer would have to be replaced. Concurrently, the clinical laboratory at Y-12 also reported the need to replace its chemical analyzer. (At that time, the Y-12 clinical laboratory was providing analytical services for both the ORGDP and Y-12 medical divisions). Consequently, R. G. Jordan, Nuclear Division Employee Relations, and the medical directors of the three Oak Ridge plants and the Paducah facility requested a proposal to implement, staff, and operate a central clinical laboratory at ORNL that could fulfill the future analytical needs of all three Oak Ridge plants (and possibly the Paducah plant). A proposal was

subsequently prepared, submitted, and approved in April 1980. After careful consideration of the commercially available analytical systems, a Rotochem (i.e., a 36-cuvette centrifugal analyzer) was purchased from the American Instrument Co. (AMINCO). In addition, an automated flame photometer was purchased to provide the analytical capability to measure serum electrolytes.

The Rotochem was delivered in September 1980 and installed by AMINCO personnel. Two medical technologists from the Health Division and a Chemical Technology staff member subsequently attended a training course in Columbia, Maryland. During September and October, the Rotochem was thoroughly evaluated, additional technologists trained, and chemical procedures, using commercially available reagent kits were adopted and evaluated.

After a final and successful comparison of analytical results obtained from the Rotochem and the miniature centrifugal analyzer, the Rotochem was placed into routine operation on November 1, 1980. Initially, only specimens from ORNL and ORGDP were analyzed; however, in January 1981, Y-12 began to submit samples for analyses. Blood chemistries that are performed on samples from every employee and those that are available on demand include blood urea nitrogen, cholesterol, creatinine, glucose (fasting), glucose (2-h post load), triglycerides, total bilirubin, uric acid, alkaline phosphatase, lactate dehydrogenase, and serum glutamate oxoglutarate transaminase. Information is also available on the electrolytes, potassium and sodium. Currently, between 60 and 90 specimens are analyzed daily by the laboratory an annual work load of between 15,000 and 23,000 specimens.

Process Development Instrumentation

The increasing emphasis upon the development of new fossil energy conversion processes has revealed a strong need for new, innovative techniques to characterize process streams both for engineering design considerations and process feedback control. Measurements must be performed on extremely complex, difficult-to-handle process samples at high temperatures and high pressures. This section is devoted to

23. N. G. Anderson, "Computer Interfaced Fast Analyzers," *Science* 166, 317 (1969).

24. C. A. Burtis, W. F. Johnson, J. C. Mailen, J. B. Overton, I. O. Tiffany, and M. B. Watsky, "Development of an Analytical System Based Around a Miniature Fast Analyzer," *Clin. Chem.* 19, 895 (1973).

a discussion of the preliminary development or investigative efforts on instrumentation to provide (1) near on-line measurements of feed quality for the Kerr-McGee Critical Solvents Deashing (CSD) unit of the Solvent Refined Coal (SRC-I) process by means of liquid chromatography, (2) on-line measurements of donor solvent quality using electron spin resonance (ESR), and (3) thermal conductivity measurements on coal-solvent slurries using the transient hot-wire technique.

Development of Automated Class Fractionation for Coal Liquids. Probably the single most necessary step in the characterization of coal-derived process streams, products, and wastes is that of class fractionation. Whether dealing with process development such as monitoring reaction conditions, upgrading products, or doing detailed characterization and identification of constituent organics, it is much easier to deal with a fractionated sample than with the total complex coal liquid matrix. Detailed characterization, however, will require additional fractionation, but it is, essentially, an extension of that used for bulk property analysis. Class fractionation for process development and or bulk physical characterization purposes (e.g., viscosity) requires reproducible fractions containing relatively large quantities of each class type, thus demanding a system capable of large throughputs.

Many class fractionation schemes have emerged in recent years. Prominent among these are the PONA (Gulf Research and Development Company),²⁵ SARA (originally the Bureau of Mines-API Research Project 60),²⁶ modified SARA (UOP Corporation),²⁷ and SESC (Mobil Research and Development Corporation)²⁸ processes. The latter, using "sequential elution" with specific solvents chromatography" on a silica-gel column, appears to be the simplest process and the most amenable to automation. Of equal importance, SESC is the most widely accepted and used of the methods that allow for convenient comparisons between fractions and, ultimately, process conditions. However, as presently employed, the procedure is laborious, time-consuming, and expensive.

In order to provide relatively rapid, reproducible fractionation of coal liquids to answer process development questions, CTD personnel developed and fabricated a preparative-scale, prototype, automated system based upon the SESC process. For initial work, a simple pumping system delivers up to 16 sequential solvents onto a silica-gel column via an automated rotary valve. The eluate is subsequently monitored by a series of three in-line detectors,

including refractive index (RI), ultraviolet-visible (uv-vis), and fluorescence photometers. Fractions, particularly from the heavy ends of coal liquids, will be made available for the measurement of fundamental properties such as viscosity, boiling point, vapor pressure, and other rheological parameters needed for process scale-up and or plant design. More detailed characterization of some fractions may be performed, as necessary, to clarify chemistry associated with process development. In addition, bioassay studies can be performed on these reproducible, individual fractions. This information would then be correlated with the original oil sample and process conditions.

The automated SESC system has been installed in a walk-in hood (see Fig. 6.11) together with a flash evaporator for recovery of fractions free of the chromatographic eluent. Safety precautions include a ventilation system and alarm, a safety cut-off on the flash evaporator, and the relocation of all power sources and lines to the outside of the hood to avoid flashing of solvent vapors in the event of sparking. Test solutions are now being run through the system to check out timing circuits in the solvent programmer and fraction collector. The programmer, which provides control for the multipoint rotary valve, and the collector, outfitted with a movable head, allow continuous and unattended operation (usually 16-24 h per run).

Automated chromatographic class fractionation has been performed on coal-derived samples from the Wilsonville pilot plant to aid in the development of instrumentation designed to monitor the feed quality of process liquids entering the Kerr-McGee CSD unit.

Monitoring feed quality for Kerr-McGee CSD unit. The economics of the SRC-I process are sensitive to recovery from the proposed Kerr-McGee CSD unit which is, in turn, dependent on the asphaltene preasphaltene ratio of the feed. The

25. J. C. Swaton and R. E. Swab, "Rapid Hydrocarbon Group-Type Analysis by High-Performance Liquid Chromatography," *J. Chromatog. Sci.* 13, 361 (1975).

26. P. H. Given, D. C. Cronauer, W. Spakman, H. L. Lovell, A. Davis, and B. Biswas, "Dependence of Coal Liquefaction Behavior on Coal Characteristics in Vitrinite-Rich Samples," *Fuel* 54, 34 (1975).

27. F. K. Schweighardt, C. M. White, S. Friedman, and J. L. Schultz, "Heteroatom Species in Coal Liquefaction Products," p. 240 in *Organic Chemistry of Coal*, ed. by J. W. Larsen, *Am. Chem. Soc. Symp. Ser.*, Washington, D.C., 1978.

28. M. Farcasiu, "Fractionation and Structural Characterization of Coal Liquids," *Fuel* 56, 9 (1977).

Fig. 6.11. Experimental system for the separation of coal products by specific solvent elution chromatography.

asphaltene preasphaltene ratio may be regulated to some degree by controlling the severity of treatment in the dissolver. The operator, however, requires rapid, analytical data in order to regulate process conditions usefully. Such process feedback is not possible using present methods of determining the asphaltene preasphaltene ratio, which rely on time-consuming laboratory extraction and analysis. On-line sampling and rapid analysis would permit process control much closer to optimum.

A system for CSD sampling and rapid analysis is being designed and will be constructed in our laboratory. Due to the nature of asphaltenes (benzene, soluble; hexane, insoluble) and preasphaltenes (pyridine, soluble; benzene, insoluble), the principle of operation of the system is based upon automated solvent elution chromatography. Commercially available chromatographic components will be procured and assembled where possible, while existing equipment is being used for preliminary studies. A microprocessor-controlled, continuous or intermittent sampling device will feed a solids-free sample to the fractionation column. A single pumping system will then deliver the eluting solvent. Subsequent detection and data manipulation will deliver the desired feed quality ratio.

Several feed samples from the Kerr-McGee CSD unit have been fractionated on the previously mentioned SESC system (see Fig. 6.12). These samples have known percentages of oils, asphaltenes, and preasphaltenes that are being correlated to SRC product yields.

Monitoring the quality of hydrogen-donor solvents. The need for solvent characterization or solvent hydrogenation information (where hydrogen-donor capability is used as a measure of solvent quality) is emerging in many coal conversion processes (e.g., solvent refining, liquefaction, pyrolysis, and extraction). A simple and, ultimately, on-line solvent quality monitoring system is needed to assist in the control of those coal conversion processes using hydrogen-donor solvents. This problem is complicated by (1) the extremely high temperature-pressure conditions existing in and around the primary process reactor, and (2) the ensuing difficulty in sampling and making meaningful measurements within a useful time frame on the process solvent under conditions similar to those in the reactor. The purpose here is to focus on the development of measurement capabilities which are capable of being operated on-line (or as close as possible to on-line) and providing a rapid measure of solvent quality for use in donor solvent coal liquefaction plants.

Recent data in the literature suggest that ESR spectroscopy might offer a means of quickly indexing solvent quality by assessing steady-state free-radical concentrations. Preliminary research by Gulf R&D involving the effect of liquefaction processing conditions on the formation and quenching of radicals in coal-free solutions has been performed by ESR under static, nonprocess conditions.²⁹ Preliminary feasibility studies have been performed by the ORNL Chemistry Division personnel using a high-temperature, flow-through ESR instrument. This particular instrument was modified to permit the use of fluid samples that are circulated and heated (up to 600°C) with pressures up to 13.8 mPa (2000 psi). A fused-silica capillary traversing the microwave cavity of the spectrometer serves as a pyrolysis cell. Preliminary ESR experiments on donor solvent samples designated "good" and "poor" hydrogen-donor quality from the Wilsonville, Alabama (Catalytic, Inc.), SRC pilot plant indicate significant differences in the fine structure and stable radical concentration at temperatures from ambient to 580°C. At run temperatures of ambient, 350, 450, and 580°C, the sample defined by plant personnel as a poor donor exhibited an increasing degree of fine structure, but no resolved structure was apparent with the sample labeled as a good hydrogen donor. The steady-state radical concentrations differed by a factor of 2 at each temperature, the poor donor having the higher concentration, as might be expected.

Additional experiments with solvents of defined quality from another process are necessary in order to verify that an actual correlation exists between free-radical population and solvent quality index. Assuming confirmatory data, a high-temperature, high-pressure cell will be fabricated and an ESR spectrometer acquired for further testing of solvent quality under actual process conditions.

Development of instrumentation for measurement of the thermal conductivity of solvent-coal slurries. To obviate the need for ultraconservative designs with concomitant high capital costs for preheaters, reactors, pumps, and other equipment for coal liquefaction processes, knowledge of physical properties such as viscosity, density, and thermal conductivity of coal liquids under process conditions is required. The Coal Liquids Flow System (CLFS)

29. I. Petrakis and D. W. Grandy, "Free Radicals in Coal and Coal Conversion: Effect of Liquefaction Processing Conditions on the Formation and Quenching of Coal-Free Radicals," *Fuel* 59, 227 (1980).

Fig. 6.12. Specific fractions obtained by chromatographing a feed sample from the Kerr-McGee CSD unit on the SESC system.

developed by the Chemical Technology Division has been designed to measure these properties at processing conditions up to 31 MPa (4500 psig) and 810 K (1000°F). Instrumentation to measure viscosity and density is already in operation on the CLFS, and we are developing instrumentation to measure the thermal conductivity of solvent-coal slurries based upon the use of the transient hot-wire technique.³⁰ This technique is based upon the imposition of a known, constant current upon a fine wire and measuring the dissipation of heat from the wire through the liquid in which it is immersed by measuring the change in the resistance of the hot wire. The thermal conductivity of the medium is inversely proportional to the slope of the temperature of the hot wire plotted against the natural logarithm of time, as indicated by the line source solution for the Fourier heat conduction equation [Eq. (1)]:

$$T_w(r, t_2) - T_w(r, t_1) = \frac{q}{4\pi k} \ln \left(\frac{t_2}{t_1} \right), \quad (1)$$

where

$T_w(r, t_i)$ = wire temperature at time t_i ,

t = time,

q = heat input per unit length,

k = thermal conductivity of the medium,

r = line source radius.

Further discussion of this solution and the simplifying assumptions are contained in refs. 30 and 31. The change in temperature of the wire can be related to the measured change in resistance of the wire which,

30. J. J. Healy, J. J. deGroot, and J. Kestin, "The Theory of the Transient Hot-Wire Method for Measuring Thermal Conductivity," *Physica* 82c, 392 (1974).

31. E. McLaughlin and J. F. Pittman, "Determination of the Thermal Conductivity of Toluene—A Proposed Data Standard from 180 to 400 K Under Saturation Pressure by the Transient Hot-Wire Method. I. The Theory of the Technique," *Phil. Trans. R. Soc. Lond. A*-270, 557 (1971).

using constant current, can be related to a voltage change, dV , across the wire. Making the appropriate substitutions and solving for k , the apparent thermal conductivity of the medium yields Eq. (2):

$$k = \frac{I^2 R \frac{dR}{dT}}{4\pi l} \left(\frac{dV}{d \ln t} \right)^{-1}, \quad (2)$$

where

I = current,

R = resistance of line source gauge at the initial temperature of the liquid,

$\frac{dR}{dT}$ = slope of resistance-vs-temperature curve for the wire.

l = length of line source gauge.

$\frac{dV}{d \ln t}$ = slope of voltage-vs- $\ln$ (time) curve.

To obtain sufficient structural strength to withstand contact with a flowing solvent-coal slurry, the line source gauge was fabricated from 0.076-mm (0.003-in.)-diam platinum (Pt) wire brazed to Pt wire having a diameter of 0.51 mm (0.020 in.) on either end for use as electrical connectors. The line source gauge was installed within the high-temperature, high-pressure cell shown in Fig. 6.13. To verify operation of the prototype instrumentation, also illustrated in this figure, a simple, unsheathed line source gauge was immersed vertically in a 500-mL graduate containing either toluene or 18-megohm distilled

ORNL-Photo 2724-80

Fig. 6.13. Transient hot-wire thermal conductivity instrument electronics and pressure vessel for the line source gauge.

water at ambient temperature, and the thermal conductivities of the two liquids were determined. Measured values were within 1% of the literature value¹² for water and within 2% of one set of literature values for toluene¹¹ but within 0.1% of another respected researcher's data.¹⁴ Measurements of $dV/d \ln(\text{time})$ were performed over short time intervals, ~0.15 to 0.4 s after initiating the current pulse to the wire, anticipating that measurements of coal slurries within the CLFS would require such fast measurements to avoid particle settling and coking problems at high temperatures with coal-solvent slurries.

Following verification of prototype instrument operation under static ambient conditions, the high-temperature, high-pressure cell was assembled into a thermostatted test flow system to simulate operation in the CLFS. The system, shown schematically in Fig. 6.14, consists of an insulated, temperature-controlled bath in which the cell and a liquid reservoir are contained. Liquid from the reservoir can be pumped at 1 to 2 mL/min through the cell, which can be isolated by means of three-way inlet and outlet valves. In this manner, liquid flow is interrupted by bypassing the cell. Rapid isolation tests will be performed with the flow-through system at ambient and elevated temperatures (<360 K) to determine if eddy heat currents are generated causing convection effects around the wire. Initial testing of the system in a static mode at ambient temperature yielded measurements that were in agreement with the literature data. The data appeared to reflect minimal heat losses

from the ends of the wire ("end effects"), as indicated by the small deviation from linearity over the time interval 0.14 to 1.5 s in Table 6.6. The absence of appreciable "end effects" was due partially to a glass encapsulation of the 0.51-mm Pt wire end leads immediately adjacent to the line source gauge.

Future efforts will be directed toward verification of operation at temperatures to ~360 K followed by installation in the CLFS. Operation of this system to date has been quite satisfactory.

32. R. C. Weast (ed.), *Handbook of Chemistry and Physics*, 55th ed., The Chemical Rubber Co. Press, Inc., Cleveland, Ohio, 1974.

33. *Ibid.*, p. 579.

34. H. Poltz and R. Jugel, "The Thermal Conductivity of Liquids. IV. Temperature Dependence of Thermal Conductivity," *Int. J. Heat Mass Transfer* 10, 1075 (1967).

Table 6.6. Effect of time interval on thermal conductivity of toluene in high-temperature, high-pressure cell

Time interval (s)	Apparent thermal conductivity ^a (mW cm ⁻¹ K ⁻¹)	Correlation ^b coefficient
0.14 0.40	1.310	0.9994
0.14 0.70	1.308	0.9998
0.14 1.0	1.312	0.9999
0.14 1.5	1.320	0.9999
0.14 2.0	1.331	0.9998
0.14 3.0	1.348	0.9997
0.14 4.0	1.361	0.9996

^aAt a power level.

^bFor linear regression of voltage vs $\ln(\text{time})$.

Fig. 6.14. Schematic of experimental setup to simulate operation of thermal conductivity instrumentation in the Coal Liquids Flow System.

6.3 ENVIRONMENTAL CONTROL TECHNOLOGY

Environmental control technology programs conducted during this reporting period included monitoring and assessment at fossil energy plants, design and development efforts for a mobile, pilot-scale wastewater treatment system for use at fossil energy plants, and bench-scale evaluations of toxicity and mutagenicity phenomena that may be associated with treatment processes proposed for handling wastewaters generated at fossil energy sites. In addition, several basic environmental sciences programs such as the characterization of nonvolatile organics in disinfected wastewater were conducted on a continuing basis. Finally, a 190-m³/d demonstration plant for wastewater treatment based on the ANFLOW system was designed, and construction was initiated. This project includes the city of Knoxville, Tennessee, as a cooperative partner. Other work on nitrate removal from wastewater is described in Sect. 3.4.

Monitoring Assessment Programs for Environmental Control Technology at Fossil Energy Plants

The Life Sciences Synthetic Fuels Program at Oak Ridge was commissioned by DOE to implement an extensive environmental monitoring and sampling program at several coal conversion facilities supported by DOE. It was proposed that during a 2- to 3-year demonstration period for each facility, information would be gathered to support the analysis and assessment of each coal conversion technology. These on-going assessments will permit DOE and other federal agencies to judge the potential environmental and health impacts and consequent environmental acceptability of further commercialization. Under this program the Chemical Technology Division has been involved in analyses and assessments for the UMD gasifier project,³⁵⁻⁴¹ the coal gasification project in Pike County, Kentucky,⁴²⁻⁴⁵ and the H-Coal project in Catlettsburg, Kentucky.⁴⁶⁻⁵⁰ A summary of these projects and the results obtained during this reporting period are given below; the data are given in detail in the indicated references.

In the UMD gasifier project, an existing oil-fired heating plant was converted to burn low-Btu gas produced by coal gasification. Tar by-products from the gasifier are being collected and used for peak heating requirements in an existing oil-fired boiler.

The design capacity for this plant is a normal 65 t/d of western subbituminous coal. The major components of the heating plant, illustrated in Fig. 6.15, include a coal-handling section, the gasifier, environmental control devices, and the boiler-steam off-gas section. A simplified flow schematic and the ORNL-defined sampling points are shown in Fig. 6.16.

Fig. 6.17 shows a timeline of the UMD operations. Run 5 (November and December 1979) and Run 6 (February 1980) were successful, with the gas

35. University of Minnesota-Duluth Coal Gasification Project Status Report for the Period Ending Sept. 30, 1979, ORNL TM-7272 (June 1980).

36. University of Minnesota-Duluth Coal Gasification Project Quarterly Progress Report for the Period Ending Dec. 31, 1979, ORNL TM-7268 (June 1980).

37. University of Minnesota-Duluth Coal Gasification Project Quarterly Progress Report for the Period Ending Mar. 31, 1980, ORNL TM-7354 (August 1980).

38. University of Minnesota-Duluth Coal Gasification Project Quarterly Progress Report for the Period Ending June 30, 1980, ORNL TM-7466 (February 1981).

39. University of Minnesota-Duluth Coal Gasification Project Semiannual Progress Report for the Period Ending Dec. 31, 1980, ORNL TM-7730 (May 1981).

40. D. L. Million and J. A. Klein, "On-Line Sampling and Analysis at the University of Minnesota-Duluth Coal Gasifier," presented at the 1980 Symposium on Instrumentation and Control for Fossil Energy Processes, Environmental Systems Session, Virginia Beach, Virginia, June 9-11, 1980.

41. J. A. Klein et al., "Health and Environmental Monitoring at the University of Minnesota-Duluth Coal Gasification Facility," presented at the Third Miami International Conference on Alternative Energy Sources, Miami Beach, Florida Dec. 15-18, 1980 (to be published in the Proceedings).

42. Pike County Coal Gasification Project Status Report for the Period Ending Sept. 30, 1979, ORNL TM-7273 (May 1980).

43. Pike County Coal Gasification Project Quarterly Progress Report for the Period Ending Dec. 31, 1979, ORNL TM-7269 (May 1980).

44. Pike County Coal Gasification Project Quarterly Progress Report for the Period Ending Mar. 31, 1980, ORNL TM-7342 (August 1980).

45. Pike County Coal Gasification Project Quarterly Progress Report for the Period Ending June 30, 1980, ORNL TM-7467 (January 1981).

46. H-Coal Pilot Plant Project Status Report for the Period Ending Sept. 30, 1979, ORNL TM-7274 (June 1980).

47. H-Coal Pilot Plant Project Quarterly Progress Report for the Period Ending Dec. 31, 1979, ORNL TM-7270 (May 1980).

48. H-Coal Pilot Plant Project Quarterly Progress Report for the Period Ending Mar. 31, 1980, ORNL TM-7345 (September 1980).

49. H-Coal Pilot Plant Project Quarterly Progress Report for the Period Ending June 30, 1980, ORNL TM-7469 (January 1981).

50. H-Coal Pilot Plant Project Semiannual Progress Report for the Period Ending Dec. 31, 1980, ORNL TM-7741 (June 1981).

STOIC TWO-STAGE GASIFIER

ORNL-DWG. 78-13526

Fig. 6.15. Schematic diagram of the University of Minnesota heating plant on the Duluth campus.

Fig. 6.16. Flow schematic and sampling points for the University of Minnesota heating plant at Duluth.

- RUN 1** - COKE; MAXIMUM CONTINUOUS OPERATION, 20 h; GAS LEAKAGE AT NUMEROUS FLANGES; MODIFICATION OF GAS CONTROL VALVE.
- RUN 2** - COKE/WYOMING (BIG HORN)/INDIANA (FREEPORT) TOP COAL; MAXIMUM CONTINUOUS OPERATION, 58 h; LEAKING COAL HOPPER; FAILURE OF ASH REMOVAL SYSTEM.
- RUN 3** - WYOMING (GRASS CREEK) COAL; MAXIMUM CONTINUOUS OPERATION, 105 h; BLOWOUT OF MERCURY SEAL.
- RUN 4** - COLORADO (SUN MINE) COAL; MAXIMUM CONTINUOUS OPERATION, 170 h; FAILURE OF ESP.
- RUN 5** - COLORADO (STEAMBOAT SPRINGS) COAL; CONTINUOUS OPERATION; CRACKED GRATE HOLDER PRODUCING CO LEAKS.
- RUN 6** - COLORADO (ROUTT COUNTY)/PENNSYLVANIA (~1 d) COAL; CONTINUOUS OPERATION; SHUTDOWN FOR REPAIRS ON COAL AND ASH HANDLING SYSTEMS.
- RUN 7** - COLORADO (STEAMBOAT SPRINGS) COAL; CONTINUOUS OPERATION; GRATE HOLDER FAILURE.

Fig. 6.17. University of Minnesota coal gasification plant on the Duluth campus; stoic two-stage gasifier.

produced being of excellent quality for use in the UMD boilers. However, the various shutdowns that have been required for repairs or modifications have prevented long-term, steady-state operation on which to base conclusions from the collected data or on which the data collection procedure can be optimized. Run 7, beginning in January 1981, has exceeded expectations and has enabled the collection of all needed samples and data. Although the gasifier will continue to operate in future years, the active data acquisition period of the monitoring and assessment program will terminate in 1981.

In the Pike County coal gasification project, two standard-design, air-blown, agitated fixed-bed Wellman-Galusha gas producers were to be installed. Each was designed to handle ~1400 kg/h (3000 lb/h) of Pike County bituminous coal selected to meet air effluent standards for sulfur emissions. The producer gas was individually piped to two steam-producing boilers. Each gasifier system was to be capable of

being operated independently or in parallel. This facility was to be designed to support a multiuse community composed of residences, a hospital, a school, municipal buildings, and industries. The project, originally scheduled for completion in 1980, is illustrated in Fig. 6.18. A simplified flow schematic and the proposed ORNL-defined sampling points are shown in Fig. 6.19. Presently, however, plans for the completion of the Pike County Project have been suspended, and it is unclear as to whether the project will be resumed.

The H-Coal project involves the catalytic hydrogenation of coal under conditions of high pressure and temperature to produce liquid hydrocarbon products. The present health and environmental plan is concerned with the 550-t/d pilot plant built with funding from the federal government and five industrial participants at Catlettsburg, Kentucky, adjacent to the existing Ashland Oil Refinery. Initial startup on oil occurred during the summer of 1980.

TWO WELLMAN-GALUSHA GASIFIERS SINGLE STAGE

Fig. 6.18. Schematic diagram of Pike County Coal Gasification Facility—Phase I Design.

Fig. 6.19. Flow schematic and sampling points for Pike County gasifier (Pikeville, Kentucky).

Fig. 6.21. Flow schematic and sampling points for the H-Coal pilot plant: process front end.

Fig. 6.22. Flow schematic and sampling points for the H-Coal Pilot Plant: effluent control units.

the processing units; thus the treatment sequence can be varied as desired.

The development of this pilot plant will occur over a period of 2 to 3 years. During FY 1981, efforts were concentrated on the design and construction of the polishing train, which will consist of ozonation, carbon adsorption, and reverse osmosis. The installation of the polishing train at the H-Coal facility is planned for October 1981. The three-unit modules and associated tanks will be installed in two 12.4-m (40-ft) covered trailers for transport to the site and for weather protection. The feed storage tanks will be located on a concrete pad adjacent to the trailers. Figure 6.24 is a schematic piping and instrumentation diagram for the polishing units and the feed storage system. These diagrams have been reviewed and accepted by Ashland Synthetic Fuels, Inc. (ASFI), which is the primary operator of the H-Coal pilot facility.

Figure 6.25 is a flow diagram for the existing wastewater treatment system at the H-Coal site. The process condensate (sour water) flow is ~20% of total flow. The other wastewater streams are several orders of magnitude less contaminated than the sour water. The polishing units will be operated on both influent and effluent streams for the existing activated sludge unit. Thus the polishing units will be evaluated as both ultimate polishing operations and as primary organics removal operations in lieu of biological oxidation.

Basic Process Evaluations for Fossil Energy Wastewater Treatment

During this reporting period a bench-scale wastewater treatment process for treating aqueous

effluents from coal conversion processes was developed, and an associated testing program was initiated. This program coupled bioassays with chemical analyses to develop assessments of these treatment processes. Experimental studies on the treatment of activated and chemical sludges were also initiated to develop environmentally acceptable handling and disposal options for sludges from coal conversion wastewater treatment.

The bench-scale process developed for treatment of coal conversion wastewaters is shown in Fig. 6.26. Sampling points to provide evaluation data are depicted. The process consists of four major unit operations: (1) stream stripping for ammonia removal, (2) biological treatment using activated sludge, (3) ozonation, and (4) sorption through resins or activated carbon. Two bioassays are used to monitor the process, namely mutagenicity tests using the Ames *Salmonella* test system and short-term toxicity tests using *Daphnia magna*. The bench-scale process was evaluated using wastewater from an ORNL coal hydrocarbonization pilot plant and found to produce an environmentally acceptable effluent.

Scrubber water from a low-Btu Chapman gasifier at the Holston Ordnance Facility, Kingsport, Tennessee, and wastewater from the solvent decanter at the Wilsonville, Alabama SRC Pilot Plant were treated using the bench-scale process. Chemical analyses and bioassays are being conducted on both the wastewaters and the samples collected from the various process steps. A comparison of the chemical data in Table 6.7 indicates that the wastewater treatment method effectively reduced the ammonia in both wastewater samples. However, the phenol

Fig. 6.24. Diagram for polishing train in wastewater treatment pilot

Fig. 6.25. Coal conversion wastewater treatment pilot plant.

Fig. 6.26. Bench-scale process for treatment of wastewater from coal conversion processes.

was effectively removed from only the Holston Ordnance scrubber water sample. The high sulfide content of the solvent decanter wastewater sample may have made the overall treatment less effective as indicated both by the high sulfide content in the process samples and by the less effective reduction in phenol concentration as compared with the Holston Ordnance scrubber water sample. The steam stripping step will be modified to optimize stripping of both ammonia and sulfide. Acute toxicity test results using the *D. magna* bioassay are presented in Table 6.8 for both the Holston Ordnance scrubber wastewater and the Wilsonville solvent decanter wastewater and their respective treatment samples.

The solvent decanter wastewater is 20-fold more toxic than the scrubber wastewater. The treatment process reduced the acute toxicity of the scrubber wastewater 140-fold and reduced the acute toxicity of the solvent decanter wastewater 470-fold. Bacterial mutagenicity tests have been completed only for the Holston Ordnance scrubber wastewater and process samples. Mutagenic activity (Ames bacterial test with metabolic activation) was found only in the basic and neutral ether-soluble organics separated from the untreated scrubber wastewater. The acidic ether-soluble organics from the scrubber wastewater and the acidic, basic, and neutral ether-soluble organics separated from the ammonia-stripped, biotreated, ozonated, and final treatment product were all found to have no mutagenic activity. The specific mutagenic activity of the neutral fraction separated from the untreated scrubber water was very high (5000 revertants/mg). This fraction includes the polynuclear aromatic hydrocarbons. The specific mutagenic activity of the basic fraction separated from the untreated scrubber wastewater was 46 revertants/mg. This fraction includes the aromatic amines and heterocyclic nitrogen-containing compounds. The neutral fraction represented only 0.3% of the total organics separated from the untreated scrubber wastewater, but the basic fraction represented 42.7% of the total organics; thus the neutral fraction contained ~40% of the total mutagenic activity in the wastewater, and the basic fraction contained ~60% of the total mutagenic activity.

Table 6.7. Chemical data for the Holston Ordnance scrubber wastewater, Wilsonville SRC Pilot Plant solvent decanter wastewater, and process treatment samples

Waste	pH	Conductivity (μ mho/cm)	Total sulfur (mg/L)	Sulfide (mg/L)	Total organic carbon (mg/L)	Ammonia- nitrogen (mg/L)	Phenol (mg/L)	Ether-soluble constituents (mg/L)		
								Neutral	Acid	Base
Holston Ordnance										
Scrubber wastewater (untreated—A)	8.00	2,630	a	a	5,300	3,600	2,500			
Ammonia stripper (B)	10.15	2,180	a	a	3,800	20	1,500			
Biotreated (C)	8.48	1,315	a	a	a	0	93			
Ozonated (D)	a	a	a	a	a	0	a			
Product (after sorption—E)	9.5	1,890	a	a	a	0	1.0			
Wilsonville										
Solvent decanter waste- water (untreated—A)	8.75	8,250	15,400	35,300 ^b		22,600	2,000	409	10,400	135
Ammonia stripped (B)	10.75	6,000	14,500	13,900		50	1,700	a	a	a
Biotreated (C)	9.00	4,650	11,300	6,300		0	200	33	1,170	21
Ozonated (D)	9.63	5,600	10,200	2,500		0	<200	20	520	6.3
Product (after sorption—E)	8.60	5,700	10,500	500		0	<200	1.8	68	6.1

^aNot Determined.

^bHigh because of organic sulfides.

Table 6.8. Acute toxicity test results (*Daphnia magna* bioassay) for Holston Ordnance scrubber wastewater, Wilsonville SRC Pilot Plant solvent decanter wastewater, and respective process treatment samples

Waste	48-h LC ₅₀ ^a (%)	Relative toxicity to raw waste
Holston Ordnance		
Scrubber wastewater (untreated—A)	0.22	1.00
Ammonia stripped (B)	0.61	0.36
Biotreated (C)	18.39	0.012
Ozonated and sorbed (E)	30.42	0.0072
Wilsonville		
Solvent decanter wastewater (untreated—A)	0.010	1.00
Ammonia stripped (B)	0.029	0.34
Biotreated (C)	2.41	0.0042
Ozonated (D)	3.07	0.0033
Product (after sorption E)	4.68	0.0021

^aPercent: by volume of test solution (e.g., 0.01% means 0.01 mL test solution per 100 mL water).

A second major objective of this research program is to assess the applicability and effectiveness of conventional technology for the treatment and disposal of sludges generated by coal conversion plant wastewater treatment facilities. The literature

concerning state-of-the-art treatment processes was reviewed, and wet-air oxidation was selected for treatment evaluation. A 1-L stirred autoclave was installed and tested in a simulated wet-air oxidation run at 300°C and 8.72 MPa (1250 psig) using 500 mL of water. An experimental program beginning with kinetic studies on model compounds (phenol, catechol) in batch treatment processes and progressing through continuous-flow treatment of actual sludges was designed and initiated during this reporting period.

Basic Environmental Sciences Program

During this reporting period, efforts included the completion of a research program on disinfection effects on nonvolatile organic constituents in wastewater effluents, the initiation of a study of bioaccumulation of lipophilic constituents from chlorinated cooling waters, and the publication of the proceedings of a third national conference on water chlorination which was conducted during this period.

Principal objectives of the disinfection effects study, which was conducted in collaboration with the Biology Division, were to examine the effects of disinfection by chlorine, ozone, or ultraviolet light irradiation on nonvolatile organic constituents relative to chemical effects and formation of mutagenic substances.

comparative study of effluents from nine wastewater treatment plants, it was determined that disinfection with chlorine or ozone destroys and produces nonvolatile organic constituents including mutagenic constituents. The chemical effects of disinfection by uv irradiation were relatively slight, although in one effluent, mutagenic constituents were eliminated by uv irradiation.

The nine wastewater treatment plants were selected using the following criteria: disinfection method, nature of wastewater source, type of wastewater treatment, standards for quality of treatment, and geographical location. The treatment plants varied from pilot-plant and small-scale [0.05-m³ s (1-mgd)] systems, treating principally domestic waste, to large-scale [4.4-m³ s (100-mgd)] systems, treating principally industrial waste. Four plants used only chlorine for disinfection, four plants used ozone for disinfection, and one plant used uv irradiation for disinfection. Eight treatment plants used conventional secondary or more advanced wastewater treatment.

The investigation utilized the following methodology: grab-sample collection of 40-L samples of undisinfected and disinfected effluents; concentration of the effluents by lyophilization; HPLC separation of nonvolatile organic constituents in effluent concentrates, using uv absorbance, cerate oxidation, and fluorescence detectors; bacterial mutagenicity testing of concentrates and chromatographic fractions; identification and characterization of nonvolatile organic constituents in mutagenic HPLC fractions.

Interplant comparison revealed considerable variability in the presence of mutagenic nonvolatile organic constituents in the undisinfected effluents as well as much variability in the destruction of the mutagenic constituents and the formation of other mutagenic constituents resulting from disinfection. Also, the effects were variable between effluent samples collected at different periods at the same wastewater treatment plant.

Although over 50 compounds were identified in the mutagenic HPLC fractions separated from the undisinfected, chlorinated, and ozonated effluents, none were known to be mutagenic. In one experiment to characterize the nature of the mutagenic activity of the nonvolatile organic constituents in a mutagenic effluent, it was determined that the activity was not attributable to organic chloramines. Most of the mutagens detected in effluents are direct acting and do not require metabolic activation. Both base pair substitution mutagens and frame shift mutagens

occur in wastewaters, but the former are more frequent. For many of the materials in effluents, strain TA-1535 was more sensitive than strain TA-100 in detecting base pair substitution mutagens.

In the second basic research program, the bioaccumulation of lipophilic halogenated organic constituents from chlorinated wastewater effluents was investigated since it has been shown to be statistically significant in several species of fish.^{51,52} A research program was initiated to determine if similar bioaccumulation occurs from chlorinated cooling waters using the freshwater clam (*Corbicula* sp.) as the indicator organism. Samples used in this study were collected from their adopted habitat in eastern Tennessee lakes. Nonexposed control samples were collected several miles downstream from any known chlorinated outfall. Clams exposed to chlorinated cooling waters were collected as near the chlorinated outfall as possible. The samples were extracted, chromatographed, and analyzed according to the method developed by Kuehl et al.⁵² Typically, the tissue was removed from the hard shells and extracted with a hexane acetone solvent. The hexane acetone solvent was removed by rotary evaporation, and the dried residue was dissolved in methylene chloride and chromatographed by gel-permeation chromatography (GPC). Eluted fractions were collected and analyzed by gas chromatography mass spectrometry. A typical GPC chromatogram with tentative identifications is shown in Fig. 6.27. Analysis of clam samples collected at the John Sevier Steam Plant, Rogersville, Tennessee, is currently under way.

The final major effort in this programmatic area involved conducting the interdisciplinary Third Conference on Water Chlorination: Environmental Impact and Health Effects,⁵³ which was held in

51. H. K. Kopperman, D. W. Hucal, and G. E. Glass, "Chlorinated Compounds Found in Waste Treatment Effluents and Their Capacity to Bioaccumulate," pp. 311-28 in *Water Chlorination: Environmental Impact and Health Effects*, vol. 1, R. L. Jolley (ed.), Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1978.

52. D. W. Kuehl, G. D. Veith, and E. N. Leonard, "Brominated Compounds Found in Waste Treatment Effluents and Their Capacity to Bioaccumulate," pp. 175-92 in *Water Chlorination: Environmental Impact and Health Effects*, vol. 2, R. L. Jolley, H. Gorchev, and D. H. Hamilton (eds.), Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1978.

53. R. L. Jolley, W. A. Brungs, and R. B. Cumming, *Water Chlorination: Environmental Impact and Health Effects*, vol. 3, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1980.

Fig. 6.27. Gel-permeation chromatogram of compounds extracted from freshwater clams (*Corbicula* sp.).

Colorado Springs, Colorado, on Oct. 28–Nov. 3, 1979. Approximately 300 participants attended, and 100 technical papers were presented; these have been edited and published. Planning has been initiated for the fourth national water chlorination conference.

Development of the ANFLOW Demonstration Project for Municipal Wastewater Treatment

The objective of the continuing ANFLOW program during this reporting period has been the demonstration of the technology for wastewater treatment on a 190-m³/d (50,000-gpd) scale using municipal wastewater. The demonstration project is being conducted in cooperation with the Wastewater Control Systems of the city of Knoxville, Tennessee, at the site of their Loves Creek treatment plant. Associated Water and Air Resources Engineers (AWARE), Inc., of Nashville, Tennessee, is serving as process and design consultant under subcontract to ORNL. Glitsch, Inc., of Dallas, Texas, is an industrial contributor (column packing material) to the project. Funds have been provided by DOE's Office of Buildings and Community Systems.

The ANFLOW Demonstration Plant to be operated at the Loves Creek Wastewater Treatment Plant in Knoxville, Tennessee (Fig. 6.28), has been designed for an average input of 2 L/s (50,000 gpd). However, it will be tested over a 1.2- to 3.2-L/s (30,000- to 80,000-gpd) range. The packed section of the bioreactor will measure 4.9 m (16 ft) in diameter and 3 m (10 ft) in height and will have a 56,000-L (15,000-gal) capacity, as shown in Figs. 6.29 and 6.30. The residence time will be 7.7 h at the design flow rate of 2 L/s (50,000 gpd). Glitsch Inc., is supplying the plastic packing (Fig. 6.31) to support the biofilm growth and is consulting with ORNL on operational procedures.

A fixed-price construction contract has been awarded to the low bidder, Cousins Construction Company of Oak Ridge, Tennessee, for approximately \$119,300. This contract covers (1) the purchase of the majority of the processing equipment, (2) installation of the new equipment and equipment already on hand at ORNL, and (3) construction of a 201.5-m² (650-ft²) building to house the demonstration plant. The system is expected to be operational for R&D by June 1981. It will be operated for ~15 months during which time it will be available as an industrial tour as part of the 1982 World's Fair in Knoxville, Tennessee.

Complete technical and economic feasibility studies will be conducted on the ANFLOW technology at this scale, and design studies for commercial-scale systems will be made. If these studies are positive, a commercial demonstration (10- to 20-fold scale-up of the Loves Creek pilot system) may be pursued.

6.4 FLUE GAS DESULFURIZATION STUDIES

Flue gas effluent control for coal-burning power plants is being mandated by the Environmental Protection Agency (EPA). The control of sulfur emissions (primarily SO₂) from high-sulfur coal is being achieved primarily through the use of aqueous scrubbers. The majority of these scrubbers use lime/limestone slurries as the basic reagent. However, these are "throw-away" systems that generate large volumes of scrubber sludge (calcium sulfite-sulfate mixtures), which cause significant disposal problems. Magnesia (MgO) scrubbing is a regenerative system that avoids sludge disposal problems by recycling the active reagent and producing a saleable sulfur-containing product. In this process the flue gas is scrubbed with a MgO slurry, and magnesium sulfite hydrate crystals are recovered from the

Fig. 6.30. A schematic of the ANFLOW R&D pilot plant.

scrubber loop and dried. The MgSO_4 is then decomposed at a high temperature to form SO_2 . The SO_2 is used to produce H_2SO_4 and MgO , which is reslaked and returned to the scrubber. An environmentally acceptable form of sulfur, such as elemental sulfur, would be a more desirable product than H_2SO_4 . Thermodynamic calculations^{54,55} indicated that under some conditions sulfur would be a major product of the high-temperature calcination of MgSO_4 in a reducing atmosphere.

The objective of this study was to provide experimental verification of the technical feasibility of reducing MgSO_4 to sulfur and MgO as a

potentially useful step in the utilization of a MgO slurry for flue gas desulfurization. Carbon monoxide and hydrogen were considered as reductants. This study included: (1) thermodynamic calculations, (2) thermogravimetric measurements, and (3) isothermal tube furnace experiments.

54. P. S. Lowell, W. F. Corbett, G. D. Brown, and K. A. Wilde, *Feasibility of Producing Elemental Sulfur from Magnesium Sulfate*, EPA 600/7-76-030 (October 1976).

55. P. S. Lowell, *Suggested Bench-Scale Support for a Reducing MgSO_4 Calciner*, Technical Memorandum 100-009-01, P. S. Lowell and Co., Inc., Austin, Texas (September 1979).

• GLITSCH 3-in. BIO RING (POLYPROPYLENE)

-WEIGHT, 3.7 lb/ft³

-SURFACE AREA, 32 ft²/ft³

-FREE SPACE, 93%

-BIOREACTOR VOLUME, ~2000 ft³

• PACKING DONATED BY GLITSCH, INC., DALLAS,

TEX. COOPERATIVE PARTICIPATION AGREEMENT

Fig. 6.31. Photograph of the packing used in the ANFLOW bioreactor.

The computer program, SOLGASMIX-PV,⁵⁶ was used to assist in the calculations of equilibrium phases that might be present during the decomposition of MgSO₃. The temperature range considered was 600 to 1300 K. Characteristic of all alkaline earth sulfites, the MgSO₃ is not a thermodynamically stable phase in the MgO-MgS-MgSO₃-MgSO₄ system but exists in metastable equilibrium with MgO or MgS. The relationships between P_{O₂} and P_{S₂} were calculated for the following equilibria:

The equilibrium values of P_{O₂} and P_{S₂} at 900 K for each of 23 mixtures of MgSO₃, with varying amounts of H₂O, C, and H, were also calculated. The results of the thermodynamic calculations can be summarized as follows:

1. The optimum pressure of elemental sulfur (S₂, S₄, S₆, and S₈) should occur at oxygen pressures between 10^{16.5} and 10^{18.0} kPa. One way of controlling this would be to maintain the appropriate CO₂/CO ratio.
2. Water, either released from hydrated MgSO₄ or formed from hydrogen reductant, tends to increase the formation of H₂S.

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

3. In the presence of CO_2 , part of the MgSO_3 is converted to MgCO_3 below 700 K; above 700 K the MgSO_3 is converted to MgO .

Thermogravimetric measurements were made to define the thermal decomposition properties of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ in both an inert atmosphere (helium) and in a slightly reducing atmosphere (0.74% CO in CO_2). The mass loss below 100°C corresponded to the dehydration reaction,

and a mass loss near 430°C corresponded to the reaction,

The final residue was identified as MgO by x-ray diffraction analysis. As in the inert atmosphere, most of the water of hydration was lost below 100°C in the slightly reducing atmosphere. However, further decomposition in the CO/CO_2 atmosphere was much more complex than in the helium atmosphere. In addition to the initial water loss, transitions occurred at 403, 563, 622, and 936°C. The reactions associated with these transitions have not been fully characterized, but probably involve the formation and decomposition of MgCO_3 , along with the decomposition of MgSO_3 and the possible formation of elemental sulfur.

The decomposition of $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$, and MgSO_4 was studied under different gas atmospheres in a tube furnace at 500, 600, 700, 750, and 800°C. Water and sulfur were collected separately, and the yield was measured gravimetrically. The results of several experiments are summarized in Table 6.9. The reported water yield is based on the theoretical amount expected for dehydration. The sulfur yield is based on the total amount of sulfur available in the sample.

The yield of sulfur from the decomposition of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ in either argon, CO_2 , 1% CO in CO_2 , or 4% H_2 in argon was 9 to 13% of theoretical in the

Table 6.9. Effects of atmosphere and temperature on sulfur yield

Gas atmosphere	Sample ^a	Temperature (°C)	Product yield (%)	
			H_2O	Sulfur
Argon	H	700	94	11
	H	750	85	10
CO_2	H	700	98	11
	H	600	94	13
1% CO/CO_2	H	700	99	12
	T	500	95	10
10% CO/CO_2	H	500-800	93	14
	H	750	79	24
CO	H	600	68	56
	H	800	79	55
	T	800	67	41
	MgSO_4	800		60
4% H_2/Ar	T	500	91	6
	H	600	80	11
H_2	H	600	79	32

^a H = hexahydrate, $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$; T = trihydrate, $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$.

temperature range 600 to 800°C. The formation of sulfur in the absence of a reducing agent (in argon and in CO_2), as well as in a slightly reducing atmosphere (1% CO in CO_2 and 4% H_2 in argon), probably results from the disproportionation of the sulfite to form sulfate and sulfur.

When pure CO was used as reductant, the sulfur yield increased to 55% at temperatures of 600 to 800°C. Use of hydrogen reductant gave a lower sulfur yield (32% at 600°C) -- a result probably due to the loss of sulfur as H_2S , as predicted by the thermodynamic calculations. The primary gaseous by-products containing sulfur were COS and H_2S . Magnesium sulfate was also reduced in pure CO at 800°C and produced a 60% yield of elemental sulfur.

Reductive calcination of MgSO_3 could be an attractive alternative to thermal decomposition when applied to the regenerable magnesia flue gas desulfurization system.

7. Special Isotope Production and Separations

7.1 TRANSURANIUM-ELEMENT PROCESSING

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

TRU Operations

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

Production and shipment. During this report period, 26 HFIR targets were processed to recover the transuranium elements. Table 7.1 provides a comparison of the amounts of key isotopes obtained during this 2-year period with the total amounts produced at TRU in 13 years of previous operation. In addition to the HFIR-target processing, six ²⁴¹Am slugs, which had been irradiated at the Savannah River Plant (SRP), were dissolved and processed to separate 16 g of ²³⁸Pu. The americium-curium fraction from this material was stored and will be processed further to recover ~3 g of curium which contains a high concentration of ²⁴³Cm (8%).

Three batches of high-purity ²⁴⁸Cm were separated from the parent ²⁵²Cf during this report period. One batch, containing 106 mg of ²⁴⁸Cm, was purified and shipped. The other two batches, containing a total of 220 mg of ²⁴⁸Cm, were stored to await final purification.

1. L. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Report of Production, Status, and Plans for the Period October 1, 1978-September 30, 1980*, ORNL-5596 (August 1981).

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

Time period	April 1979 to March 1981	August 1966 to March 1979
Number of years	2	13
Number of target campaigns	2	39
Number of targets processed	26	448 ^a
Amounts of key isotopes recovered:		
²³⁸ Pu	0	141 g
²⁴¹ Am	19 g	252 g
²⁴⁴ Cm	128 (253) ^b g	1852 g
²⁴⁸ Bk	100 mg	456 mg
²⁵² Cf	845 mg	4131 mg
²⁵⁴ Es	4.7 mg	18.3 mg
²⁵⁶ Fm	1.8 ^c pg	10 pg

^aNumber of targets includes 251 HFIR targets, 176 SRP slugs and targets, and 21 SRP Pu-Al tubes.

^bValue in parentheses is total curium.

^cEstimated amount.

A total of 97 shipments of transuranium elements was made during the 2-year report period. The total amounts of each type of product shipped are listed in Table 7.2.

Table 7.2. Amounts of transuranium elements shipped during the period April 1, 1979–March 31, 1981

^{239}Pu	29.2 g
^{240}Pu	0.15 g
^{241}Am	38.3 g
Curium (mixed)	21.5 g
^{24}Cm (56%)	7.2 mg
^{24}Cm (>99%)	3.2 mg
^{24}Cm (99%)	2.2 μg
^{24}Cm (97%)	140.1 mg
^{24}Cm (92%)	9.2 mg
^{24}Bk	96.3 mg
^{25}Cf	0.2 mg
^{25}Cf	0.23 mg
^{25}Cf	357.2 mg
^{25}Es (mixed)	2.56 mg
^{25}Es	3.2 μg
^{25}Fm	2 μg^a

^aEstimated.

Processes and equipment. A new vessel off-gas (VOG) charcoal adsorber system has been installed in a pit south of the TRU building. This system consists of two parallel trains each containing a small electrical resistance heater, a flow-rate element, and a housing for two standard, replaceable charcoal beds and a HEPA filter. The new system is being used as a backup to the Hopcalite-charcoal iodine retention system, which is located upstream in the VOG system.

Target fabrication. The supply of feed material for HFIR targets was increased by acquisition of 277 g of curium from the Savannah River Laboratory (SRL). This material is part of the Californium-I Program product that was recovered at TRU previously and shipped to SRL in 1972. The material was returned to TRU as the result of an exchange for a similar quantity of curium from the Space Nuclear Systems program.

Fifty HFIR targets were fabricated from curium oxide and/or americium oxide for transuranium element production. In addition, two special HFIR targets were fabricated for the ORNL Operations Division. Each special target contained 4 g of isotopically separated ^{118}Sn and one target also contained 1 g of ^{54}Fe . These materials were encapsulated in quartz ampuls which were carefully sized to fit into a standard HFIR target rod.

Special Projects

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

Fabrication of neutron sources from ^{252}Cf . Some of the californium recovered at TRU is incorporated into neutron sources, which are subsequently loaned to researchers. Five sources containing 2.1 to 18.3 mg of ^{252}Cf were fabricated in this report period; three of these were doubly encapsulated in type 304L stainless steel in a standard TRU configuration (NSD).² Two sources were prepared for the National Bureau of Standards in a special point-source configuration.³

Sources returned. Neutron sources are returned to TRU when the projects for which they were requested are completed or when replacements are ordered to make up for decay of the ^{252}Cf . These sources are available for reassignment until the appropriate time for reprocessing to recover the ^{248}Cm daughter. During this report period, 17 sources were returned and 4 were reassigned; 87 are now on loan and 18, which contain from 1 μg to 7.7 mg of ^{252}Cf , are available for reassignment.

Electroplated ^{252}Cf fission sources. Procedures were developed to allow the electroplating of various amounts of purified ^{252}Cf from dry isopropanol solutions onto platinum foils or disks. Nine fission sources, ranging in size from 0.16 to 339 μg of ^{252}Cf , were prepared using a modified electroplating cell in which a brass heat sink was used to minimize the formation of gas bubbles in the plating solution. An insulating mask was used to confine the californium deposit to a circular area of the desired size.

Repurification of Campaign 56 einsteinium. At the request of the Transplutonium Program Committee, the residues remaining from experiments that made use of the Campaign 56 einsteinium product were collected, concentrated by evaporation, and purified by ion exchange techniques. The final

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

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

product, containing 2.97 μg of ^{254}Es and 3.1 ng of ^{255}Es , amounted to $\sim 75\%$ of the material in the original Campaign 56 einsteinium product after correction for decay.

Production of ^{250}Cf . Approximately 235 μg of ^{250}Cf , produced by irradiation of ^{249}Bk in the HFIR Hydraulic Rabbit Facility, was recovered and purified at TRU. Prior to the irradiation, approximately 1.2 mg of ^{249}Bk was purified using a microseparations column to remove the ingrown ^{249}Cf . The purified ^{249}Bk was blended with magnesium nitrate solution and loaded onto Dowex 50 resin beads which were subsequently dried, calcined, and mixed with aluminum powder. The mixture was pressed into three pellets which were heat-treated to remove volatile impurities and then encapsulated in a HFIR rabbit. The rabbit capsule was irradiated for 20 h and then cooled for 9 h before it was transferred to Shielded Cave B at TRU via the hydraulic transfer tube.

After dissolution of the aluminum pellet matrix in caustic, the magnesium-berkelium microspheres were recovered by filtration and dissolved off the filter frit by small additions of 1 M HNO_3 . The solution was diluted to 0.2 M HNO_3 and processed by means of a high-pressure ion exchange run to separate the californium from the berkelium and most of the fission products. The californium fraction was concentrated and purified by means of a cation exchange cleanup run, and the product solution was evaporated in a quartz cone and packaged for shipment. The final product consisted of 274 μg of californium with the following isotopic composition (as of August 23, 1979): 4.79% ^{249}Cf , 86.78% ^{250}Cf , 7.42% ^{251}Cf , 1.01% ^{252}Cf , <0.001% ^{253}Cf , and <0.02% ^{254}Cf .

After decay of the ^{250}Bk , the ^{249}Bk residue was recovered and purified. The amount of ^{249}Bk recovered was 718 μg .

Radiography of stainless steel specimens. Twenty-eight irradiated fracture-strain specimens of stainless steel alloy were radiographed remotely using the TRU target fabrication facilities. This service was performed because the TRU facilities contain an x-ray machine capable of operating at 80 kV. The machine normally used for postirradiation examination (50 kV) was not adequate for these examinations. A special effort was required to prevent contamination of the specimens with ^{244}Cm or ^{252}Cf while they were in the TRU cells.

Preparation for production of 40 μg of ^{245}Es . A special request for a 40- μg sample of ^{245}Es has been made. Under normal conditions, the isotope ^{245}Es

(half-life = 276 d) is very difficult to produce by neutron irradiation in the HFIR because the isotope has a thermal neutron fission cross section of 3000 b; thus the effective half-life in the HFIR would be only about 1.3 d. The production ^{245}Es relative to ^{253}Es possibly may be enhanced via capture and fission occurring in the epithermal region if the thermal neutrons can be filtered out with a material such as cadmium. Calculations have indicated that the production ratio of ^{245}Es to ^{253}Es in a standard HFIR target might be increased by a factor of 10.

However, currently available values for the capture cross sections of ^{253}Es leading to the production of ^{245}Es are not consistent with the observed production of ^{245}Es . Thus, our present effort is directed toward making new measurements of the thermal and epithermal capture cross sections in the HFIR, using the Hydraulic Rabbit Facility. This task is significantly more complicated than it would be in a reactor operated at a lower flux. A rabbit with a cadmium insert designed to meet the exacting requirements has been fabricated and tested by irradiation in the HFIR. No difficulties were encountered. Preparations are under way to encapsulate a sample of ^{253}Es into a similar rabbit.

7.2 ISOTOPIC SEPARATIONS

The current separations program has two primary objectives. The first is to maintain viable sales and Research Materials Collection (RMC) inventories for use in fundamental neutronics research and in diverse medical, commercial, and applications research such as nuclear medicine, analytical instrumentation, atomic clocks, and lasers. Sixty-one new loans were made from the RMC inventory during each of the last two fiscal years, representing more than 3.2 and 1.5 kg of electromagnetically separated isotopes, respectively. During the same intervals, sales of about 1.5 and 1.7 kg of the separated isotopes accounted for revenues to the program of approximately \$1.85 million in 1979 and more than \$2 million in 1980. For the first time in a number of years, the sales volume to domestic customers in FY 1980 was greater than to foreign customers.

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

The isotopic separations program during the past two years was dominated by two long separations, plutonium and thallium, which were made for very different reasons. The plutonium campaign, which consumed the greater part of 8 months in 1979, had as its objective the recovery of about 250 g of ~99.9% ^{241}Pu for heavy-element research. The thallium collection, which extended from early December 1979 to October 1980, was ultimately intended for nuclear medicine application since enriched ^{203}Tl is the precursor for the production of ^{201}Tl in cyclotrons. Thallium-201 is finding ever-increasing use as a screening agent and diagnostic tool in heart ailments.

In all, three isotopic separations were completed while two others were in progress at the end of the reporting period. Table 7.3 presents a summary of the separations with the isotope of major interest highlighted. The quantity recovered (or expected to be recovered), along with the average isotopic purity of the isotope of interest, is also shown. Three of the five isotopes are precursors for the production of radioisotopes currently being used in nuclear medicine. The other two, ^{242}Pu and ^{208}Pb , are needed for programs in nuclear research. The remaining isotopes of each element, which could be collected concurrently, will be available for potential sales or RMC inventories.

Table 7.3. Summary of isotopic separations

Element	Percent of total effort	Major isotope	Quantity (g)	Assay (%)
Plutonium	28	242	250.8	99.932
Thallium	49	203	3083.6	95.69
Zinc	8	68	270 ^a	>99.2 ^a
Tellurium	10	124	96 ^b	>95.5 ^b
Lead	5	208	650 ^a	>98 ^a

^aEstimated recovery and assay; chemical recovery incomplete.

^bEstimated recovery and average assay; separation incomplete.

In addition to the production separations, a research and development collection of titanium isotopes was made in order to find an improved charge material for future isotopic separations and to provide a small quantity of >95% enriched ^{50}Ti for physics research.

The ^{242}Pu enrichment campaign began in early May 1979 in two electromagnetic isotope separators which are housed in a radioactively contained area.

However, more than a month of intensive efforts was needed by the members of the separation group prior to beginning the separation in order to prepare the facility for the campaign and to review safety procedures. The last previous separation in the facility was completed in September 1975, and the area had been in standby since that time. All stable isotope separation activities were curtailed while the plutonium enrichment was under way.

The charge material for the separation consisted of 975 g of plutonium in the chemical form of "low-fired" oxide enriched to ~95% in ^{242}Pu . A volatile form of plutonium was obtained in situ by passing carbon tetrachloride vapors over the heated oxide in the ion sources of the separators. Through a recovery-and-recycle program, a total of 1601 g of plutonium was vaporized into the separator tanks.

The ^{242}Pu , which was collected in 17 separate graphite receiver pockets during the separation, was recovered from individual collector pockets and chemically refined to an end product which consisted of 250.812 g of 99.932% ^{242}Pu .

Following the completion of the physical separation, all of the calutron components were stripped with acid, and the unresolved feed material was chemically recovered and refined. The facility was cleaned to remove extraneous activity and again placed in a standby condition.

The thallium isotopic separation, as noted in Table 7.3, accounted for almost half of the production effort during the past 2 years. The separation was initiated early in December 1979 in a segment of eight beta-type calutrons on a 5-d, week, 24-h/d basis. After approximately 4 months, the separation was expanded into a second eight-tank segment in order to meet the anticipated needs for enhanced ^{203}Tl .

The separation, which yielded more than 3 kg of >95% ^{203}Tl product, surpasses a ^{184}W separation several years ago for quantity of "wanted" isotope recovered from a single separation series.

Separator Research and Development

Xenon. During this reporting period, ion source and receiver developments needed to ensure satisfactory separation of xenon isotopes were completed. The attainment of a 10-mA Xe^+ beam having acceptable focal qualities required the use of a reduced-size arc chamber with a drift space between the filament and the principal region of the arc. The size of the ion exit slit was also reduced in length to accommodate the smaller chambers. Without such changes, the attainment of a well-focused beam in excess of 0.15 mA was impossible. Higher levels of ion output (15- to 20-mA Xe^+) were attainable in

conventional ion sources, but the beam quality was never acceptable.

Experimentation with various arc-support gases fed into the drift space adjacent to the filament finally provided a breakthrough in the attainment of an improved process efficiency. With many gases, including xenon, efficiencies were ~7%; however, when helium was introduced in a He/Xe volume ratio of 25-50/1, a process efficiency of 30% could be sustained for short intervals (hours) and an efficiency of 15 to 18% could be averaged throughout an entire run. This improvement could be achieved without losses in either ion output or beam quality.

Under the above conditions, ^{124}Xe ions were collected in a continuously deposited layer of antimony, condensed upon a 250-cm² plate at a rate approaching that which would give a Sb/Xe weight ratio of 100/1. Under these conditions ^{124}Xe at 78.3% isotopic purity was collected from a 10.4-mA Xe⁺ beam at greater than 50% ion retention and 15% source efficiency. Prior to development of the Sb-Xe⁺ technique, large-scale collections of isotopes of inert gases such as xenon were considered infeasible. Therefore, this pilot work has expanded the applicability of electromagnetic separations into new areas.

Titanium. A joint venture between the development and operations groups addressed two problems in titanium separation: (1) to improve on the charge material (TiCl_4), which in the past had limited the isotopic purity of ^{50}Ti to ~80%, and (2) to provide a small quantity of ^{50}Ti enriched to >95% for a physics experiment. Typically, the separation of ^{50}Ti from TiCl_4 feed generated neutral-vapor contamination within the collector pocket, which limited the purity of ^{50}Ti to 80% although beam resolution would indicate that >95% should easily be achieved.

A charge system to produce a mixture of the lower chlorides of titanium (which have lower vapor pressures) by passing TiCl_4 vapors over titanium heated in the charge bottle was evaluated. The operating pressure was not significantly reduced; hence no appreciable improvement in isotopic purity (83% vs 80%) resulted. The use of TiCl_4 in conjunction with calcium-vapor pumping reduced the operating pressure tenfold while the ion output of Ti^+ was increased and the ^{50}Ti purity was elevated to >98%. This work provided >800 mg of the needed isotope and established the basis for use in future separations to acquire titanium isotopes. The method allows for sample collection at slightly improved output and a 20-fold reduction in isotopic contamination.

Mercury. Ion source development is one avenue of approach to influencing both the availability and the cost of high-volume, repetitive-use isotopes such as ^{196}Hg and ^{203}Tl . The problems associated with the acquisition of the mercury isotope, which is a medical precursor, are more complex than those usually encountered in isotopic separations. Difficulties have been experienced with the charge material (Hg, HgCl , HgO , HgS , etc.), low ion output, "dirty equipment" (influencing both output and purity), and the collector (with regard to retention and contamination). Each area has been addressed in the past, and in general, an improvement in one area has introduced a compromise in another. Elemental mercury as a feed improves the operational stability but reduces the useful ion output by >50%; oil used as a collection medium reduces contamination but puts limits on the quantity collected per run.

All attempts to increase the useful ion output from metallic mercury feed failed to produce favorable results. At full output (approaching 10- to 15-mA Hg^+), beam resolution was unattainable. Parameters and geometries found useful in other separations failed to provide positive improvement. Acceptable focus disappeared at an output in excess of 2- to 3-mA Hg^+ .

Problems with HgS feed were postulated to be associated with decomposition of HgS at the temperature necessary to transport the required amount of HgS into the arc region. This problem was addressed by placing the HgS feed directly below the arc column, by providing water-cooled heat sinks to minimize the variations introduced during optimizations of arc current and voltage, and by alterations in ion extraction geometry. The combined effects were promising. At the time the effort was switched from mercury to thallium, an ion output of 7-mA Hg^+ was routinely achieved in a well-focused state; the stability of operation approached that experienced with the low-output mercury feed system. The collection problem continues to exist. Efforts to utilize the antimony collection matrix as in Xe⁺ collection failed due to the neutral-vapor contamination problem. The ^{196}Hg isotope collected on continuously deposited antimony was diluted up to 1500 wt % by normal mercury.

Thallium. In all the thallium separations, an instability in the ion output has limited the purity of the ^{203}Tl attained and has also added to the cost of the isotope. The instability evidenced itself as a randomly occurring loss of ~50% of ion output with an attendant defocusing of the ion beam. This condition may last for a few seconds and then correct itself, or it

may persist until the operating parameters are manually reoptimized. The R&D effort produced some improvement, but the problem is still unsolved. In a series of experiments directed at altering the arc pressure and changing the ion-to-neutral ratio in the ion-acceleration region, little effect on beam stability was noted; however, the total ion output peaked broadly about a particular slit size. The addition of an arc-chamber insert reduced both the intensity and frequency of the instability by forming a very shallow arc chamber in which the insert actually contacted the back edge of the arc column. This flat-plate insert reduced the ion output slightly, but after several alterations in shape, a system was produced in which the output was undiminished. The final shape involved direct contact with only one-fourth of the area of the arc surface; the contacted area was located directly behind the ion exit slot of the source.

With this insert and the attendant improvement adopted into the ongoing separations program, further changes were introduced into the developmental system. Attempts to utilize the ion source geometry which was so successful in mercury separation failed; neither ion output nor beam quality approached acceptable levels. Subsequent changes in arc geometry, including multiple-aperture collimating slots, produced results that were sometimes favorable but seldom in agreement with predicted values. A three-hole collimating slot which

formed three arc columns within the arc chamber increased ion output significantly at acceptable beam quality; the adverse effect was a drastic (50%) reduction in filament life, which offset the derived benefits. Similarly, filaments placed within the arc chamber produced favorable increases in ion output; however, such filaments operated at a higher temperature, causing filament deformation as a result of magnetic field forces and softening of the filament at the elevated temperature.

During the above work and throughout the scheduled separations, it was recognized that problems existed with the use of Tl_2S as a feed material due to its decomposition and subsequent introduction of sulfur into the arc region. The use of Tl_2S as feed was predicated on the excessive ion source sparking experienced with metallic thallium in prior separations. More recent attempts to use a metallic thallium feed with abbreviated extraction electrodes are showing promise. Increases in ion output of up to 40% have been achieved, although beam quality suffers at the higher output and reproducibility is difficult to achieve. Sustained improvement in output amounting to 10-15% is now almost routine without undue compromise in stability or beam quality. A proper change in electrode configuration and spacing is a promising approach to the achievement of further improvements in thallium separation.

8. Nuclear Regulatory Commission Programs

8.1 REACTOR SAFETY RESEARCH

Severe Accident Sequence Analysis (SASA)

The objective of this Nuclear Regulatory Commission (NRC) program, in which four laboratories are contributors (ORNL, Sandia, Idaho National Engineering Laboratory, and Los Alamos), is improved understanding of the consequences of severe light-water reactor accidents. Although the activities of the laboratories differ, each contributes toward this general goal. ORNL's role, performed within both the Engineering Technology and the Chemical Technology divisions, is to analyze the sequence of events and resulting consequences for a series of postulated severe accidents at the Browns Ferry reactor.

Thus, far, we have concentrated on an accident sequence initiated by loss of ac power and subsequent failure of the auxiliary ac power source. This event leads to loss of core cooling, core melt, pressure vessel failure, and containment breach. A detailed sequence of events and conditions within the reactor during this accident has been derived.

We are in the process of determining fission product pathways from the fuel source through the reactor pressure vessel and the containment and building structures for this accident sequence. Each fission product category is being treated separately in order to properly account for chemical reactions that may affect the transport rate. Calculation of the noble gas transport pathway has been completed; estimation of iodine transport rates is currently in progress.

Aerosol Technology Support for the LMFBR

Vapor-condensation aerosols likely to comprise the mixtures of importance in various nuclear reactor accidents are being systematically generated and characterized in a 5-m³ (CRI-II) test vessel operated as part of a larger Liquid-Metal Fast Breeder Reactor

(LMFBR) Aerosol Release and Transport Program at ORNL.

Effective generation techniques based principally upon powdered metal-oxygen combustion in a dc plasma arc have been used to generate 100-g quantities of pure metal-oxide aerosols, and liquid sodium metal has been ignited spontaneously in a high-pressure spray to generate Na₂O₂ aerosols separately or in combination with another aerosol generated by the metal-oxygen process.

The results obtained thus far indicate that all aerosol materials formed by the vapor condensation methods in use exhibit a uniquely similar closed-vessel aerodynamic behavior and deposition rate, although the numbers and sizes of primary particles comprising a branched-chain agglomerate vary by more than an order of magnitude. At similar mass concentrations, all aerosols apparently quickly mature to about the same "self-preserving" aerodynamic size distribution, which is only slightly modified by vessel size and geometry. This observation may be illustrated in the four comparison photographs of the spiral centrifuge collections of the size-distributed aerosols of U₃O₈, Fe₂O₃, SnO₂, and SiO₂ in Fig. 8.1. The virtual lack of any significant time-dependent change in size distribution is apparent in each photograph. In each case, during a period of several hours over which the samples were collected, the airborne mass concentration diminished by a factor of at least 100. While this observation may be an oversimplification of systematics, it promises to be helpful in establishing radiological consequence levels as derived from aerosol behavior codes.

Experimental Program in LWR Core-Melt Aerosol Release and Transport

Aerosol behavior may be expected eventually to assume an importance in LWR Class IX accident assessment essentially equal to its importance in LMFBR safety analysis. Fission products, core

ORNL-OWG 81-13461

Fig. 8.1. Samples of centrifuge collector foils showing similar size distributions for four pure oxide aerosols.

components, and structural materials may be vaporized in large quantity from a core melt, giving rise to extra-high aerosol mass concentrations in the containment or dry well. At such high concentrations, they should initiate a coagglomeration scavenging process followed by rapid settling and thereby relieve a potentially harmful threat to the environment. Volatile fission products, including halogens in any oxidation state, may be adsorbed on the surface of the chemically active aerosols and could be expected to attenuate at about the same rate as the particulate solids.

Therefore a new program has been proposed to investigate closed-vessel, core-melt aerosol release and deposition behavior under the most realistic environmental conditions possible involving metal-water reaction followed by complete melting. A survey of the requirements of an experimental approach to a demonstration of core-melt aerosol release has clearly indicated that the most practical technique would be "skull melting" by direct rf induction. Aerosols generated by this method may be readily introduced into the present CRI-II containment for further examination where well-characterized aerosol instrumentation is already available.

The initial part of the effort has been dedicated to the development of a demonstration-scale (0.5- to 1.0-kg), water-cooled skull container with segmented copper components. This concept permits induction melting with kilocycle-frequency rf power by direct coupling to the mixed-fuel charge. Such a complete aerosol generation system has been constructed on a demonstration scale using a 50-kW rf power supply that was already on hand, and a few test melts have been conducted in the 300- to 700-g range.

A sample test melt is shown in Fig. 8.2 with the skull-melt residue in the split crucible at right, the overhead rubble in the center, and the vaporized aerosol (mainly metallic tin) on an off-gas filter at the left.

A second part of the effort has been concerned with the design of a future, full-scale (5- to 10-kg) furnace and selection of a 250-kW rf power unit to match the furnace. At this scale, aerosol releases of 100 g or more could then be expected. Combined with activated surrogate fission product tracers and gamma spectrometry, this configuration would afford a special opportunity to characterize simultaneously the core component as well as the fission product vaporization rates.

The major emphasis of the project will be to investigate chemical states and adsorption processes for tracer fission products—particularly halogens, cesium, and tellurium—and the coagglomeration of fuel, radioactive species, and structural material aerosol particles as a measure of the total attenuation rates.

Several approaches to the determination of chemical species have been investigated including x-ray diffraction, which is applicable to the mixed metal and metal oxides, and hydrogen reduction, which will identify some particular metal oxides. Maypack differential adsorption and liquid-liquid extraction will be used to identify most of the radioiodine species.

Characterization of Iodine Species in LWR Accident Environments

An aqueous iodine chemistry research program has been initiated in order to determine the redox chemistry of molecular iodine and its related products at temperatures up to 300°C. Although aqueous iodine chemistry has been a subject of considerable interest for several decades, there are no data available at the temperatures, pH, and concentrations at which most reactor accident sequences would occur.

This laboratory effort is intended to fill these obvious deficiencies; it is being performed in stages that are defined principally by the temperature because many of the materials of containment are limited to definite temperature regimes. Absorption spectrophotometry is being used to monitor individual iodine species in both liquid and vapor phases; and by using cell path lengths of up to 30 cm, it is possible to monitor some iodine species at concentrations as low as 10^{-6} M.

A titanium cell with sapphire windows has been modified to accommodate iodine kinetics studies up to 150°C. In addition, a sealed silica cell enclosed in a steel pressure-ballast system has been developed for studying equilibria between liquid and vapor phases of aqueous iodine solutions at temperatures of up to 150°C.

The major objectives of this program, confined to temperatures up to 150°C for the first year, have been (1) to identify and characterize the iodine species that occur in both liquid and vapor phases; (2) to obtain liquid-vapor distribution coefficient data for these iodine species as a function of temperature and

ORNL DWG 81-888

128

OFF-GAS AEROSOL FILTER

OVERHEAD RUBBLE

SEGMENTED INDUCTION CRUCIBLE

Fig. 8.2. Typical core-melt test for Zircaloy-clad UO_2 in the split crucible assembly.

concentration; and (3) to determine rates of reaction for iodine with water as a function of temperature, concentration, and pH.

Fission Product Release from LWR Fuel Under Overheat Conditions

Fission product release tests were performed with commercial fuel irradiated to 13,000 MWd/t in the Peach Bottom-2 BWR at high heat ratings and temperatures.¹ The amounts of krypton, cesium, and iodine released in-reactor to the plenum and gap space of the Peach Bottom-2 fuel are compared in Table 8.1 with the amounts in the previously tested H. B. Robinson-2 fuel. The concentrations of cesium and iodine in the gap space were 36 times greater in the Peach Bottom-2 fuel rods. Most commercial fuel rods should have concentrations within this range. These gap inventories were measured by purging the pellet-to-cladding gap space with purified helium while the test segments were at temperatures of 700 to 1100°C. This method was devised to measure the total quantity of fission products potentially releasable from a ruptured fuel rod in a controlled loss-of-coolant accident.

Results of the fission product release and gap purge tests with 30.5-cm lengths of high-gap-inventory fuel are summarized in Table 8.2. The burst tests were performed by inductively heating 15.2 cm of the test segment prepressurized with purified argon so that the Zircaloy cladding expanded and ruptured into flowing steam at the temperatures shown. The pressure required to rupture the cladding at 850°C was 2.8 times greater than that required at 960°C. The large volume of gas vented at rupture in the 850°C test caused the release of cesium and iodine to be almost the same as that in the 960°C test.

Table 8.2 also lists measured and estimated releases of cesium and iodine, the estimates being

projected by a source term model applicable to these low-temperature release conditions.^{2,3} Measured and predicted values agree quite well, considering that the model was based on tests with low-gap-inventory fuel and with simulated fuel rods. The mass of cesium (sum of all isotopes) released in each of the three tests with Peach Bottom-2 fuel ranged from 7150 to 7950 μg . The releases of cesium during similar tests with H. B. Robinson-2 fuel were much smaller—130 to 280 μg .

Currently, preparations are being made to extend the tests to the melting point of the fuel element ($\sim 2600^\circ\text{C}$). In order to do this in the required steam atmosphere, a tungsten-susceptor type furnace design has been adopted. The rf-heated susceptor is protected from steam oxidation by a helium bleed stream. Procedures for loading fuel and for disassembly in a hot-cell environment, as required in these tests, are compatible with this furnace design.

8.2 REGULATORY DIFFERENCES BETWEEN THORIUM AND CURRENT URANIUM FUEL CYCLES

A study is being conducted to assess the health, safety, and environmental aspects of thorium nuclear fuel cycles, how these aspects differ from those of the

1. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, O. L. Kirkland, and R. L. Towns, *Fission Product Release from Highly Irradiated LWR Fuel*, ORNL/NUREG/TM-287R2 (NUREG/CR-0722) (February 1980).
2. R. A. Lorenz, J. L. Collins, and A. P. Malinauskas, *Fission Product Source Terms for the LWR Loss-of-Coolant Accident: Summary Report*, ORNL/NUREG/TM-206 (NUREG/CR-0091) (June 1978).
3. R. A. Lorenz, J. L. Collins, and A. P. Malinauskas, "Fission Product Source Terms for the Light Water Reactor Loss-of-Coolant Accident," *Nucl. Technol.* 46, 404 (1979).

Table 8.1 Amounts of fission products in the pellet-to-cladding gap space

Fuel type	Burnup (MWd/t)	Krypton (%) ^a	Fission products in the gap space			
			Cesium		Iodine	
			(%) ^c	($\mu\text{g}/\text{cm}^2$) ^b	(%) ^c	($\mu\text{g}/\text{cm}^2$) ^b
H. B. Robinson-2	30,000	0.25 ^c	0.30	13	0.50	1.2
Peach Bottom-2	12,400	11.4 ^d	12.5	470	12.1	42

^aPercent of total produced.

^b μg of total element per cm^2 of cladding surface.

^cMeasured in room-temperature fuel rod puncture.

^dFrom measurement of room-temperature fuel rod puncture adjusted for local burnup and heat rating.

Table 8.2. Amounts of fission products released

Test	Test type	Amounts (%) ^a released				
		Measured "Kr" ^b	Cesium		Iodine	
			Measured	Calculated ^c	Measured	Calculated ^c
BWR-1	900°C burst	1.7	1.71	1.26	1.18	1.67
BWR-2	850°C burst	1.0	1.70	1.81	2.54	3.18
SRW-3	1200°C diffusion	1.1	1.85	1.07	2.99	2.70
BWR-4	700—1100°C gap purge	1.2	12.2	d	12.1	d

^aPercent of total produced in-reactor in heated length of test fuel rod segment.

^bThese amounts are in addition to the 11 to 15% released to plenum and void spaces in-reactor.

^cCalculated using source term model.

^dNot applicable.

uranium fuel cycles, and how these differences could affect the regulatory process. The study encompasses two specific tasks. Task I, Thorium Fuel Cycle Impacts Assessment, includes a literature review of thorium fuel cycles and an evaluation of the health, safety, and environmental (HS&E) impacts that might result from them. The entire thorium fuel cycle is evaluated including mining, milling, refining and conversion, fresh fuel fabrication, chemical separation of spent fuel, recycle fuel fabrication, and waste management. Task II, Comparison of Uranium and Thorium Fuel Cycles, is to compare the HS&E impacts in Task I with those from uranium fuel cycles and to identify any modifications or additions to the existing regulations that may be necessary for regulating thorium fuel cycles. Task I of the study was completed, and a report is being readied for publication. A report on Task II is in the review process.

8.3 SAFETY REVIEW OF NUCLEAR FACILITIES

The objective of this program is to provide technical assistance to the Nuclear Regulatory Commission in evaluating the safety of nuclear fuel cycle facilities and preparing related generic reports.

The safety review of the General Electric Morris Operation, which was performed in 1979 as part of the fuel storage facility license renewal, was reevaluated for conformance with Code of Federal Regulations, Title 10, Part 72, "Licensing Requirements for the Storage of Spent Fuel in an Independent Spent Fuel Storage Facility." A revised safety evaluation report has been prepared and will be issued as ORNL/NUREG/TM-439 (NUREG/CR-1697).

An evaluation of the effects of a tornado on the Nuclear Fuel Services Fuel Reprocessing Plant at West Valley, N.Y., has been completed. The results of

the evaluation indicate that a potential for the release of radioactivity from the general purpose cell to the operating aisle via the unplugged manipulator sleeves exists as a result of the ventilation air flow being reversed. The preparation of a final report has been initiated.

8.4 DEFINITION OF PARAMETERS FOR MAJOR ACCIDENTS IN SPENT FUEL STORAGE, FUEL REPROCESSING, AND WASTE SOLIDIFICATION FACILITIES

This program is part of a larger NRC program dealing with fuel cycle facility accidents. In addition to ORNL, it involves Los Alamos National Laboratory (LANL) and Battelle Pacific Northwest Laboratories (BPNL). A part of the LANL program includes the development of computer codes for predicting the response of ventilation and off-gas systems in fuel cycle facilities. The ORNL part of the program is to establish accident scenarios and define accident parameters for spent fuel storage, fuel reprocessing, and waste solidification facilities. A part of the BNPL program includes accident scenarios and parameters for fuel fabrication facilities. The ORNL and BPNL scenarios and parameters are contributions to an NRC Accident Analysis Handbook (AAH).

The first and second sections of the AAH, entitled "Summary" and "Background," are the responsibility of NRC; the third through the sixth sections are the responsibility of ORNL and BPNL (each for their assigned type of facility). The third section of the AAH, "Preaccident Parameters," describes the processes and process equipment, contents, and ventilation as well as the off-gas systems of selected facilities. It provides the essential characteristics of each type of facility and process subject to the

accidents to be considered in later sections. The fourth section, "Rationale for Accidents Considered," considers the accidents that have been experienced by, or can be realistically postulated for, the types of facilities described in the third section of the AAH. The main emphasis of these accident analyses is to identify accidents with potential for offsite releases. The prime objective of the list of postulated accidents summarized in this section is the identification of potential hazardous releases (i.e., of mass and/or energy). The accidents that were considered for the types of facilities described include criticality excursions, equipment failures, explosions, fires, and spills. The fifth section, "Event Defining Parameters," is to illustrate the determination of significant parameters (for an initiating event)

which provide input to near-field energy and mass transport calculations. The parameters generally required as a function of time for the initiating incident (source term) in most accident analyses are energy released, mass (and/or volume) released, temperature generated, pressure generated, and properties of aerosols formed. Examples of the determination of event-defining parameters for several of the accidents postulated in the fourth section of the AAH are presented in this section. The sixth and last section (other than appendixes) of the AAH, "Physicochemical Properties of Materials and Events," is to provide a preliminary basic data base on, and a guide to, the kinds of information needed in the analysis of accidents such as those postulated in the fourth section.

9. Three Mile Island Support Studies

Chemical Technology Division (CTD) staff members became involved with recovery operations at the Three Mile Island (TMI) Nuclear Power Station two days after the 1979 accident, when an ORNL response team was formed at the request of the U.S. Nuclear Regulatory Commission (NRC). The CTD was asked to provide technical guidance in chemical engineering, especially in the area of effluent control. During the three months following the accident, ten CTD staff members were on site as technical advisors to the Waste Management Group of the TMI Recovery Team. The major concerns of CTD personnel at TMI were in the areas of (1) release of ^{131}I to the environment, (2) treatment and storage of contaminated water, and (3) decontamination of surface and equipment. This work has been described in a report¹ written at the request of the President's Commission on the Accident at Three Mile Island (the Kemeny Commission).

Since the accident, CTD personnel have been involved continuously in the conception, development, and evaluation of chemical processes for the decontamination of the high-activity-level water (HALW) remaining in the reactor containment building (CB) and the reactor coolant system (RCS). All water cleanup work has been coordinated through the three-person Technical Advisory Group (TAG); one member of this group is a CTD staff member.

Samples of RCS water obtained shortly after the accident were used to characterize the water and to evaluate methods and materials considered for use in decontaminating the HALW. Personnel from CTD performed distribution coefficient measurements and tracer-level column loading tests on a variety of ion exchange media with potential value for HALW treatment. The TAG selected a treatment method, and the TMI owner, General Public Utilities, contracted for the design of a submerged demineralizer system (SDS).²

In December 1979, 3 L of CB water were obtained, and both hot-cell and laboratory tests were then performed in the CTD Transuranium Processing

Plant (TRU) to evaluate the SDS process flowsheet.³ The flowsheet was found to meet the design criterion which specifies that, except for tritium, the treated water, when diluted with normal TMI plant discharges, should contain <10% of the limits in 10CFR20;⁴ however, discharge of the diluted, treated water was not approved by the NRC. Two 1900-m³ (500,000-gal) storage tanks were built to contain the SDS effluent pending resolution of the disposal question and to permit removal and treatment of the water from the containment building. Since the SDS effluent would not meet NRC criteria then in use for storage in undiked tanks that were not seismically designed, further tests were made at TRU to develop flowsheet modifications that would produce SDS effluent suitable for storage in the existing tanks. The results of these tests have been reported⁵ to the TAG.

Another project involving CTD personnel was the coordination of ORNL participation in DOE studies to identify research and development programs that were shown, as a result of the TMI accident, to be of generic interest to the nuclear power industry. The draft report of the long-range plan⁶ was submitted to DOE by CTD personnel.

---

1. R. E. Brooksbank and L. J. King, *Involvement of the ORNL Chemical Technology Division in Contaminated Air and Water Handling at the Three Mile Island Nuclear Power Station*, ORNL/TM-7044 (August 1979).

2. R. R. Reust, *CNSI/TMI Water Cleanup System Process Description*, AGNS Draft Report, Allied-General Nuclear Services (August 1979).

3. D. O. Campbell, E. D. Collins, L. J. King, and J. B. Knauer, *Evaluation of the Submerged Demineralizer System (SDS) Flowsheet for Decontamination of High-Activity-Level Water at the Three Mile Island Unit 2 Nuclear Power Station*, ORNL/TM-7448 (July 1980).

4. 10CFR, Part 20, Appendix B, Table II, Column 2.

5. D. O. Campbell, E. D. Collins, L. J. King, and J. B. Knauer, *Process Improvement Studies for the Submerged Demineralizer System (SDS) at the Three Mile Island Unit 2 Nuclear Power Station*, ORNL/TM-7756 (in press).

6. *TMI Technical Information and Examination Program Preliminary Long-Range Plan for Generic Research and Development*, Draft DOE Report (July 1980).

Staff members of CTD participated in a DOE-SDS task force⁷ to evaluate the technical and financial impacts of loading the SDS ion exchange columns to radioactinide levels higher than those proposed in the reference SDS flowsheet. This effort also included a study of the radiation stability of inorganic ion exchange materials.⁸

---

7. *Evaluation of Increased Cesium Loadings on Submerged Demineralizer System Zeolite Beds*, DOE-SDS Task Force, Draft DOE Report (April 1981).

8. J. W. Roddy, *A Survey: Utilization of Zeolites for the Removal of Radioactivity from Liquid Waste Streams*, ORNL/TM-7782 (August 1981).

10. Miscellaneous Programs

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

A total of 1047 kg of uranium (76.5% ^{235}U , 9.67% ^{233}U , 1.40% ^{234}U , 5.63% ^{236}U , 6.84% ^{238}U , and 120 parts of ^{232}U per million parts of total uranium) is stored as a nitrate solution in an 18,900-L (5000-gal) vessel in Building 3019. This uranium resulted from reprocessing the Consolidated Edison Indian Point Reactor core, which produced 2.8 billion kWh of electricity between 1962 and 1965. Reprocessing was performed at the Nuclear Fuels Services Plant in West Valley, New York, and the product solution was transferred to ORNL in 1968-69.

The solution is maintained subcritical with two soluble neutron poisons (gadolinium and cadmium). Although the vessel was packed with borosilicate glass rings prior to introduction of the solution, neither the integrity nor the boron poison content of these rings can be verified. In addition, the pit housing the vessel does not contain borosilicate rings; therefore, we must rely on soluble poisons to prevent criticality in the event of leakage from the vessel into the pit. The measured concentrations of the poisons have varied widely over the 12-year storage period. However, at no time did the sum of the measured gadolinium and cadmium poison concentrations drop below values adequate to ensure criticality control. No evidence of significant corrosion in the vessel was found in analysis of samples of the solution for stainless steel constituents. However, localized corrosion could have occurred and would present a problem since the vessel walls are only 0.53 cm (0.21 in.) thick. Both DOE-CRO and ORNL safety committees have stated that continued storage for longer than an additional 3 years may be unwise.

We are presently designing and fabricating equipment for converting the uranium from nitrate solution to U_3O_8 for long-term storage in stainless steel cans (~3.2 kg U per can) in a previously constructed earthquake-proof storage facility. The process, demonstrated with the stored solution in a hot cell, concentrates the uranium while destroying

excess nitric acid and then, using rising-zone furnaces, converts the uranium to U_3O_8 in the storage cans.

The detailed design of equipment to perform this operation is 96% complete. The fabrication and procurement of equipment are 55% complete. We plan to begin the solidification operation in fiscal year 1983 after mock-up testing of the mechanical components.

10.2 $^{233}U_3O_8$ PACKET LOADING FOR ARGONNE NATIONAL LABORATORY

This program, described previously,¹ was completed during the present report period. A total of 1743 packets (1128 during this period), each containing 33 g of U_3O_8 , was transferred to the Zero Power Reactor site in Idaho for criticality experiments. The overall yield (fraction of loaded packets that met specifications) was 72%. Leakage caused by poor welding was the principal reason for rejection (~20%). Fusion welding of the tops onto the packets was difficult because of the precision required of the tracking mechanism, the changes in the welding current due to heat build-up in the programmer, and the length and taper of the welding rods.

10.3 URANIUM-233 PROCESSING

Oak Ridge National Laboratory serves as a national distribution center for ^{233}U . The facility includes shielded wells for storing up to 454 kg of ^{233}U in solid form (density = 1 g/cm³) and tanks (containing borosilicate glass rings for neutron poisoning) which can store 900 kg of ^{233}U in the form of uranyl nitrate solution at ^{233}U concentrations up to 250 g/L. An adjacent vault, constructed to meet criteria for withstanding earthquake and tornado damage, can be used to store up to 200 kg of fissile material.

1. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1979, ORNL-5542, pp. 90-92.

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

During this report period, four dissolution cycles were performed to convert 69.3 kg of ^{233}U from aged UO_2 and U_3O_8 to nitrate solution. Twenty-five additional dissolution cycles were performed to dissolve 21.7 kg of ^{233}U and 980 kg of thorium contained in $\text{UO}_2\text{-ThO}_2$ pellets. Five solvent extraction runs were made to recover 80.2 kg of ^{233}U . Five ion exchange runs were made to purify 60.2 kg of ^{233}U suitable for conversion to UO_2 or U_3O_8 . Two conversion runs were made to convert 9.3 kg of ^{233}U from nitrate solution to UO_2 . An additional four runs were made to convert 47.2 kg of ^{233}U to U_3O_8 .

Receipts during this report period amounted to 11 shipments containing a total of 26.4 kg of ^{233}U as UO_2 , $\text{UO}_2\text{-ThO}_2$, and metal; 2.3 kg of ^{239}Pu as PuO_2 ; 697 kg of thorium as $\text{UO}_2\text{-ThO}_2$ pellets and microspheres; and 5.8 kg of ^{235}U as $\text{UO}_2\text{-ThO}_2$ microspheres. Fourteen shipments from the facility contained 47.8 kg of ^{233}U as U_3O_8 , 4.0 kg of ^{233}U as UO_2 , 0.8 kg of ^{239}Pu as PuO_2 or $\text{PuO}_2\text{-UO}_2$ microspheres, and 0.3 kg of ^{235}U as $\text{PuO}_2\text{-UO}_2$ microspheres.

We are presently fabricating a replacement extraction pulse column and scrap dissolver for installation in the facility during this fiscal year. The existing extraction column, installed 25 years ago, operates inefficiently, resulting in excessive ($>1.0\%$) loss of uranium to the raffinate stream. The scrap dissolver developed a leak after the dissolution of $\sim 7 \times 10^4$ kg of $\text{UO}_2\text{-ThO}_2$ scrap in fluoride-catalyzed nitric acid. We have redesigned the top disengaging section of the replacement extraction column to eliminate dependence on borosilicate glass rings to render the solution subcritical in the event of a combination of equipment failure and human error. The use of glass rings requires annual verification of their integrity by x-raying the disengaging section and interpreting the film. This hazardous task must be performed 6 m (20 ft) above the cell floor by an x-ray technician dressed in two pairs of coveralls, a hood, and an assault mask. The redesigned section will utilize an annular space [section of 46-cm (18-in.) pipe inside 61-cm (24-in.) pipe] with the center section filled with sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$). Calculations show the neutron multiplication factor to be within the acceptable range using this technique.

A baffled tank has been installed in the vessel off-gas system to contain the radon for 20 half-lives. This holdup will permit essentially all of the radon to decay to particulate daughters that can be removed by absolute filtration prior to release to the central ORNL stack. We are presently designing a de-entrainment system that will remove entrained liquids from the dissolver off-gas stream.

A Safety Analysis Report for the operations in Buildings 3019 and 3100 (Source and Nuclear Materials Vault) was submitted to the Office of Radiation Safety for transmittal to and review by DOE-ORO.

A proposal for the recovery of 306 kg of ^{233}U from unirradiated light-water breeder reactor fuel elements was prepared and submitted to DOE. The proposal includes a preliminary cost estimate and a schedule for performing the task.

10.4 IMPROVEMENTS TO SAFEGUARDS IN BUILDING 3019

A number of improvements to the physical security system—new alarmed fencing, perimeter lighting, TV monitoring, and a "hardened" guard post—were completed and placed in operation. Internal modifications included conversion to a programmable key-card system and remotely monitored intrusion detection devices.

The Facility Integrated Computer System was placed in operation and debugged during this report period. This system receives signals from recently installed electronic transmitters that operate in parallel with the pneumatic transmitters, sending signals to the control room.

After the computer terminals had been installed in the Building 3019 control room and the Building 2026 analytical facility, operating personnel and Analytical Chemistry Division personnel were given training in computer access and information input and retrieval.

Although the system was originally plagued with hardware problems, operation during the past 4 months has been excellent.

10.5 SAFEGUARDS ENGINEERING

The principal objective of the Safeguards Engineering Program has been to demonstrate process monitoring as it might be accomplished by inspectors of a nuclear fuel recycle facility. A proposed multiphase work plan covering five fiscal years has been developed, but lack of support has prevented significant progress this last fiscal year. The four major contributions to the proposed

program would be: (1) analytical development, which could generate the instrumental capability; (2) computer system safeguards, which should provide a balanced, overall process view of near-real-time inventory, internal security, physical protection, and external surveillance; (3) project support, which would comply with the external program function requirements such as operator training and nuclear materials documentation; and (4) operations and processing monitoring, which should supplement internal security, physical protection, and external surveillance with a partial, element-by-element evaluation of the separate system components.

Improved instrumentation and computer interfaces initially permitted the solvent extraction system operations conducted in the Building 3019 Pilot Plant to be monitored as an accurate, but passive and static, volume balance. The volume balance is now made via an active, dynamic method of almost instantaneous process monitoring. Appropriate instrumentation for measuring flow and concentration, which could be added to the Pilot Plant later, would permit determination of the fissile-material mass balance within a period of ~ 15 s to 30 min.

An in-line, uranium-fluorescence analyzer is being tested in the laboratory. Preliminary calibration tests have been completed with three light excitation sources: a mercury vapor bulb, a krypton vapor bulb, and a helium-cadmium laser. The calibration is linear over the range of uranium concentration from 0.4 to more than 100 g/L. Both the light for solution excitation and that from uranium fluorescence are transmitted in a random-mix, bifurcated optical fiber bundle. The bundle interfaces with the solution in a minimum 6- to 7-mm-diam excitation face.

An ultrasonic, liquid-level detector has been installed in the 15-cm (6-in.)-diam titer tube of the 91-cm (36-in.)-diam S-4 solvent extraction feed tank. The instrument precision is ± 1 mm, an equivalent of ± 20 mL in the titer tube and ± 650 mL of the ~ 1150 -L working volume of S-4. An accurate flow rate is determined within 2 min by comparing liquid level with time; the previous method of flow-rate estimation required a minimum of 30 min.

10.6 REMOVAL OF HAZARDOUS RADIONUCLIDES FROM URANIUM MILL TAILINGS

Uranium mill tailings contain radionuclides that are a potential hazard for thousands of years. The long-term risks are mainly caused by the presence of the uranium decay chain members ^{230}Th and ^{226}Ra ,

whose respective half-lives are 80,000 and 16,000 years. The Uranium Mill Tailings Remedial Action Project (UMTRAP) has sponsored research on methods of treatment of the tailings to reduce their hazard. As a part of this program, we are continuing the investigation^{2,3} of methods of leaching, isolating, and concentrating radium and thorium. The major emphasis has been on the use of nitric acid as the leaching agent and the use of precipitation, adsorption, and solvent extraction for recovery of the radium and thorium.

Samples of tailings (from the Vitro site in Salt Lake City) remaining from previous work were used to measure the effectiveness of various reagents for leaching radium. Comparison of several agents is shown in Fig. 10.1. Multistage contact with either 1 or 3 M HNO_3 reduces the radium with each additional crosscurrent stage. The first three stages are more effective than later stages. The curves show

2. A. D. Ryon, F. J. Hurst, and F. G. Seeley, *Nitric Acid Leaching of Radium and Other Significant Radionuclides from Uranium Ores and Tailings*, ORNL/TM-5944 (August 1977).

3. F. M. Scheitlin and W. D. Bond, *Removal of Hazardous Radionuclides from Uranium Ore and/or Mill Tailings: Progress Report for the Period October 1, 1978 to September 30, 1979*, ORNL/TM-7065 (January 1980).

Fig. 10.1. Multistage, crosscurrent leaching of radium from Vitro tailings at 80°C for 1 h.

several inflections, the first corresponding roughly to the dissolution of the gypsum in the tailings; the inflection occurs later with 1 *M* than with 3 *M* HNO₃. The last three stages show a constant slope, which is characteristic of uniform distribution of radium between the solid and liquid phases. In contrast to leaching by HNO₃, the leaching of radium by 0.5 *M* ethylenediaminetetraacetic acid (EDTA) appears to level off after the second stage at a radium concentration of ~60 pCi/g as opposed to 22 pCi/g for 3 *M* HNO₃ after six stages. The effect of the liquid-to-solid ratio in crosscurrent leaching shows that leaching can be improved slightly by using more stages at a lower liquid-to-solid ratio to obtain the same total consumption of leaching agent.

Comparison of leachants at three temperatures is shown in Table 10.1. The effectiveness of 1 *M* HNO₃ improved progressively as the temperature increased

Table 10.1. Percentage of radium leached from Vitro tailings in three stages at 2:1 liquid-to-solid ratio

Reagent	Time (h)	Temperature (°C)		
		60	80	100
1 <i>M</i> HNO ₃	6		85	
1 <i>M</i> HNO ₃	1	71	84	90
3 <i>M</i> HNO ₃	1	87	95	94
0.5 <i>M</i> EDTA	1		91	
2 <i>M</i> Na ₂ CO ₃ -3 <i>M</i> HNO ₃	1		86	
1 <i>M</i> HNO ₃ -3 <i>M</i> HNO ₃	1		91	

from 60 to 80 to 100°C. With 3 *M* HNO₃, radium leaching improved as the temperature increased from 60 to 80°C, but showed no further improvement at 100°C. The use of a Na₂CO₃ solution to metathesize the gypsum and remove the sulfate before leaching with HNO₃ was demonstrated to be effective.

Removal of radium from the sand fraction of the tailings would permit use of the sand as cover material to attenuate the radon from the mines. Several tests were made to determine leaching of radium from the sand (+140 mesh) from Vitro tailings. Multistage data with 3 *M* HNO₃ show that most of the radium is leached in two stages; and thereafter it is removed at a low, uniform fraction indicative of a constant distribution. Grinding causes a stepwise release followed by the same gradual release down to a radium concentration of <20 pCi/g after six stages. The results show that 2 *M* HNO₃ is only slightly less effective than 3 *M* HNO₃, and that 3

M HCl is equivalent to 3 *M* HNO₃. Neither 1 *M* NaCl nor 10 *M* H₂SO₄ was very effective. The effectiveness of 0.5 *M* EDTA was greater than that of 1 *M* HNO₃ but less than that of 2 *M* HNO₃. Leaching with 3 *M* HNO₃ for 24 h at room temperature was as effective as 1 h at 80°C, which would indicate that heap leaching may offer a simple, practical treatment step.

10.7 CHATTANOOGA SHALE AS A SOURCE OF OIL AND VALUABLE METALS

Devonian shale is being considered as a source of oil. It contains about the same amount of carbon as the more-studied western shale and, when retorted with hydrogen, yields about the same amount of oil. The Chattanooga shale is of special interest because, in addition to oil, it contains enhanced concentrations of certain metals that are valuable or strategic. A few scouting tests have been made to determine the feasibility of oil and metal recovery.

Retorting Experiments

To determine the oil yields achievable from Chattanooga shale and to provide spent shale samples for metal recovery tests, a series of retorting experiments was performed by heating ~500-g batches of shale (~6-mm particles) from ambient temperature to about 937 °C (220° F) at a heatup rate of about 0.1 K/s (11° F/min). Experiments were performed at atmospheric pressure under argon and at 3.6 MPa (500 psig) under a hydrogen atmosphere. The experiments were done in a reactor (0.032 m ID × 0.76 m long) heated by an electric furnace. Thermocouples for temperature control were located on the external surface and internally at approximately the center of the bed. Purge gas was metered into the top of the reactor. Effluent from the bottom of the reactor passed through a series of air-cooled, ice-cooled, and dry-ice-cooled traps and a charcoal bed for collection of liquid products. Aqueous and oil phases were separated by decantation for oil yield determination. The volume and composition of the gas downstream of the liquid collection system were measured with an orifice meter and a gas chromatograph.

Experiments were performed on samples of the Gassaway member of Chattanooga shale from three sources. Sample A was collected from a Chattanooga shale at a road cut near Cookeville, Tennessee; samples B and C were obtained from the Institute of Gas Technology (IGT) from an unspecified location.

Run conditions and oil and gas yields for the experiments are given in Table 10.2 along with carbon distributions and gas compositions. Sample C was run under only a hydrogen atmosphere. Oil yields from the argon atmosphere tests with samples A and B were 0.050 m³/Mg (12 gal/ton), whereas the oil yields from hydroretorting under 3.6-MPa hydrogen pressure were 0.083 m³/Mg (19.7 gal/ton), 0.096 m³/Mg (22.9 gal/ton), and 0.058 m³/Mg (14.2 gal/ton) for samples A, B, and C, respectively. The hydrogen consumption during the three hydroretorting experiments was ~75 m³/Mg. The results indicate that a significant increase in oil yield can be obtained by retorting under hydrogen pressure. Oil yields are in general agreement with those reported in the literature⁴ for eastern Devonian shales.

Metal Recovery Experiments

Shale contains several minerals with value sufficient to justify the consideration of recovery. Economic recovery of these metals could enhance the economics of shale processing, decrease this country's dependence on foreign sources, and minimize environmental concerns of spent shale disposal. Metals of interest include Al, Co, Fe, Mo, and U.

A scouting study is presently under way to investigate mineral recovery from eastern shale. The experimental program has two objectives: to determine both the shale metal values that can be extracted and the research and development work necessary to advance the concept of metal recovery toward commercialization. Experiments to date have concentrated on the metal removal step.

The reference feed material (Table 10.3) is a Chattanooga oil shale that has been retorted with hydrogen under pressure. This material is considered to be indicative of the solid waste generated by the IGT Retort Process, which represents the state of the art in eastern oil shale development. Other feeds tested include raw shale, shale that has been subjected to gasification, and retort residue that has been subjected to roasting-gasification.

Maximum extraction values via direct acid leach with HCl or H₂SO₄ for Al, Co, Fe, and U were found to be 77, 99, 99, and 65%, respectively. An ambient-

4. S. A. Weil et al., "The IGT HYTORT Process for Hydrogen Retorting of Devonian Oil Shales," presented at the Sixth National Conference on Energy and the Environment, Pittsburgh, May 21-24, 1979.

Table 10.2. Run conditions and results from retort tests with Chattanooga shale

Conditions and parameters	Sample A		Sample B		Sample C
	In Ar	In H ₂	In Ar	In H ₂	In H ₂
Pressure, MPa	0.1	3.6	0.1	3.6	3.6
Purge rate, m ³ /s × 10 ³	0.003	0.06	0.004	0.06	0.06
Final temperature, K	934	941	936	932	933
Heat-up rate, K/s	0.1	0.08	0.1	0.1	0.1
Oil yield, m ³ /Mg ^a	0.050	0.083	0.050	0.096	0.058
Gas yield, m ³ /Mg	41	36	37	28	20
Original carbon content, %	16.4	16.4	14.1	14.1	10.1
Carbon distribution, ^b %					
Liquid	26	48	29	60	48
Gas	5	9	6	6	7
Residue	69	43	65	34	45
Gas composition, %					
H ₂	34	c	34	c	c
CH ₄	24	49	24	45	48
C ₂	5	7	4	7	6
CO	3	9	5	7	8
CO ₂	3	0.2	9	0.4	0.4
H ₂ S	31	35	24	41	38
H ₂ consumption, m ³ /Mg		76		76	74

^aMultiply by 240 to convert to gal/ton.

^bNormalized to 100%; carbon balances ranged from 88 to 106%.

^cHydrogen-free basis.

Table 10.3. Composition of Chattanooga shale retort residues

Element	Composition (ppm)	Element	Composition (ppm)
Al	76,400	Na	3,419
B	114	Nb	15
Ba	1,055	Ni	311
Be	3	P	617
Ca	3,632	Pb	31
Co	75	Sc	13
Cr	123	Sr	79
Cu	121	Th	3
Fe	71,600	Ti	4,610
K	24,700	U	58
Li	37	V	447
Mg	8,164	Y	33
Mn	138	Zn	507
Mo	205	Zr	88

temperature leach of retort residue followed by a reflux-temperature leach results in substantial Al-Fe separation. The initial leach extracts ~90% of the iron and <5% of the aluminum. The reflux leach extracts >70% of the aluminum and the remainder of the iron. In the HCl system aluminum could be recovered as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ via sparge crystallization and calcined to marketable alumina (Al_2O_3). Scouting studies indicate the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ can be recovered at sufficient purity in two crystallization stages. The iron in the first-stage leach liquor can be recovered as Fe_2O_3 , with HCl recovered for recycle.

An ambient-temperature H_2SO_4 leach of raw shale resulted in a 59% removal of uranium with a total feed weight loss of <3%. Thus, uranium extraction prior to treatment for oil and gas recovery may be possible.

Leaches of retort residue subjected to gasification at temperatures ranging from 550 to 750°C showed increased extraction values for Cu, K, Mo, and P. At temperatures greater than 800°C, sintering occurs and results in decreased extraction values for all metals.

10.3 POST-ACCIDENT SAMPLING IN NUCLEAR REACTORS (SUPPORT TO TVA)

The Tennessee Valley Authority (TVA) is receiving short-term assistance from ORNL in the review and adaptation of nuclear reactor sampling equipment for the nuclear power plants at Browns Ferry, Sequoyah, and Watts Bar. The sampling equipment was first designed for the Commonwealth Edison Company by the Sentry Equipment Corporation and the NUS Corporation. The January 1981 deadline originally imposed upon the utilities by the NRC for installation and operability of the equipment has been extended to January 1982.

Thus far, ORNL and TVA personnel have observed an operational demonstration of the equipment and instrumentation by the Sentry Equipment Corporation in Oconomowoc, Wisconsin, and drawings of the equipment have been reviewed at ORNL. This equipment will be supplied to TVA for post-accident sampling and on-line analysis. A report has been written to document results from the equipment demonstration and drawing review.

Administrative Summary

PUBLICATIONS, ORAL PRESENTATIONS, AND PATENTS

A. Basic Science and Technology

1. Bahner, C. T.,¹ R. R. Shoun, and W. J. McDowell, "Stability of Diethyl[(diethylcarbamoyl)methyl] Phosphonate," presented at the Southeastern Regional Meeting of the American Chemical Society, Roanoke, Va., Oct. 24-26, 1979.
2. Barker, R. E., "Granular Filtration in an Electric Field," presented at the Department of Chemical Engineering, Clemson University, Clemson, S.C., Nov. 9, 1979.
3. Beahm, E. C., and C. A. Culpepper,² "Basic Chemical Compatibility of Uranium Carbides with Cr-Fe-Ni Alloys," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11-16, 1979.
4. Beahm, E. C., and C. A. Culpepper,² "Basic Chemical Compatibility of Uranium Carbides with Cr-Fe-Ni Alloys," *Trans. Am. Nucl. Soc.* 33, 262-63 (1979).
5. Begovich, J. M., and W. G. Sisson, "A Rotating Annular Chromatograph for Continuous Metal Separations: The Role of Column Dimensions," presented at the Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., May 5-8, 1980.
6. Begovich, J. M., and W. G. Sisson, "Continuous Ion Exchange Separation of Zirconium and Hafnium," presented at the Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Chicago, Ill., Feb. 22-26, 1981.
7. Benker, D. E., F. R. Chattin, E. D. Collins, J. B. Knauer, P. B. Orr, R. G. Ross, and J. T. Wiggins, "Chromatographic Cation Exchange Separation of Decigram Quantities of Californium and Other Transplutonium Elements," presented at the Symposium on Industrial-Scale Production-Separation-Recovery of Transplutonium Elements, Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
8. Besmann, T. M., "Thermodynamics of Actinide-Carbon-Oxygen Systems: Potential Fuels for the Breeder," presented at the Department of Chemistry, University of California, Berkeley, Oct. 27, 1980.
9. Besmann, T. M., and E. C. Beahm, "Thermodynamic Studies of Thorium Carbide Fuel Preparation and Fuel-Clad Compatibility," presented at the International Symposium on Thermodynamics of Nuclear Materials, Jülich, Federal Republic of Germany, January 1979; published in the *Proceedings*, IAEA-SM-236/61, International Atomic Energy Agency, 1980, pp. 277-95.
10. Besmann, T. M., and C. A. Culpepper,² "Thermodynamic Measurements in the $\text{PuO}_{1.5}\text{-PuC}_{1.5}\text{-C}$ System," presented at the Fall Meeting of the Nuclear Division of the American Ceramic Society, San Francisco, Oct. 26-29, 1980.
11. Besmann, T. M., and T. B. Lindemer, "Thermodynamic Calculations on Coal Ash Oxide-CaO Interactions," presented at the Annual Meeting of the American Ceramic Society, Cincinnati, Apr. 28-May 2, 1979; published in *Am. Ceram. Soc. Bull.* 58, 352 (1979).

1. Present address: Bluefield College, Bluefield, W. Va.

2. Solid State Division.

12. Besmann, T. M., and T. B. Lindemer, "Thermodynamic Measurements in the Th-C-O System," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 27-30, 1980; published in *Am. Ceram. Soc. Bull.* **59**, 396 (1980).
13. Besmann, T. M., and T. B. Lindemer, "High-Temperature Equilibrium Between Thorium Dioxide, Thorium Dicarbide, and Carbon," *J. Inorg. Nucl. Chem.* **43**, 981 (1981).
14. Besmann, T. M., T. B. Lindemer, and C. Ling,³ "Thermodynamic Calculations on Coal Ash and CaO Interactions," *Am. Ceram. Soc. Bull.* **59**, 484 (1980).
15. Bigelow, J. E., E. D. Collins, and L. J. King, "The 'CLEANEX' Process: A Versatile Solvent Extraction Process for Recovery and Purification of Lanthanides, Americium, and Curium," presented at the Actinide Separations Symposium, Pacific Chemical Conference of the American Chemical Society, Honolulu, Apr. 1-6, 1979; published in ACS Symposium Series 117, 1980, pp. 147-55.
16. Bratzler, R. L.,⁴ and J. M. Begovich, *A Mathematical Model for Multicomponent Separations on the Continuous Annular Chromatograph*, ORNL/TM-6706 (December 1980).
17. Brown, C. H., Jr., *Mass Transfer in Two-Phase Nondispersing Liquid-Liquid Contactors with a High-Density-Difference System*, ORNL/TM-6670 (April 1979).
18. Brunton, G. D.,⁵ J. R. Hightower, Jr., I. L. Thomas,⁶ W. R. Grimes, H. D. Cochran, Jr., J. S. Johnson, Jr.,⁶ J. S. Watson, and F. W. Wiffen,⁷ "Assessment of Basic Research Needs and Priorities in Support of Fossil Energy," pp. 97-139 in *Basic Research Needs in Seven Energy-Related Technologies*, DOE/ER-0060 (1980).
19. Campbell, D. O., "The Application of Pressurized Ion Exchange to Separations of Transplutonium Elements," presented at the Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
20. Canon, R. M., *High-Temperature Oxidation of Graphite Rods with Temperature Control by Combustion Gas Recycle*, ORNL/TM-5683 (April 1980).
21. Canon, R. M., and J. M. Begovich, "Pressurized Continuous Chromatography," presented at the Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., Oct. 30-Nov. 2, 1979.
22. Canon, R. M., J. M. Begovich, and W. G. Sisson, "Pressurized Continuous Chromatography," *Sep. Sci. Technol.* **15**, 655-78 (1980).
23. Canon, R. M., A. D. Kelmers, W. J. McDowell, F. G. Seeley, and J. S. Watson, "Metal Removal from Coal Ashes and Wastes," presented at the Solid Waste Research and Development Needs for Emerging Coal Technologies Workshop, San Diego, Apr. 22-25, 1979; published in the *Proceedings*, American Society of Civil Engineers, 1979, pp. 120-34.
24. Canon, R. M., W. J. McDowell, F. G. Seeley, and J. S. Watson, "Recovery of Resource Material from Fly Ash and Coal Conversion Residue," presented at the Solid Waste Research and Development Needs for Emerging Coal Technologies Workshop, San Diego, Apr. 22-25, 1979; published in *Solid Waste Research and Development Needs for Emerging Coal Technologies*, American Society of Civil Engineers, 1979.

---

3. Co-op student from University of Tennessee, Knoxville.

4. Polaroid Corp., Cambridge, Mass.

5. Present address: Office of Nuclear Waste Isolation, Battelle, Columbus, Ohio.

6. Chemistry Division.

7. Metals and Ceramics Division.

25. Canon, R. M., F. G. Seeley, and J. S. Watson, "Engineering Analysis and Comparison of New Processes for the Recovery of Resource Materials from Coal Ash," presented at the Fifth International Ash Utilization Symposium, Atlanta, February 1979; published in the *Proceedings*, METC/SP-79/10 (1979), pp. 56-67.
26. Chattin, F. R., D. E. Benker, M. H. Lloyd, P. B. Orr, R. G. Ross, and J. T. Wiggins, "Preparation of Curium-Americium Oxide Microspheres by Resin-Bead Loading," presented at the Symposium on Industrial-Scale Production-Separation-Recovery of Transplutonium Elements, Second Chemical Congress of the American Chemical Society, Las Vegas, Aug. 24-29, 1980.
27. Clinton, S. D., and J. J. Perona, "Mass Transfer in a Bubble-Agitated Liquid-Liquid System," presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, Nov. 16-20, 1980.
28. Clinton, S. D., and J. S. Watson, "The Solubility of Tritium in Yttrium at Temperatures from 250 to 400°C," *J. Less-Common Met.* **66**(1), 51-57 (1979).
29. Collins, E. D., and D. E. Benker, *Iodiox Process Tests in a Transuranium Element Production Campaign*, ORNL/TM-6182 (June 1979).
30. Collins, E. D., D. E. Benker, F. R. Chattin, P. B. Orr, and R. G. Ross, "Multigram Group Separation of Actinide and Lanthanide Elements by LiCl-Based Anion Exchange," presented at the Symposium on Industrial-Scale Production-Separation-Recovery of Transplutonium Elements, Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
31. Counce, R. M., and J. J. Perona, "Gaseous Nitrogen Oxide Absorption in a Sieve-Plate Column," *Ind. Eng. Chem. Fundam.* **18**, 400-406 (1979).
32. Counce, R. M., and J. J. Perona, "A Mathematical Model for Nitrogen Oxide Absorption in a Sieve-Plate Column," *Ind. Eng. Chem. Process Des. Dev.* **19**, 426-31 (1980).
33. Counce, R. M., and J. J. Perona, "The Scrubbing of Gaseous Nitrogen Oxides in Packed Towers," presented at the National Meeting of the American Institute of Chemical Engineers, Houston, Apr. 5-9, 1981.
34. Egan, B. Z., F. G. Seeley, and A. D. Kelmers, "Chemistry of the Calsinter Process for Alumina Recovery from Fly Ash," presented at the Symposium on Hydrometallurgy, Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Las Vegas, Feb. 24-28, 1980; published as preprint 80-47, Society of Mining Engineers, 1980.
35. Egan, B. Z., F. G. Seeley, and A. D. Kelmers, "Recovery of Aluminum from Fly Ash by the Calsinter Process," pp. 169-76 in *Process and Fundamental Considerations of Selected Hydrometallurgical Systems*, M. C. Kuhn, Ed., Society of Mining Engineers, New York, 1981.
36. Felker, L. K., and F. G. Seeley, "Chemical Development of the Calsinter Process for Recovering Resource Materials from Fly Ash," presented at the Chemical Technicians Symposium, National Meeting of the American Chemical Society, Washington, D.C., Sept. 10-15, 1979.
37. Fellows, R. L., and M. H. Lloyd, "The Precipitation of Thorium Molybdate," presented at the National Meeting of the American Chemical Society, Washington, D.C., Sept. 9-14, 1979.
38. Fellows, R. L., and M. H. Lloyd, "The Solubility and Precipitation of Molybdenum Oxides in Nitric Acid," presented at the Symposium on the Chemistry of Early Transition Metal Oxides, Polyoxoanions, and Oxo Complexes, Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
39. Fisher, P. W., and J. S. Watson, "Cryosorption Pumping for Fusion Reactors," presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, Nov. 16-20, 1980.

40. Friedman, H. A., *Feasibility Study for the Oxidation of Am(III) by Photolysis*, ORNL/TM-7359 (December 1980).
41. Friedman, H. A., and L. M. Toth, "Absorption Spectra of Np(III), (IV), (V), and (VI) in Nitric Acid Solution," *J. Inorg. Nucl. Chem.* 42, 1347 (1980).
42. Friedman, H. A., and L. M. Toth, "Photochemically Induced Reduction of Trace Np(VI) in U(VI)-HNO₃ Solutions," *J. Inorg. Nucl. Chem.* 43, 1611-13 (1981).
43. Friedman, H. A., L. M. Toth, and M. M. Osborne, "The Photochemistry of Neptunium in Aqueous Perchloric Solutions," *J. Inorg. Nucl. Chem.* 41, 1339 (1979).
44. Fuller, E. L., Jr.,⁶ S. D. Clinton, K. J. Fallon,⁸ C. M. Jones,⁹ J. J. Perona, J. S. Watson, and S. M. Senkan,⁸ "Sorption of SF₆ by Activated Charcoal," *J. Chem. Eng. Data* 23, 4-7 (1981).
45. Gilliam, T. M., "Development of the Krypton Absorption in Liquid CO₂ (KALC) Process: Mass Transfer Efficiencies of Packed Columns," *Nucl. Technol.* 43, 75 (April 1979).
46. Gilliam, T. M., and R. M. Canon, "Removal of Metals from Coal Ash," presented at the 15th Intersociety Energy Conversion Engineering Conference, Seattle, Aug. 18-22, 1980; published in the *Proceedings*, American Institute of Aeronautics and Astronautics, 1980, pp. 970-77.
47. Horner, D. E.,¹⁰ J. C. Mailen, J. R. Coggins, Jr.,¹¹ S. W. Thiel,¹² T. C. Scott,³ N. Pih,³ and R. G. Yates,¹¹ *Interphase Transfer Kinetics of Thorium Using the Single Drop and the Lewis Cell Techniques*, ORNL/TM-6903 (November 1979).
48. Horner, D. E.,¹⁰ J. C. Mailen, J. R. Coggins, Jr.,¹¹ S. W. Thiel,¹² T. C. Scott,³ N. Pih,³ and R. G. Yates,¹¹ "Interphase Transfer Kinetics of Thorium Using the Drop Method and the Lewis Cell Method," presented at the National Meeting of the American Chemical Society, Houston, Mar. 23-28, 1980.
49. Horner, D. E.,¹⁰ J. C. Mailen, J. R. Coggins, Jr.,¹¹ S. W. Thiel,¹² T. C. Scott,³ N. Pih,³ and R. G. Yates,¹¹ "Interphase Transfer Kinetics of Thorium Between Nitric Acid and Tributyl Phosphate Solutions Using the Single Drop and the Lewis Cell Techniques," *Ind. Eng. Chem. Fundam.* 19, 287-91 (1980).
50. Horner, D. F.,¹⁰ J. C. Mailen, S. W. Thiel,¹² T. C. Scott,³ and R. G. Yates,¹¹ *Interphase Transfer Kinetics of Uranium Using the Drop Method, Lewis Cell, and Kenics Mixer*, ORNL/TM-6786 (May 1979); also published in *Ind. Eng. Chem. Fundam.* 19, 287-91 (1980).
51. Jones, G., Jr., and R. M. Canon, "Resource Recovery from Coal Residues," presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, Nov. 16-20, 1980.
52. Keller, O. L.,⁶ W. R. Grimes, M. R. Guerin,¹³ M. L. Poutsma,⁶ and J. S. Watson, *ORNL Coal Chemistry Report—1979*, ORNL-5629 (February 1980).
53. Kelmers, A. D., "The Recovery of Uranium from Seawater—Status of Technology and Needed Future Research and Development," presented at a Topical Meeting on the Recovery of Uranium from Seawater, Massachusetts Institute of Technology, Cambridge, Dec. 1-2, 1980; to be published in the *Proceedings*.

---

8. Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge.

9. Physics Division.

10. Retired.

11. Co-op student from Auburn University, Auburn, Ala.

12. Co-op student from Virginia Polytechnic Institute, Blacksburg.

13. Analytical Chemistry Division.

54. Kelmers, A. D., B. Z. Egan, F. G. Seeley, and G. D. Campbell, "Direct Acid Dissolution of Aluminum and Other Metals from Fly Ash," presented at the Symposium on Hydrometallurgy, Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Chicago, Feb. 22-26, 1981.
55. Kelmers, A. D., and H. E. Goeller, *Uranium Recovery from Low-Level Aqueous Sources*, ORNL/TM-7652 (March 1981).
56. Kelmers, A. D., F. G. Seeley, G. D. Campbell, and B. Z. Egan, "Direct Acid Dissolution of Aluminum and Other Metals from Ten Fly Ashes," presented at the Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Chicago, Feb. 22-26, 1981.
57. Kinard, W. F.,¹⁴ and W. J. McDowell, "Liquid-Liquid Extraction of Alkali and Alkaline Earth Metals by Crown Ethers and a Liquid Cation Exchanger," presented at the Annual Meeting of the South Carolina Academy of Science, College of Charleston, Charleston, S.C., Mar. 27-29, 1980.
58. Kinard, W. F.,¹⁴ W. J. McDowell, and R. R. Shoun, "Studies of the Size-Selective Extraction of Alkali Metals Ions by the Synergistic Extraction System, Crown Ether-Di(2-ethylhexyl) Phosphoric Acid-Benzene," presented at the Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., Oct. 30-Nov. 2, 1979; published in *Sep. Sci. Technol.* 15, 1013-24 (1980).
59. King, L. J., "Current Status of the Transuranium Processing Plant," presented at the American Nuclear Society Conference on Remote Systems Technology, San Francisco, Nov. 11-16, 1979; published in *Trans. Am. Nucl. Soc.* 33, 882-83 (1979).
60. King, L. J., J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Report of Production, Status, and Plans for the Period January 1, 1978-September 30, 1978*, ORNL-5531 (June 1979).
61. King, L. J., J. E. Bigelow, and E. D. Collins, "Transuranium Processing Plant," presented at the Energy Resources Workshop, Oak Ridge National Laboratory, Oak Ridge, Tenn., Sept. 24-26, 1979.
62. King, L. J., J. E. Bigelow, and E. D. Collins, "Experience in the Separation and Purification of Transplutonium Elements in the Transuranium Processing Plant at the Oak Ridge National Laboratory," presented at the Symposium on Industrial-Scale Production-Separation-Recovery of Transplutonium Elements, Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
63. Lindemer, T. B., "Engineering Applications of Chemical Thermodynamics to Metal and Oxide Systems," presented during the visit of the American Chemical Society delegation to the Peoples Republic of China, June 9-20, 1980.
64. Lindemer, T. B., "Oxide Phase Equilibria Involving Cesium and Rubidium," presented at the Fall Meeting of the Nuclear Division, American Ceramic Society, San Francisco, Oct. 26-29, 1980.
65. Lindemer, T. B., T. M. Besmann, and C. E. Johnson,¹⁵ "Thermodynamic Review and Calculations—Alkali Metal Oxide Systems with Nuclear Fuels, Fission Products, and Structural Materials," *J. Nucl. Mater.* 100 (1981).
66. Mailen, J. C., "An Empirical Equation for Estimating Nitric Acid Extraction by Tri-*n*-Butyl Phosphate from Nitric Acid and Nitric Acid-Sodium Nitrate Solutions," *Nucl. Technol.* 52, 310 (1981).
67. Mailen, J. C., and D. E. Horner,¹⁰ "Calculated and Experimental Studies of Nonequilibrium Solvent Extraction of Uranium-Thorium and Uranium-Zirconium," presented at the National Meeting of the American Institute of Chemical Engineers, Portland, Oreg., Aug. 17-20, 1980.

---

14. College of Charleston, Charleston, S.C.; formerly of the Chemical Technology Division.

15. Argonne National Laboratory, Argonne, Ill.

68. Mailen, J. C., D. E. Horner,¹⁰ N. Pih,³ S. M. Robinson, and R. G. Yates,¹¹ "Solvent Extraction Chemistry and Kinetics of Zirconium," presented at the Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., Oct. 30–Nov. 2, 1979; published in *Sep. Sci. Technol.* 15, 959–73 (1980).
69. McDowell, W. J., "Alpha Liquid Scintillation Counting: Past, Present, and Future," presented at the International Conference on Liquid Scintillation Counting, San Francisco, Aug. 21–24, 1979; published in *Liquid Scintillation Counting, Recent Applications and Development. Vol. 1. Physical Aspects*, C.-T. Peng, D. L. Horrocks, and E. L. Alpen, Eds., Academic Press, New York, 1980, pp. 315–32.
70. McDowell, W. J., "Separations Chemistry and Hydrometallurgy Research at Oak Ridge National Laboratory: Background and Opportunities," presented at the University of New Mexico, Albuquerque, Sept. 26, 1979.
71. McDowell, W. J., "Alpha Liquid Scintillation Counting Method Development at Oak Ridge National Laboratory and Arizona State University," presented at Arizona State University, Tempe, Sept. 29–Oct. 3, 1979.
72. McDowell, W. J., "Possibilities for the Use of Crown Ethers as Size-Selective Extractants in Process Applications," presented at the National Meeting of the American Chemical Society, Atlanta, Mar. 29–Apr. 3, 1981.
73. McDowell, W. J., E. J. Bouwer,¹⁶ J. W. McKlveen,¹⁷ and G. N. Case, "Application of the Combined Solvent Extraction–High Resolution Liquid Scintillation Method to the Determination of ²³⁰Th and ^{234–238}U in Phosphatic Materials," presented at the International Conference on Liquid Scintillation Counting, San Francisco, Aug. 21–24, 1979; published in *Liquid Scintillation Counting, Recent Applications and Development. Vol. 1. Physical Aspects*, C.-T. Peng, D. L. Horrocks, and E. L. Alpen, Eds., Academic Press, New York, 1980, pp. 333–46.
74. McDowell, W. J., and G. N. Case, "New Advances in Alpha Spectrometry by Liquid Scintillation Methods," presented at the American Nuclear Society Topical Meeting on Measurement Technology for Safeguards and Materials Control, Kiawah Island, S.C., Nov. 26–30, 1979; published in *Trans. Am. Nucl. Soc.* 33, 8–10 (1979); also published in National Bureau of Standards special publication 582, T. R. Canada and B. S. Carpenters, Eds., 1980, pp. 111–20.
75. McDowell, W. J., W. F. Kinard,¹⁴ and R. R. Shoun, "Recent Advances in Size-Selective Synergistic Extraction with Crown Ethers and Liquid Cation Exchangers," presented at the Third Symposium on Macrocyclic Compounds, Brigham Young University, Provo, Utah, Aug. 6–8, 1979.
76. McDowell, W. J., W. F. Kinard,¹⁴ and R. R. Shoun, "Crown Ethers as Size-Selective Synergists in Solvent Extraction Systems," presented at the International Solvent Extraction Conference (ISEC '80), Liege, Belgium, Sept. 6–12, 1980; published in the *Proceedings*, L. Delvaux and G. Duyckaerts, Eds., vol. 1, Sect. 80-6.
77. McDowell, W. J., and R. R. Shoun, "An Evaluation of Crown Compounds in Solvent Extraction of Metals," p. 95 in *Solvent Extraction, Proceedings of the International Conference, ISEC '77, Toronto, September 1977*, CONF-770907, B. H. Lucas, G. M. Ritcey, and H. W. Smith, Eds., Canadian Institute of Mining and Metallurgy, CIM special vol. 21 (1979).
78. Metzger, R.,¹⁷ J. W. McKlveen,¹⁷ R. Jenkins,¹⁸ and W. J. McDowell, "Specific Activity of Uranium and Thorium in Marketable Rock Phosphate as a Function of Particle Size," *Health Phys.* 39, 69–75 (1980).

---

16. Stanford University, Palo Alto, Calif.

17. Arizona State University, Tempe.

18. Phillip Morris Research Center, Richmond, Va.

79. Pearson, R. L., "Heat Exchanger Tube-CaSO₄ Deposit Interaction in the Fluidized-Bed Combustion of Coal," presented at the Pacific Coast Regional Nuclear Division Meeting of the American Ceramic Society, San Francisco, Oct. 26-29, 1980.
80. Pearson, R. L., "Thermodynamic Analysis of Heat Exchanger Tube-CaSO₄ Deposit Interaction in the Fluidized-Bed Combustion of Coal," presented at the Department of Metallurgy and Metallurgical Engineering, University of Utah, Salt Lake City, Oct. 29, 1980.
81. Pruett, D. J., "The Solvent Extraction Behavior of Nitrosylruthenium Complexes in Nitric Acid-Tri-*n*-Butyl Phosphate Systems," presented at the National Meeting of the American Chemical Society, Houston, Mar. 23-28, 1980.
82. Pruett, D. J., "The Solvent Extraction Behavior of Nitrosylruthenium Complexes. Part I. The Nitric Acid-Tri-*n*-Butyl Phosphate System," *Radiochim. Acta* **27**, 115-20 (1980).
83. Raschella, D. L.,¹⁹ R. L. Fellows, and J. R. Peterson,⁶ "Novel Sample Container for Solution Calorimetry," *Rev. Sci. Instrum.* **50**, 1481-82 (1979).
84. Roddy, J. W., "Distribution of Ethanol-Water Mixtures to Organic Liquids," *Ind. Eng. Chem. Process Des. Dev.* **20**, 104-8 (1981).
85. Roddy, J. W., and W. J. McDowell, *Separations Systems Data Base: A User's Manual. Revision 1*, ORNL/TM-6593/R1 (January 1981).
86. Scott, C. D., "Continuous Annular Chromatography: A New Tool for High-Resolution, Large-Scale Separations," presented at the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Jan. 14, 1980; also presented at the Department of Chemical Engineering, University of Virginia, Charlottesville, Apr. 17, 1980.
87. Seeley, F. G., L. K. Felker, and A. D. Kelmers, "Dissolution and Recovery of Aluminum and Other Metals from Calsinter Process Sinter Product," presented at the Symposium on Hydrometallurgy, Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Chicago, Feb. 22-26, 1981.
88. Seeley, F. G., and W. J. McDowell, "Fe(III) Extraction Equilibria in the System Fe₂(SO₄)₃-(NH₄)₂SO₄ vs Primene JM-T Sulfate-Toluene," *J. Inorg. Nucl. Chem.* **43**, 375-78 (1981).
89. Seeley, F. G., W. J. McDowell, L. K. Felker, A. D. Kelmers, and B. Z. Egan, "Determination of Extraction Equilibria for Several Metals in the Development of a Process Designed to Recover Aluminum and Other Metals from Coal Combustion Ash," *Hydrometallurgy* **6**, 277-90 (1981).
90. Shoun, R. R., "The Investigation of Lanthanide-Carbamoylmethylphosphonate Complexes by Extraction Equilibria and NMR," presented at the Actinide Workshop IV, Los Alamos, N.M., May 13-14, 1980.
91. Shoun, R. R., and W. J. McDowell, "Actinide Extractants—Development, Comparison, and Future," presented at the Pacific Chemical Conference of the American Chemical Society, Honolulu, Apr. 1-6, 1979; published in *Actinide Separations*, ACS Symposium Series No. 117, 1980, pp. 71-87.
92. Shoun, R. R., W. J. McDowell, and B. Weaver,¹⁰ "Bidentate Organophosphorus Compounds as Extractants from Acid Waste Solutions: A Comparative and Systematic Study," p. 101 in *Solvent Extraction, Proceedings of the International Conference, ISEC '77, Toronto, September 1977*, CONF-770907, B. H. Lucas, G. M. Ritcey, and H. W. Smith, Eds., Canadian Institute of Mining and Metallurgy, CIM special vol. 21 (1979).

---

¹⁹ University of Tennessee, Knoxville.

93. Stinton, D. P.,⁷ W. J. Lackey,⁷ and R. D. Spence, *Production of Spherical Uranium Dioxide-Uranium Dicarbide for Nuclear Fuel Applications Using Thermochemical Principles*, ORNL/TM-7651 (March 1981).
94. Stinton, D. P.,⁷ and R. D. Spence, "Sintering of Gel-Derived Uranium Trioxide + Carbon to Produce Highly Dense Uranium Dioxide + Uranium Dicarbide Microspheres," presented at the Fall Meeting of the American Ceramic Society, New Orleans, Oct. 14-19, 1979.
95. Stinton, D. P.,⁷ S. M. Tiegs,²⁰ W. J. Lackey,⁷ and T. B. Lindemer, "Rate Controlling Factors in the Carbothermic Preparation of Uranium Dioxide-Uranium Dicarbide-Carbon Microspheres," presented at the Annual Meeting of the Nuclear Division, American Ceramic Society, Cincinnati, Apr. 28-May 2, 1979; published in *J. Am. Ceram. Soc.* **62**, 596-99 (1979).
96. Talbot, J. B., "An Evaluation of Hydroclone Operation for the Removal of Micron-Sized Particles from Viscous Liquids," presented at the Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., Oct. 30-Nov. 2, 1979; published in *Sep. Sci. Technol.* **15**, 277-96 (1980).
97. Talbot, J. B., *The Performance of Hydroclones for Removing Particles from Viscous Liquids*, ORNL/TM-5684 (August 1980).
98. Talbot, J. B., and S. D. Clinton, "Liquid Lithium Blanket Processing Studies," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11-16, 1979; published in *Engineering Problems of Fusion Research, Proceedings of the Eighth Symposium*, Institute of Electrical and Electronic Engineers Publication 79CH1441-5 NPS, pp. 389-93.
99. Talbot, J. B., and S. D. Clinton, "Recovery of Tritium from Molten Lithium Using Yttrium Getters," *J. Nucl. Mater.* **85/86**, 341-44 (1979).
100. Toth, L. M., and G. M. Begun,⁶ "Raman Spectra of Uranyl Ion and Its Hydrolysis Products in Aqueous HNO₃," *J. Phys. Chem.* **85**, 547-49 (1981).
101. Toth, L. M., J. T. Bell, and H. A. Friedman, "Photochemistry of the Actinides," presented at the Pacific Chemical Conference of the American Chemical Society, Honolulu, Apr. 1-6, 1979; published in *Actinide Separations*, ACS Symposium Series No. 117, 1980, pp. 253-66.
102. Toth, L. M., and H. A. Friedman, "The Photochemistry of Neptunium in Aqueous Nitric Acid Solutions," *Radiochim. Acta* **27**, 173-76 (1980).
103. Watson, J. S., "Recovery of Metals from Fly Ash," seminar presented at the Department of Chemical Engineering, Georgia Institute of Technology, Atlanta, Mar. 3, 1980.
104. Watson, J. S., P. W. Fisher, and J. B. Talbot, "Tritium in Fusion Reactor Components," presented at the American Nuclear Society Topical Meeting on Tritium Technology in Fission, Fusion, and Isotopic Applications, Dayton, Ohio, Apr. 29-May 1, 1980; published in the *Proceedings*, CONF-800427 (1980), pp. 319-22.
105. Weiss, J. F.,²¹ H. E. Walburg, Jr.,²² and W. J. McDowell, "Placental Transfer of Americium and Plutonium in Mice," *Health Phys.* **39**, 903-11 (1980).

---

20. Central Management Office.

21. Tennessee Valley Authority Analytical Laboratory, Muscle Shoals, Ala.; formerly of the Comparative Animal Research Laboratory, Oak Ridge, Tenn.

22. Comparative Animal Research Laboratory, Oak Ridge, Tenn.

B. Biotechnology and Environmental Studies

1. Amrhein, M.,²³ F. Ngan,²³ R. K. Genung, and A. L. Rivera, *Response of a Packed-Bed, Fixed-Film Bioreactor to Zinc Toxicant*, ORNL/MIT-309 (May 1980).
2. Arcuri, E. J., and H. L. Ehrlich,²⁴ "Electron Transfer Coupled to Mn(II) Oxidation in Two Deep-Sea Pacific Ocean Isolates," presented at the Fourth International Symposium on Environmental Biogeochemistry, Canberra, Australia, Aug. 27-Sept. 5, 1979; published in *Environmental Biogeochemistry in Relation to the Mining Industry and Environmental Pollution*, Australian Academy of Science, 1980, pp. 339-44.
3. Arcuri, E. J., S. E. Shumate II, and S. M. Gibson, "Film Growth and Phenol Removal in a Fixed-Film Bioreactor," presented at the Sixth International Fermentation Symposium, London, Ontario, Canada, July 20-25, 1980.
4. Arcuri, E. J., R. M. Worden,¹⁹ and S. E. Shumate II, "Ethanol Production in Fixed-Film Bioreactors Employing *Zymomonas mobilis*," presented at the Meeting on Trends in the Biology of Fermentation of Fuels and Chemicals, Brookhaven National Laboratory, Upton, N.Y., Dec. 7-11, 1980.
5. Arcuri, E. J., R. M. Worden,¹⁹ and S. E. Shumate II, "Ethanol Production of Immobilized Cells of *Zymomonas mobilis*," *Biotechnol. Lett.* 2, 499-504 (1980).
6. Bostick, W. D., "Kinetic Methods of Analysis," presented at the Department of Chemistry, University of Tennessee, Chattanooga, Oct. 23, 1979.
7. Bostick, W. D., "Postcolumn Chromatographic Applications of Enzymes," presented at the Department of Laboratory Medicine and Pathology, University of Minnesota Medical School, Minneapolis, Oct. 13, 1980.
8. Bostick, W. D., M. L. Bauer, R. McCracken, and J. E. Mrochek, "Portable Centrifugal Analyzer for the Determination of Rapid Reaction Kinetics," *Anal. Chem.* 52, 300-306 (1980).
9. Bostick, W. D., and C. A. Burtis, "Hydroxylamine as a Competitive Inhibitor for the Kinetic Enzymatic Assay of Ethanol in Relatively Concentrated Solutions," *Biotechnol. Bioeng.* 22, 2437-39 (1980).
10. Bostick, W. D., M. S. Denton, and S. R. Dinsmore, "New Developments in On-Line Isoenzyme Monitoring for Use in Clinical Diagnostics," presented at the International Liquid Chromatography Symposium III: Biological and Biomedical Applications, Boston, Oct. 11-12, 1979.
11. Bostick, W. D., M. S. Denton, and S. R. Dinsmore, "Liquid Chromatographic Separation and On-Line Bioluminescence Detection of Creatine Kinase Isoenzymes," presented at the Southeast Regional Meeting of the American Association for Clinical Chemistry, Charleston, S.C., Apr. 17-19, 1980; published in *Clin. Chem.* 26, 712-17 (1980).
12. Bostick, W. D., and J. B. Overton, "Modified Kit Procedure for the Kinetic Assay of Ethanol," *Biotechnol. Bioeng.* 22, 2383-92 (1980).
13. Bostick, W. D., J. B. Overton, and C. A. Burtis, "The Use of Competitive Inhibitors to Increase the Dynamic Range of the Enzymatic Kinetic Assay of Ethanol," presented at the National Meeting of the American Chemical Society, Atlanta, Mar. 29-Apr. 3, 1981.
14. Brand, J. I., and J. A. Klein, "The Effect of the Oak Ridge National Laboratory Bench-Scale Aqueous Treatment Train on Mutagenicity and Toxicity of Aqueous Effluents from Coal Conversion Processes," presented at the Annual Purdue Industrial Waste Conference, West Lafayette, Ind., May 13-15, 1980.

23. Massachusetts Institute of Technology School of Chemical Engineering Practice, Oak Ridge, Tenn.

24. Rensselaer Polytechnic Institute, Troy, N.Y.

15. Brand, J. I., J. A. Klein, B. R. Parkhurst,²⁵ and K. T. Rao,²⁶ "Mutagenicity and Toxicity of Treated Aqueous Effluents from Coal Conversion Processes," presented at the Annual Purdue Industrial Waste Conference, West Lafayette, Ind., May 13-15, 1980.
16. Burtis, C. A., "Dynamic Introduction of Liquids into Centrifugal Analyzers," presented at the Symposium on Centrifugal Analysers in Clinical Chemistry, University of Southampton, Southampton, England, Sept. 5-7, 1979.
17. Burtis, C. A., "Data Processing for Centrifugal Analyzers," pp. 51-70 in *Methods in Laboratory Medicine*, vol. 1, Praeger Scientific, New York, 1980.
18. Burtis, C. A., W. D. Bostick, and J. E. Mrochek, "Analytical Applications of Centrifugal Analysis Coupled with Response Surface Methodology," presented at the Annual Summer Symposium of the American Chemical Society, Duke University, Durham, N.C., June 5-7, 1980.
19. Burtis, C. A., and J. E. Mrochek, "Data Processing for Centrifugal Analyzers," presented at the Symposium on Centrifugal Analysers in Clinical Chemistry, University of Southampton, Southampton, England, Sept. 5-7, 1979.
20. Carpenter, J. H.,²⁷ R. M. Bean,²⁸ W. J. Blogoslawski,²⁹ W. Davis,³⁰ and R. L. Jolley, "Chlorination Products," presented at the Workshop on Scientific Problems Relating to Ocean Pollution, Estes Park, Colo., June 10-14, 1978; published in *Scientific Problems Relating to Ocean Pollution*, U.S. Department of Commerce, 1979, pp. 23-24.
21. Cumming, R. B.,²⁶ M. L. Bauer,³¹ R. K. Genung, D. D. Willis,³² N. E. Lee, W. D. Bostick, G. B. Johnson,³³ and J. E. Mrochek, "The Development of a Fast Rotary Electrophoresis System with Capacity for High Sample Throughput and Great Resolving Power," presented at the Symposium on Advanced Analytical Concepts for the Clinical Laboratory, Oak Ridge, Tenn., Apr. 26-27, 1979.
22. Cumming, R. B.,²⁶ N. E. Lee, L. R. Lewis,²⁶ J. E. Thompson, and R. L. Jolley, "The Relationship of Disinfection to Mutagenicity in Wastewater Effluents," pp. 881-98 in *Water Chlorination: Environmental Impact and Health Effects*, vol. 3, Ann Arbor Science, Ann Arbor, Mich., 1980.
23. Denton, M. S., "Open-Pore Polyurethane as a Medium for Coal Conversion Process Effluent Cleanup," presented at the Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., Oct. 30-Nov. 2, 1979.
24. Denton, M. S., "Characterization and Identification of Organics in Coal-Conversion Aqueous Waste-Treatment Effluents," *Analytical Specialists Group Newsletter*, Union Carbide Corp., Tarrytown, N.Y., June 13, 1980.
25. Denton, M. S., and S. R. Dinsmore, "Characterization and Identification of Organics in Coal Conversion Processes: Products and Aqueous Waste-Treatment Effluents," presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N.J., Mar. 10-14, 1980.
26. Denton, M. S., and S. R. Dinsmore, "A Comparison of Synthetic Adsorbents, Including Open-Pore Polyurethane as Applied to Coal Conversion Process Aqueous Effluent Cleanup," presented at the Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.

---

25. Environmental Sciences Division.

26. Biology Division.

27. University of Miami, Miami, Fla.

28. Battelle Pacific Northwest Laboratories, Richland, Wash.

29. National Marine Fisheries, Milford, Conn.

30. U.S. Environmental Protection Agency, Johns Island, S.C.

31. Instrumentation and Controls Division.

32. Separation Systems Division, ORGDP.

33. UCC-ND Engineering.

27. Denton, M. S., and S. R. Dinsmore, "Portable Field Monitor for PCBs," presented at the National Meeting of the American Chemical Society, Atlanta, Mar. 29-Apr. 3, 1981.
28. Denton, M. S., S. R. Dinsmore, J. I. Brand, J. Beams,¹⁰ and F. L. Ball,¹³ "Open-Pore Polyurethane as a Medium for Coal Conversion Process Aqueous Effluent Cleanup," presented at the Symposium on Separation Science and Technology for Energy Application, Gatlinburg, Tenn., Oct. 30-Nov. 2, 1979; published in *Sep. Sci. Technol.* 15, 587-613 (1980).
29. Egan, B. Z., "Review of *Immobilized Enzymes: Research and Development*, I. Chibata, Ed., Halsted Press, 1978," *Am. Sci.* 67, 481-82 (1979).
30. Egan, B. Z., and C. D. Scott, "Use of Cell-Free Biological Systems for Hydrogen Production," presented at a Chemical Engineering Graduate Seminar, University of Tennessee, Knoxville, Nov. 13, 1979.
31. Genung, R. K., "A Critique of the DOE Workshop on Anaerobic Filters," pp. 253-54 in *Proceedings of the U.S. Department of Energy Seminar on Anaerobic Filters*, Argonne National Laboratory, Argonne, Ill., January 1980.
32. Genung, R. K., and W. W. Pitt, Jr., "Pilot Plant Demonstration of an Anaerobic, Fixed-Film Bioreactor for Wastewater Treatment," presented at the Solar Energy Research Institute Symposium on Fuels from Biomass, Golden, Colo., June 5-7, 1979.
33. Genung, R. K., W. W. Pitt, Jr., G. M. Davis,³⁴ and J. H. Koon,³⁴ "Energy Conservation and Scale-up Studies for a Wastewater Treatment System Based on a Fixed-Film, Anaerobic Bioreactor," presented at the Second Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, Tenn., Oct. 2-5, 1979; published in *Biotechnol. Bioeng. Symp.* 10, Wiley, 1980.
34. Genung, R. K., W. W. Pitt, Jr., G. M. Davis,³⁴ and J. H. Koon,³⁴ "Development of a Wastewater Treatment System Based on a Fixed-Film, Anaerobic Bioreactor," presented at the U.S. Department of Energy Workshop on Anaerobic Filters, Howey-in-the-Hills, Fla., Jan. 8-10, 1980; published in the *Proceedings*.
35. Greenbaum, E., "Simultaneous Photoproduction of Hydrogen and Oxygen by Photosynthesis," presented at the Second Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, Tenn., Oct. 2-5, 1979; published in *Biotechnol. Bioeng.* 10, 1-13 (1980).
36. Greenbaum, E., "Simultaneous Photoevolution of Hydrogen and Oxygen by Photosynthetic Systems: The Role of the Electron Transport Chain Linking the Two Photosystems," presented at the Gordon Conference on Physicochemical Aspects of Photosynthesis, Santa Barbara, Calif., Feb. 4-8, 1980.
37. Greenbaum, E., "Photobiological Solar Energy Conversion: Simultaneous Photoproduction of Hydrogen and Oxygen by Photosynthetic Systems," presented at the Annual Meeting of the American Society for Photobiology, Colorado Springs, Colo., Feb. 17-21, 1980.
38. Greenbaum, E., "Biological Energy Production," presented at the short course on Research Topics in Biophysics, Annual Meeting of the American Physical Society, New York, Mar. 23, 1980.
39. Greenbaum, E., "Solar Energy Conversion by Photosynthetic Systems," presented at the Annual Meeting of the Electrochemical Society, Inc., St. Louis, May 11-16, 1980.
40. Greenbaum, E., "Photosynthetic Hydrogen Production," presented to the Hydrogen Coordinating Committee, U.S. Department of Energy, Washington, D.C., July 15, 1980.
41. Greenbaum, E., "Stoichiometry of Hydrogen and Oxygen Photoproduction by Chloroplasts, Ferredoxin, and Hydrogenase," presented at the Sixth International Fermentation Symposium, London, Ontario, Canada, July 20-25, 1980.

---

34. Associated Water and Air Resources Engineers, Inc., Nashville, Tenn.

42. Greenbaum, E., "Biosolar Hydrogen Production," *ORNL Review*, Oak Ridge National Laboratory, Summer 1980, pp. 25-29.
43. Greenbaum, E., "Photobiological Hydrogen Production," presented at the Annual Meeting of the American Association for the Advancement of Science, Toronto, Ontario, Canada, Jan. 3-8, 1981.
44. Greenbaum, E., "Hydrogen Production by Photosynthesis," presented at the Fifth Annual Institute of Gas Technology Meeting on Energy from Biomass and Wastes, Lake Buena Vista, Fla., Jan. 26-30, 1981.
45. Greenbaum, E., "Using Plants for Hydrogen Production," presented at the Annual Meeting of the Southern Section of the American Society of Plant Physiologists, Atlanta, Feb. 1-3, 1981.
46. Greenbaum, E., "Biophysics of Hydrogen and Oxygen Evolution by Photosynthesis," presented at the Annual Meeting of the Biophysical Society, Denver, Feb. 23-25, 1981.
47. Greenbaum, E., "Photosynthetic Water Splitting," presented at the First Solar Energy Research Institute Solar Hydrogen Production Program Contractors' Review Meeting, Washington, D.C., Mar. 26-27, 1981.
48. Greenbaum, E., J. W. Woodward, J. P. Eubanks, and D. A. McWhirter, "Photoproduction of Hydrogen and Oxygen," *The Bio-Energy Directory*, 4th ed., P. F. Bente, Jr., Ed., The Bio-Energy Council, 1981, p. 264.
49. Haag, W. R.,³⁵ "The Formation of *N*-Bromo-*N*-Chloroamines in Chlorinated Saline Waters," *J. Inorg. Nucl. Chem.* 42, 1123-27 (1980).
50. Hamza, A. V.,²³ J. F. Dolan,²³ E. W. Wong,²³ R. K. Genung, C. W. Hancher, and J. F. Walker, *Three-Phase Fluidized Bioreactors for Denitrification*, ORNL/MIT-324 (March 1981).
51. Hancher, C. W., *ANFLOW Demonstration Plant Groundbreaking Ceremony*, publicity brochure, Oak Ridge National Laboratory, 1980.
52. Hancher, C. W., and W. W. Pitt, Jr., "Denitrification of High-Strength Nitrate Waste Using a Fluidized-Bed Biological Reactor," presented at the Annual Conference of the Water Pollution Control Federation, Houston, Oct. 7-12, 1979.
53. Hancher, C. W., W. W. Pitt, Jr., and B. D. Patton, "Biological Reduction of Nitrate Wastewater Using a Fluidized-Bed Bioreactor," presented at the Hydrometallurgy Meeting, Toronto, Ontario, Canada, Nov. 11-13, 1979.
54. Hines, D. C. M.,¹⁹ D. W. Weeter,¹⁹ and R. K. Genung, "Production of Ammonia in a Packed-Bed Anaerobic Upflow (ANFLOW) Bioreactor," presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, Nov. 19, 1980.
55. Hunter, C. A.,²³ S. F. Sciamanna,²³ J. V. Tormo, Jr.,²³ C. D. Scott, and C. D. West,³⁶ *Recovery of ORGDP Waste Heat as an Energy Source for Converting Biomass to Fuels*, ORNL/MIT-315 (February 1981).
56. Jennings, H. L., A. L. Rivera, and R. K. Genung, "Kinetic Studies in a Packed-Bed Bioreactor," presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, November 1980.
57. Jolley, R. L., "Water Analysis: An Odyssey of Expedience and Necessity," presented at Expochem '79, Houston, Oct. 22-25, 1979.

---

³⁵ Graduate student from University of Tennessee, Knoxville, on Oak Ridge Associated Universities Fellowship.

³⁶ Engineering Technology Division.

58. Jolley, R. L., "Concentration of Organic Compounds in Water. A Literature Survey," presented at the Workshop on Protocol Development: Criteria and Standards for Potable Reuse and Feasible Alternatives, Warrenton, Va., July 29-31, 1980; published in the *Proceedings*.
59. Jolley, R. L., "Chloramine Reactions and Products," pp. 166-82 and 236-39 in *Drinking Water and Health II*, National Academy Press, Washington, D.C., 1980.
60. Jolley, R. L., W. A. Brungs,³⁷ and R. B. Cumming,²⁶ "Introduction," *Water Chlorination: Environmental Impact and Health Effects*, vol. 3, Ann Arbor Science, Ann Arbor, Mich., 1980.
61. Jolley, R. L., W. A. Brungs,³⁷ and R. B. Cumming,²⁶ Eds., *Water Chlorination: Environmental Impact and Health Effects*, vol. 3, Ann Arbor Science, Ann Arbor, Mich., 1980, 1171 pp.
62. Jolley, R. L., and R. B. Cumming,²⁶ "Oxidant Effects on Complex Mixtures of Nonvolatile Organics in Polluted Waters: Examination by HPLC and Bioscreening," *Ozone Sci. Eng.* 1, 31-37 (1979).
63. Jolley, R. L., R. B. Cumming,²⁶ N. E. Lee, L. R. Lewis,²⁶ and J. E. Thompson, "Characterization of Mutagenic Chromatographic Fractions from Ozonated and Chlorinated Wastewater Effluents," presented at the Tenth Annual Symposium on the Analytical Chemistry of Pollutants, Dortmund, Federal Republic of Germany, May 28-30, 1980.
64. Jolley, R. L., N. E. Lee, L. R. Lewis,²⁶ C. I. Mashai,³⁸ W. W. Pitt, Jr., J. E. Thompson, and R. B. Cumming,²⁶ "Chromatography, Bioscreening, and Characterization of Mutagenic Organic Constituents in Nondisinfected and Disinfected Wastewater Effluents," presented at the Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
65. Jolley, R. L., N. E. Lee, W. W. Pitt, Jr., and J. E. Thompson, "Characterization of Nonvolatile Organics in Disinfected Wastewater Effluents," presented at the National Meeting of the American Chemical Society, Honolulu, Apr. 1-6, 1979.
66. G. H. Kemker,²³ S. J. Roadcap,²³ R. Sitchin,²³ J. I. Brand, and J. A. Klein, *The Ozonolysis of Aqueous Solutions of Phenol and Thiocyanate*, ORNL/MIT-318 (December 1980).
67. Klein, J. A., B. R. Clark,¹³ K. E. Cowser,²⁰ S. D. Van Hoesen,²⁰ T. J. Wood,³⁹ and A. P. Duhamel,⁴⁰ "Health and Environmental Monitoring at the University of Minnesota-Duluth Coal Gasification Facility," presented at the Third Miami International Conference on Alternative Energy Sources, Miami Beach, Fla., Dec. 15-18, 1980.
68. Klein, J. A., M. R. Guerin,¹³ and B. R. Clark,¹³ "Characterization and Control of Toxic Organic Materials from Coal Conversion Processes," presented at the Joint Meeting of the Southeastern and Southwestern Regions of the American Chemical Society, New Orleans, Dec. 8-12, 1980.
69. Lee, D. D., C. D. Scott, and C. W. Hancher, "Fluidized-Bed Bioreactor for Coal-Conversion Effluents," *J. Water Pollut. Control Fed.* 51, 974-84 (1979).
70. Lee, N. E., W. R. Haag,⁴¹ and R. L. Jolley, "Effects of Chlorinated Cooling Water Effluents on Freshwater Clams," presented at the Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
71. Lee, N. E., R. L. Jolley, M. S. Denton, S. R. Dinsmore, J. E. Thompson, and W. W. Pitt, Jr., "Native Fluorescence: An Aid to the Identification of Nonvolatile Organics in Secondary Wastewater Effluents," presented at the National Meeting of the American Chemical Society, Washington, D.C., Sept. 9-14, 1979.

---

37. U.S. Environmental Protection Agency, Duluth, Minn.

38. U.S. Environmental Protection Agency, Cincinnati.

39. University of Minnesota, Duluth.

40. U.S. Department of Energy, Washington, D.C.

41. University guest from University of Tennessee, Knoxville.

72. Million, D. L.,⁴² and J. A. Klein, "On-Line Sampling and Analysis at the University of Minnesota, Duluth, Coal Gasifier," presented at the Symposium on Instrumentation and Control for Fossil Energy Processes, Analysis and Sampling Session, Virginia Beach, Va., June 9-11, 1980; published in the *Proceedings*.
73. Pitt, W. W., Jr., and R. K. Genung, "Information on ANFLOW Project," in *Bio-Energy Directory 1979*, Bio-Energy Council.
74. Pitt, W. W., Jr., and R. K. Genung, "Energy Conservation and Production in a Packed-Bed Anaerobic Bioreactor," presented at the Symposium on Energy from Biomass and Wastes, Lake Buena Vista, Fla., Jan. 21-25, 1980; published in the *Proceedings*, Institute of Gas Technology, 1980, pp. 451-72.
75. Pitt, W. W., Jr., C. W. Hancher, and B. D. Patton, "Biological Reduction of Nitrate Wastewater Using a Fluidized-Bed Bioreactor," presented at the Annual Hydrometallurgical Meeting, Toronto, Canada, Nov. 11-13, 1979.
76. Pitt, W. W., Jr., C. W. Hancher, B. D. Patton, and S. E. Shumate II, "Advanced Biological Treatment of Aqueous Effluent from the Nuclear Fuel Cycle," presented at the Second Environmental Control Symposium, sponsored by the U.S. Department of Energy, Reston, Va., Mar. 17-19, 1980.
77. Pitt, W. W., Jr., R. L. Jolley, and G. Jones, Jr., "Characterization of Organics in Aqueous Effluents of Coal Conversion Processes," *Environ. Int.* 2, 167-71 (1979).
78. Pitt, W. W., Jr., and G. Jones, Jr., *Continuous Environmental Monitoring for Aqueous Effluents*, ORNL/TM-6118 (May 1980).
79. Pitt, W. W., Jr., and D. D. Lee, "Recovery of Ethanol from Fermentation Broths Using Selective Sorption-Desorption," presented at the Intersociety Energy Conversion Engineering Conference, Seattle, Aug. 18-22, 1980.
80. Roadcap, S. J.,²³ R. A. Trevino-Lozano,²³ S. Znaimer,²³ R. K. Genung, C. W. Hancher, and J. F. Walker, *Residence-Time Distribution Studies in Fluidized-Bed Bioreactors*, ORNL/MIT-319 (March 1981).
81. Roberts, M. H., Jr.,⁴³ N. E. Blanco,⁴⁴ D. R. Wheeler,⁴⁴ N. E. Lee, J. E. Thompson, and R. L. Jolley, "Production of Halogenated Organics During Wastewater Disinfection," Special Report in Applied Marine Science and Ocean Engineering No. 239, Virginia Institute of Marine Science, College of William and Mary, December 1980.
82. Schuresko, D. D.,⁴⁵ "A Portable Fluorometric Monitor to Detect PNA Contamination of Work Area Surfaces," presented at the Symposium on Instrumentation and Control for Fossil Energy Processes, Denver, Aug. 20-22, 1979; also presented at the Fourth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Columbus, Ohio, Oct. 2-4, 1979.
83. Schuresko, D. D.,⁴⁵ "A Portable Spotter to Detect PNA Contamination of Work Area Surfaces," presented at the National Meeting of the American Chemical Society, Washington, D.C., Sept. 10-14, 1979.
84. Schuresko, D. D.,⁴⁵ "Portable Fluorometric Spotter for Detection of Surface Contamination by Polynuclear Aromatic Hydrocarbon Compounds," presented at the Seventh Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, Sept. 28-Oct. 3, 1980; also presented at the Fifth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Columbus, Ohio, Oct. 28-30, 1980; published in *Anal. Chem.* 52, 371-73 (1980).

---

42. Computer Sciences Division.

43. Virginia Institute of Marine Science, Gloucester Point, Va.

44. Hampton Roads Sanitation District Commission, Virginia Beach, Va.

45. Health and Safety Research Division; formerly of the Chemical Technology Division.

85. Schuresko, D. D.,⁴⁵ W. D. Bostick, S. R. Dinsmore, and J. E. Mrochek, "Induction of Cytochrome-P450 Mixed Function Oxidase (MFO) Activity in Hamster Embryo Culture (HEC) by Exposure to Coal-Derived Tars," presented at the Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, Sept. 28-Oct. 3, 1980.
86. Scott, C. D., "Advanced Biotechnology for Energy Production," presented at the Southern Regional Research Center, U.S. Department of Agriculture, New Orleans, Feb. 13, 1980.
87. Scott, C. D., "Fixed-Film Bioreactors for Environmental Control and Energy Production," presented at the Department of Chemical Engineering, University of Missouri, Columbia, Mar. 11, 1980.
88. Scott, C. D., "Introduction," *Proceedings of the Second Symposium on Biotechnology in Energy Production and Conservation, Biotechnol. Bioeng. Symp. 10*, Wiley, New York, 1980.
89. Scott, C. D., "Introduction to the Proceedings of the 12th Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory," *Clin. Chem.* **26**(10), 1379 (1980).
90. Scott, C. D., "Biotechnology in Energy Production and Conservation," briefing to the World Press Institute, Oak Ridge, Tenn., Feb. 2, 1981.
91. Scott, C. D., C. W. Hancher, and E. J. Arcuri, "Tapered Fluidized-Bed Bioreactor for Environmental Control and Fuel Production," presented at the Sixth International Fermentation Symposium, London, Canada, July 20-25, 1980.
92. Scott, C. D., R. S. Melville,⁴⁶ and D. S. Young,⁴⁷ "Introduction to the Proceedings of the 11th Symposium on Advanced Analytical Concepts for the Clinical Laboratory," *Clin. Chem.* **25**, 1547 (1979).
93. Scott, C. D., S. E. Shumate II, and E. J. Arcuri, "Fixed-Film Columnar Bioreactors for the Production of Chemicals and Fuels from Biomass," presented at the First Solar Energy Research Institute International Workshop on Biotechnology for the Production of Chemicals and Fuels from Biomass, Vail, Colo., Oct. 1-3, 1980.
94. Shumate, S. E., II, G. W. Strandberg, D. A. McWhirter, J. R. Parrott, Jr., G. M. Bogacki,⁴⁸ and B. R. Locke,⁴⁹ "Separation of Heavy Metals from Aqueous Solutions Using Biosorbents—Development of Contacting Devices for Uranium Removal," presented at the Second Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, Tenn., Oct. 2-5, 1979; published in *Biotechnol. Bioeng. Symp. 10*, Wiley, 1980, pp. 27-34; also presented at the Hydrometallurgy Meeting sponsored by the Canadian Institute of Mining and Metallurgy, Toronto, Canada, Nov. 11-13, 1979.
95. Shumate, S. E., II, G. W. Strandberg, J. R. Parrott, Jr., and B. R. Locke,⁵⁰ "Separation of Uranium from Process Wastewaters Using Microbial Cells as Sorbents," presented at the Hydrometallurgy Meeting sponsored by the Canadian Institute of Mining and Metallurgy, Toronto, Canada, Nov. 11-13, 1979.
96. Sitchin, R.,²³ P. F. Gubanc,²³ J. V. Tormo, Jr.,²³ E. J. Arcuri, and C. D. Scott, *Ethanol Production by Zymomonas mobilis in a Tapered-Bed Bioreactor*, ORNL/MIT-320 (February 1981).
97. Strandberg, G. W., "A Cyclic Pattern of Hydrogen Evolution by *Anabaena flos-aque*," *Eur. J. Appl. Microbiol. Biotechnol.* **9**, 19-20 (1980).
98. Strandberg, G. W., and S. E. Shumate II, "Association and Accumulation of Dissolved Heavy Metals by Microbial Cells," presented at the Symposium on Inorganic Pollutants in the Environment, Pacific Chemical Conference of the American Chemical Society, Honolulu, Apr. 3, 1979.

---

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

47. Mayo Clinic, Rochester, Minn.

48. Oak Ridge Associated Universities summer student from University of Vermont.

49. Participant in the Southern College-University Union Science Semester Program.

50. Vanderbilt University, Nashville, Tenn.

99. Strandberg, G. W., and S. E. Shumate II, "Biosorbents for Removal of Certain Heavy Metals from Aqueous Process Streams," presented at the Symposium on Novel Solutions to Problems of Waste, Pollution, and Energy, ASM/U.S.-Japan Intersociety Microbiology Congress, Honolulu, May 8-11, 1979.
100. Strandberg, G. W., S. E. Shumate II, and J. R. Parrott, Jr., "Microbial Cells as Biosorbents for Heavy Metals: Accumulation of Uranium by *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa*," *J. Appl. Environ. Microbiol.* 41(1), 237-45 (1981).
101. Strandberg, G. W., S. E. Shumate II, J. R. Parrott, Jr., and D. A. McWhirter, "Microbial Uptake of Uranium, Cesium, and Radium," presented at the Symposium on Microbial Processes for Metals Accumulation and Sulfur/Nitrogen Removal from Fuels, Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
102. Tanner, R. D.,⁵¹ C. J. Wei,⁵¹ and J. Woodward, "The Development of a Semi-Solid Fermentation System for the Production of Lysine-Enriched Yeast and Ethanol," pp. 323-28 in *Advances in Biotechnology*, vol. 1, M. Moo-Young, C. W. Robinson, and C. Vezina, Eds., Pergamon, Oxford, 1981.
103. Woodward, J., and S. L. Arnold,³ "The Effect of D-Glucose and D-Fructose on the Activity of β -Glucosidase in *Trichoderma reesei* C30 Cellulase," presented at a conference on Trends in the Biology of Fermentations, Brookhaven National Laboratory, Upton, N.Y., Dec. 7-11, 1980.
104. Woodward, J., and S. L. Arnold,³ "The Inhibition of β -Glucosidase Activity in *Trichoderma reesei* C30 Cellulase by Isomers and Derivatives of Glucose," *Biotechnol. Bioeng.* 23, 1553-62 (1981).

C. Fission Energy

1. Beatty, R. L.,⁷ R. E. Norman, and K. J. Notz, *Gel-Sphere-Pac Fuel for Thermal Reactors—Assessment of Fabrication Technology and Irradiation Performance*, ORNL-5469 (November 1979).
2. Campbell, D. O., "Physical and Chemical Characterization of Insolubles in Irradiated Fuels," presented at a Seminar on Reactor Fuel Dissolution under the U.S. Department of Energy/U.K. Atomic Energy Agency Exchange Agreement on Fast Reactor Collaboration, Windscale, England, October 1979.
3. Campbell, D. O., "Chemical Aspects of LWR Fuel Reprocessing," Chap. 3 in *Light Water Reactor Nuclear Fuel Cycle*, R. G. Wymer and B. L. Vondra,⁵² Eds., CRC Press, Boca Raton, Fla., 1981.
4. Campbell, D. O., and W. L. Pattison, *The Effect of Heat Treatments on Tritium Volatility and the Behavior of Other Radioactive Constituents in Irradiated Fuel*, ORNL/TM-7326 (April 1981).
5. Carter, W. L., and A. R. Olsen,⁷ *An Evaluation of Fuel Fabrication and the Back End of the Fuel Cycle for Light-Water- and Heavy-Water-Cooled Nuclear Power Reactors*, ORNL/TM-6685 (June 1979).
6. Clark, W. E.,¹⁰ and W. B. Howerton, *The Removal of Organic Material from Recycle Nitric Acid by Ozone*, ORNL/TM-6672 (April 1979).
7. Collins, E. D., D. E. Benker, J. E. Bigelow, F. R. Chattin, L. J. King, M. H. Lloyd, R. G. Ross, and H. C. Savage, "Solvent Extraction Studies of Coprocessing Flowsheets," presented at the American Chemical Society Topical Meeting on Fuel Cycles for the '80s, Gatlinburg, Tenn., Sept. 29-Oct. 2, 1980.
8. Davis, W., Jr., L. Maya,⁶ D. Y. Valentine,⁵³ and A. D. Kelmers, *Kinetics of the Reaction of Nitrous Acid with Hydroxylammonium Nitrate in Nitric Acid Media*, ORNL/TM-7264 (May 1980).

---

⁵¹. Department of Chemical Engineering, Vanderbilt University, Nashville, Tenn.

⁵². Deceased.

⁵³. Formerly of the Chemistry Division.

9. Dodson, K. E., "Hydrazine Carbonate: An Alternate Reagent for the Cleanup of Solvents Used in Radiochemical Separation Processes," presented at the National Meeting of the American Chemical Society, San Francisco, Aug. 25-29, 1980.
10. Dyer, F. F., and R. P. Wichner, "A Study of the Behavior of Tritium in the Peach Bottom HTGR," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11-16, 1979; published in *Trans. Am. Nucl. Soc.* 33, 312 (1979).
11. Eatherly, W. P.,⁷ C. R. Kennedy,⁷ and R. P. Wichner, "Mechanical Properties of Several Graphites Affected by Steam Oxidation," presented at the Fall Meeting of the American Ceramic Society, San Francisco, Oct. 26-29, 1980.
12. Engel, J. R.,³⁶ H. F. Bauman,³⁶ J. F. Dearing,³⁶ W. R. Grimes, E. H. McCoy,⁷ and W. A. Rhoades,⁵⁴ *Conceptual Design Characteristics of a Denatured Molten-Salt Reactor with Once-Through Fueling*, ORNL/TM-7207 (July 1980).
13. Evans, R. B., III,⁵² W. Davis, Jr., and A. L. Sutton, Jr., *Cesium Diffusion in Graphite*, ORNL-5648 (May 1980).
14. Fitzgerald, C. L., and V. C. A. Vaughen, "Head-end Reprocessing Studies with Irradiated High-Temperature Gas-Cooled Reactor (HTGR) Fuels," presented at the American Nuclear Society National Topical Meeting on Fuel Cycles for the '80s, Gatlinburg, Tenn., Sept. 29-Oct. 2, 1980; published in the *Proceedings*, CONF-800943.
15. Goode, J. H., and R. G. Stacy, *Voloxidation and Dissolution of Irradiated (Th,U)O₂*, ORNL/TM-6643 (May 1979).
16. Goode, J. H., and R. G. Stacy, *Head-End Processing Studies with Mixed (U,Pu)O₂ and UO₂ Reactor Fuels*, ORNL/TM-6757 (November 1979).
17. Goode, J. H., R. G. Stacy, and V. C. A. Vaughen, "The Release of Tritium and Other Radionuclides During the High Temperature Oxidation of Irradiated Urania," presented at the American Chemical Society Joint Fall Meeting of Basic Science and Nuclear Divisions, New Orleans, Oct. 14-17, 1979.
18. Goode, J. H., R. G. Stacy, and V. C. A. Vaughen, *Head-end Reprocessing Studies of H. B. Robinson-2 Fuel. II. Parametric Voloxidation Studies*, ORNL/TM-6888 (May 1980).
19. Goode, J. H., R. G. Stacy, and V. C. A. Vaughen, *Comparison Studies of Head-end Reprocessing Using Three LWR Fuels*, ORNL/TM-7103 (June 1980).
20. Gray, L. M.,⁵⁵ "The Effect of Soluble Zirconium on the Dissolution Rates of ThO₂ and ThO₂-UO₂," presented at the National Meeting of the American Chemical Society, Houston, Mar. 23-28, 1980.
21. Groenier, W. S., A. D. Mitchell, and R. T. Jubin, "Computational Techniques Used in the Development of Coprocessing Flowsheets," presented at the Fast Reactor Fuel Reprocessing Symposium, Dounreay, Scotland, May 15-18, 1979.
22. Haas, P. A., "Heating of Uranium Oxides in a Microwave Oven," *J. Am. Ceram. Soc.* 58(9), 873 (1979).
23. Haas, P. A., J. M. Begovich, A. D. Ryon, and J. S. Vavruska,⁵⁶ "Chemical Flowsheet Conditions for Preparing Urania Spheres by Internal Gelation," presented at the Northwest Regional Meeting of the American Chemical Society, Richland, Wash., June 13-15, 1979; published in CONF-790666-1 (1979); published as ORNL/TM-6850 (July 1979); and published in *Ind. Eng. Chem. Prod. Res. Dev.* 19, 459-67 (1980).

---

⁵⁴. Engineering Physics Division.

⁵⁵. Formerly of the Chemical Technology Division.

⁵⁶. Los Alamos National Laboratory, Los Alamos, N.M.; formerly of the Chemical Technology Division.

24. Kasten, P. R.,²⁰ R. G. Wymer, W. D. Burch,⁵⁷ B. L. Vondra,⁵² A. L. Lotts,²⁰ A. R. Olsen,⁷ W. L. Carter, R. H. Rainey,⁵⁸ D. R. Johnson,⁷ and L. S. Abbott,⁵⁴ *Research and Development Requirements for the Recycle of Bred Fuels in Uranium and Thorium Fuel Cycles*, ORNL/TM-6504 (May 1979).
25. Katz, S.,¹⁰ and W. D. Bond, *A Method of Estimating Distribution Coefficients of Degradation Products from Organophosphorus Extractants*, ORNL/TM-6776 (May 1979).
26. Katz, S.,¹⁰ and W. D. Bond, "Estimation of Phosphorus-Containing Impurities in Organophosphorus Extractants and Their Distribution Coefficients from the Total Phosphorus Content of the Phase in Equilibrium with the Extractant Phase," *J. Inorg. Nucl. Chem.* **41**, 1781-86 (1979).
27. Kelmers, A. D., L. Maya,⁶ D. N. Browning,⁵⁹ and W. Davis, Jr., "The Chloride-Catalyzed Decomposition of Ammonium Nitrate in Nitric Acid Media at 100°C," *J. Inorg. Nucl. Chem.* **41**, 1583-88 (1979).
28. Knauer, J. B., J. H. Paehler, Jr., M. H. Lloyd, and M. G. Stewart, *Uranium and Plutonium Distribution Coefficients in the 6 vol % and 30 vol % TBP-NDD Systems*, ORNL/TM-7493 (March 1981).
29. Lamb, C. E., C. L. Fitzgerald, and V. C. A. Vaughen, *Behavior of Fission Product Iodine in the Head-end Reprocessing of HTGR Fuel: Iodine-129 Studies (Series I)*, ORNL/TM-6642 (July 1979).
30. Lamb, C. E., A. D. Mitchell, V. C. A. Vaughen, and R. J. Shannon, *Thorex Solvent Extraction Studies with Irradiated HTGR Fuel: Series I*, ORNL/TM-7108 (October 1980).
31. Leuze, R. E., "An Overview of the Light Water Reactor Fuel Cycle," presented at a training session for health physics personnel, Oak Ridge Associated Universities, Oak Ridge, Tenn., Apr. 9, 1979.
32. Leuze, R. E., "The Nuclear Fuel Cycle," presented at the Energy Resources Workshop, Oak Ridge National Laboratory, Oak Ridge, Tenn., Sept. 24-26, 1979.
33. Leuze, R. E., "Nuclear Waste Management—A Perspective," presented at a meeting of the Tulsa Chapter, American Nuclear Society, Tulsa, Okla., Jan. 15, 1980.
34. Leuze, R. E., "Review of Foreign Reprocessing," presented at the Nuclear Fuel Cycle Information Workshop, Oak Ridge National Laboratory, Oak Ridge, Tenn., Sept. 16-18, 1980.
35. Leuze, R. E., "An Introduction to the Nuclear Fuel Cycle," presented at the Nuclear Fuel Cycle Information Workshop, Oak Ridge National Laboratory, Oak Ridge, Tenn., Feb. 10, 1981.
36. Leuze, R. E., "An Overview of the LWR Fuel Cycle in the United States," Chap. 2 in *Light Water Reactor Nuclear Fuel Cycle*, R. G. Wymer and B. L. Vondra,⁵² Eds., CRC Press, Boca Raton, Fla., 1981.
37. Leuze, R. E., W. D. Bond, and F. M. Scheitlin, "Recovery of Plutonium from HEPA Filters by Ce(IV)-Promoted Dissolution of PuO₂ and Recycle of the Cerium Promoter," presented at the International Conference on Nuclear Waste Transmutation, Austin, Tex., July 22-24, 1980; published in the *Proceedings*, p. 361 (1980).
38. Lindemer, T. B., "Recent Research on the Interaction of Simulated Fission Products with SiC in HTGR Particles," presented at the Japan Atomic Energy Research Institute, Tokai-mura, Japan, June 23-24, 1980.
39. Lloyd, M. H., and G. O. Ledergerber, "Preparation of (U-Pu)O₂ Microspheres from Coprocessed Feed Solutions," presented at the Annual Meeting of the American Ceramic Society, Cincinnati, Apr. 28-May 2, 1979.

---

57. Fuel Recycle Division.

58. Oak Ridge Associated Universities, Oak Ridge, Tenn.; consultant to the Chemical Technology Division.

59. Student on assignment from Great Lakes Colleges Association.

40. Mailen, J. C., D. E. Horner,¹⁰ S. M. Robinson, and S. E. Dorris,³ *Solvent Scrubbing Kinetics of Uranium- and Zirconium-Dibutylphosphate Complexes Using Sodium Carbonate, Hydrazine Carbonate, and Hydrazine Oxalate*, ORNL/TM-7244 (February 1981).
41. Mailen, J. C., D. E. Horner,¹⁰ and J. K. Storey,⁵⁵ *Comparison of the Extraction Kinetics of Uranium(VI) by Tri-n-butyl Phosphate and Alternative Trialkyl Phosphate Extractants*, ORNL/TM-7231 (October 1980).
42. Mailen, J. C., O. K. Tallent, D. E. Horner,¹⁰ and K. E. Dodson, *Interphase Transfer Kinetics of Plutonium(IV) Using the Lewis Cell Technique*, ORNL/TM-7073 (July 1980).
43. Mailen, J. C., and L. M. Toth, "Chemistry of Volatile Fission Product Elements," Chap. 5 in *Light Water Reactor Nuclear Fuel Cycle*, R. G. Wymer and B. L. Vondra,⁵² Eds., CRC Press, Boca Raton, Fla., 1981.
44. Meyer, H. R.,⁶⁰ J. E. Till,⁶¹ E. S. Bomar,⁷ W. D. Bond, L. E. Morse, and V. J. Tennerly,⁷ "Recycle of Thorium/Uranium Carbide Fuels—A Radiological Assessment," presented at the Annual Meeting of the Health Physics Society, Philadelphia, July 8–13, 1979.
45. Mitchell, A. D., *SEPHIS-MOD4: A User's Manual to a Revised Model of the Purex Solvent Extraction System*, ORNL-5471 (May 1979).
46. Mitchell, A. D., *Modification of the SEPHIS-MOD4 Computer Program to Simulate the Thorex Solvent Extraction Process*, ORNL/TM-6825 (December 1979).
47. Notz, K. J., D. W. Holladay, C. W. Forsberg, and G. L. Haag, "Processes for the Control of $^{14}\text{CO}_2$ During Reprocessing," presented at the International Symposium on Management of Gaseous Wastes from Nuclear Facilities, Vienna, Feb. 18–22, 1980; published as ORNL/TM-7338 (July 1980).
48. Osborne, M. F., and R. B. Briggs,⁶² "Iodine Adsorption on Steel in Helium," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11–16, 1979; published in *Trans. Am. Nucl. Soc.* 33, 294–96 (1979).
49. Pearson, R. L., and T. B. Lindemer, "SiC-Fission Product Interaction in Triso-Coated HTGR Fuels," presented at the Annual Meeting of the American Ceramic Society, Cincinnati, Apr. 28–May 2, 1979.
50. Pearson, R. L., and T. B. Lindemer, *Simulated Fission Product Oxide Behavior in Triso-Coated HTGR Fuel*, ORNL/TM-6741 (August 1979).
51. Pearson, R. L., T. B. Lindemer, and E. C. Beahm, *Simulated Fission Product-SiC Interaction in Triso-Coated LEU or MEU HTGR Fuel Particles*, ORNL/TM-6991 (November 1980).
52. Ryon, A. D., and P. E. Hart,²⁸ "Gel Sphere Processes for Product Conversion," presented at the American Nuclear Society Topical Meeting on Fuel Cycles for the '80s, Gatlinburg, Tenn., Sept. 29–Oct. 2, 1980.
53. Ryon, A. D., A. E. Pasto,⁶³ P. A. Haas, J. M. Begovich, and J. S. Vavruska,⁵⁶ "Development of Processes for the Production of UO_2 Microspheres for Sphere-Pac and Sphere-Cal-Pellet Nuclear Fuels," presented at the Summer Meeting of the American Nuclear Society, Atlanta, June 3–7, 1979.
54. Smith, F. J.,⁶ R. E. Mesmer,⁶ and D. R. McTaggart, "The Solubility of Thorium Fluoride in Nitric Acid-Hydrofluoric Acid Solution Between 25 and 100°C," *J. Inorg. Nucl. Chem.* 43, 541–47 (1981).

---

60. Health and Safety Research Division.

61. Consultant to the Health and Safety Division.

62. Consultant.

63. Formerly of the Metals and Ceramics Division.

55. Spence, R. D., and P. A. Haas, "Preparation of Thorium-Uranium Gel Spheres," presented at the National Meeting of the American Institute of Chemical Engineers, Portland, Oreg., Aug. 17-20, 1980; published in the *Proceedings*, pp. 1-25.
56. Spence, R. D., P. A. Haas, and D. P. Stinton,⁷ "Development of a Thoria-Urania Sphere Preparation Process," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 27-30, 1980.
57. Tallent, O. K., J. C. Mailen, and K. E. Dodson, "Thorium Dibutyl Phosphate Complexes," *Inorg. Nucl. Chem. Lett.* **16**, 101-4 (1980).
58. Tallent, O. K., J. C. Mailen, L. M. Gray,⁵⁵ D. O. Campbell, and S. R. Buxton,¹⁰ *Study of the Effects of Zirconium on the Dissolution of Thoria in Nitric-Hydrofluoric Acid Solutions With and Without Aluminum Nitrate*, ORNL/TM-6770 (August 1979).
59. Tallent, O. K., J. C. Mailen, S. K. Whatley, K. E. Dodson, W. B. Howerton, and T. L. Yount,³ *The Use of H₂ in Secondary Dissolution for the Recovery of Plutonium*, ORNL/TM-7007 (May 1980).
60. Tiegs, S. M.,²⁰ and P. A. Haas, "Improved Fuel Pellet Fabrication Using Gel Microspheres," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11-16, 1979; published in *Trans. Am. Nucl. Soc.* **33**, 273-75 (1979).
61. Tiegs, S. M.,²⁰ P. A. Haas, and R. D. Spence, *The Sphere-Cal Process: Fabrication of Fuel Pellets from Gel Microspheres*, ORNL/TM-6906 (September 1979).
62. Tiegs, S. M.,²⁰ W. B. Stines,⁷ and M. H. Lloyd, "Fabrication of (Uranium, Plutonium) Dioxide Fuel Pellets Using Gel Microspheres," presented at the Fall Meeting of the American Ceramic Society, San Francisco, Oct. 26-29, 1980.
63. Tiegs, T. N.,⁷ J. M. Robbins,⁷ R. L. Hamner,¹⁰ B. H. Montgomery,³⁶ M. J. Kania,⁷ T. B. Lindemer, and C. S. Morgan, Jr.,⁷ *Irradiation Performance of HTGR Fuel in HFIR Capsule HT-31*, ORNL-5510 (May 1979).
64. Till, J. E.,⁶¹ H. R. Meyer,⁶⁰ L. E. Morse, W. D. Bond, E. S. Bomar,⁷ and V. J. Tennery,⁷ "Reprocessing Nuclear Fuels of the Future: A Radiological Assessment of Advanced (Th, U) Carbide Fuel," *Nucl. Technol.* **48**, 54-62 (1980).
65. Toth, L. M., H. A. Friedman, and M. M. Osborne, "The Polymerization of Pu(IV) in Aqueous Nitric Acid Solution," presented at the American Nuclear Society Topical Meeting on Fuel Cycles for the '80s, Gatlinburg, Tenn., Sept. 30-Oct. 2, 1980; published as ORNL/TM-7180 (October 1980).
66. Vaughn, V. C. A., "Experience with a U.K. Dissolution Test Using Irradiated Mixed-Oxide Fuels," presented at a Seminar on Reactor Fuel Dissolution under the U.S. Department of Energy/U.K. Atomic Energy Agency Exchange Agreement on Fast Reactor Collaboration, Windscale, England, October 1979.
67. Vaughn, V. C. A., and J. H. Goode, "Dissolution of Irradiated Mixed-Oxide Fuel," presented at a Seminar on Reactor Fuel Dissolution under the U.S. Department of Energy/U.K. Atomic Energy Agency Exchange Agreement on Fast Reactor Collaboration, Windscale, England, October 1979; also presented at the American Nuclear Society Topical Meeting on Fuel Cycles for the '80s, Gatlinburg, Tenn., Sept. 25-Oct. 2, 1980.
68. Vavruska, J. S.,³⁶ P. A. Haas, and A. E. Pasto,⁶³ "Preparation of Dense Oxide Spheres of 10- to 100-Micron Diameter for Sphere-Pac Nuclear Fuels," presented at the Annual Meeting of the American Ceramic Society, Cincinnati, Apr. 28-May 2, 1979; published in the *Proceedings*.
69. Vondra, B. L.,⁵² "LWR Fuel Cycle—Past, Present, Future," Chap. 1 in *Light Water Reactor Nuclear Fuel Cycle*, R. G. Wymer and B. L. Vondra, Eds., CRC Press, Boca Raton, Fla., 1981.

70. Wichner, R. P., and F. F. Dyer,¹³ *Distribution and Transport of Tritium in the Peach Bottom HTGR*, ORNL-5497 (August 1979).
71. Wichner, R. P., and F. F. Dyer,¹³ *Carbon-14 Production in the Peach Bottom HTGR Core*, ORNL-5597 (July 1980).
72. Wichner, R. P., M. F. Osborne, R. A. Lorenz, and R. B. Briggs,⁶² "Iodine Sorption/Desorption from Low-Alloy Steel and Graphite," presented at the Specialists Meeting on Coolant Chemistry, Plate-out, and Decontamination in Gas-Cooled Reactors, sponsored by the International Atomic Energy Agency, Jülich, Federal Republic of Germany, Dec. 2-4, 1980.
73. Williams, D. F., and C. C. Haws, *Design of and Operating Procedures for an Interim Facility for Preparing Kilogram Quantities of UO₂ Spheres by Internal Gelation*, ORNL/TM-6950 (October 1980).
74. Wymer, R. G., "Selected Chemistry of the Nuclear Fuel Cycle," presented to the American Chemical Society Student Affiliate Chapter of Maryville College, Maryville, Tenn., Oct. 11, 1979.
75. Wymer, R. G., "Nuclear Power and Its Fuel Cycle," presented at the Executive Seminar Center, Oak Ridge, Tenn., Dec. 12, 1979, and Nov. 6, 1980; also presented at Oak Ridge Associated Universities, Oak Ridge, Tenn., Feb. 9, 1980.
76. Wymer, R. G., and B. L. Vondra,⁵² Eds., *Light Water Reactor Nuclear Fuel Cycle*, CRC Press, Boca Raton, Fla., 1981.

D. Fossil Energy

1. Cochran, H. D., "Coal Liquefaction and Gasification," presented to the Southern College University Union, Oak Ridge, Tenn., July 1980.
2. Cochran, H. D., "Technical Details of European Coal Technology," presented to the International Energy Technology Assessment Management Group, Oak Ridge National Laboratory, August 1980.
3. Cochran, H. D., "Coal Liquefaction," *ORNL Review*, Oak Ridge National Laboratory, Winter 1980, pp. 38-43.
4. Cochran, H. D., "Technical Status of Direct Coal Liquefaction Projects," presented at the Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass., November 1980.
5. Cochran, H. D., "Pseudocomponents and Whole Syncrudes," report to the Workshop on Design Properties of Coal Liquids, Arrowhead Lodge, Okla., Mar. 2-4, 1981.
6. Cochran, H. D., "ORNL/UCC-ND Technical Support to Major Liquefaction Projects," presented to Solvent Refined Coal International, Inc., Inglewood, Colo., January 1981; and presented to the International Coal Refining Company, Allentown, Pa., February 1981.
7. Cochran, H. D., "Liquid and Gaseous Fuels from Coal," ORNL National Energy Perspective Overview Paper requested by the Program Planning and Analysis Group of Oak Ridge National Laboratory.
8. Cochran, H. D., and C. W. Di Bella,⁶⁴ "SRC-I and SRC-II Demonstration Plant Projects: A Technical Status Report," presented at the Seventh Annual Conference on Coal Gasification, Liquefaction, and Conversion to Electricity, University of Pittsburgh, August 1980.
9. Dickerson, L. S., "Laboratory Studies Supporting In Situ Coal Gasification: A Chemical Engineering Technician's Role," presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, Nov. 16-20, 1980.

---

64. U.S. Department of Energy, Oak Ridge Operations, SRC Projects Office.

10. Edwards, M. S.,⁶⁵ B. R. Rodgers, C. H. Brown, P. K. Carlson,³⁶ W. R. Gambill, T. M. Gilliam, J. M. Holmes,³⁶ R. P. Krishnan,³⁶ and L. F. Parsly,³⁶ *Technical Support to the Solvent-Refined Coal (SRC) Demonstration Projects: Assessment of Current Research and Development*, ORNL/TM-6952 (December 1980).
11. Edwards, M. S.,⁶⁵ W. C. Ulrich, and R. Salmon, "Economics of Gasoline Production from Underground Coal Gasification via Mobile-M Process," presented at the American Institute of Chemical Engineering Fuels and Petrochemicals Division Session, Houston, Apr. 1-5, 1979.
12. Edwards, M. S.,⁶⁵ W. C. Ulrich, and R. Salmon, "Economics of Producing Gasoline from Underground Coal Gasification Synthesis Gas," presented at the Fifth Underground Coal Conversion Symposium, Alexandria, Va., June 18-21, 1979.
13. Forrester, R. C., III,⁶⁶ "Coal and the Energy Crisis: A Perspective," presented to the Research and Engineering Staff of Dresser Industries, Magcobar Division, Houston, Feb. 6, 1980.
14. Forrester, R. C., III,⁶⁶ M. S. Edwards,⁶⁵ and R. Salmon, "Fuel-Grade Methanol Synthesis: A Technology Assessment," presented at the Second International Coal Utilization Exhibition and Conference, Houston, Nov. 6-8, 1979.
15. Forrester, R. C., III,⁶⁶ and R. Johnston,⁶⁷ "The Economics of Near-Term Alternatives for Coal-Based Electricity Generation," presented at the Second Miami International Conference on Alternative Energy Sources, Miami Beach, Fla., Dec. 10-13, 1979.
16. Forrester, R. C., III,⁶⁶ and P. R. Westmoreland,⁶⁸ "Two-Dimensional Pyrolysis Effects During In Situ Coal Gasification, Preliminary Results," *J. Pet. Technol.* 20, 571-73 (1979).
17. Gambill, W. R., "Overview Presentation on Heat Transfer Equipment for Coal Conversion," presented at the Workshop on Critical Coal Conversion: Equipment, Huntington, W. Va., Oct. 1-3, 1980; published in FE-2468-88, Engineering Society's Commission on Energy, Inc., Washington, D.C., 1981, pp. 42-53.
18. Gibson, M. R., R. L. Andrews, and L. S. Dickerson, "Continuous Flow Measurement of Coal Liquids Physical Properties—The Chemical Engineering Technician's Role," presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, Nov. 16-20, 1980.
19. Gilliam, T. M., and J. I. Brand, "Improved Filtration Rates of Coal Liquefaction Streams," presented at the Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., Oct. 30-Nov. 2, 1979.
20. Gilliam, T. M., J. I. Brand, and B. R. Rodgers, *Coal Dissolution Studies: Particle Size Distribution in Coal-Derived Liquids as a Function of Degree of Coal Conversion*, ORNL/TM-6681 (May 1979).
21. Gilliam, T. M., J. I. Brand, and B. R. Rodgers, "Particle Size Distribution in Coal-Derived Liquids as a Function of Degree of Coal Conversion," presented at the 14th Intersociety Energy Conversion Engineering Conference, Boston, Aug. 5-10, 1979.
22. Hewitt, J. D., and B. R. Rodgers, "Chemical Class Fractionation and Thermophysical Property Measurements of Solvent-Refined Coal Liquids," presented at the Chemical Technicians Symposium, National Meeting of the American Chemical Society, Las Vegas, Aug. 24-29, 1980.
23. Hightower, J. R., Jr., "Physical Properties of Coal Liquids," presented at the Department of Chemical Engineering, State University of New York, Buffalo, Feb. 4, 1981.

---

65. Mobil Research and Development Corp., Paulsboro, N.J.; formerly of the Chemical Technology Division.

66. Fluor Engineers and Constructors, Irvine, Calif.; formerly of the Chemical Technology Division.

67. AMOCO UK Exploration, Ltd.

68. On leave of absence.

24. Hwa, V. W.-S.,²³ W. K. Fraizer,²³ W. C. Ulrich, and H. D. Cochran, Jr., *Determination of Price-Ratio Constraints on Synthetic Fuel Products*, ORNL/MIT-302 (April 1980).
25. Johnson, P. J., and S. P. N. Singh, "Impact of Different Environmental Constraint Levels on the Indirect Coal Liquefaction Process," presented at the Seventh National Conference on Energy and the Environment, Phoenix, Ariz., Nov. 30-Dec. 3, 1980.
26. Kelmers, A. D., "Analysis of Pellets from the Magnesite Regeneration Calciner," presented at the Philadelphia Electric Company, Philadelphia, Jan. 21, 1980.
27. Larsen, J. W.,⁶ and B. R. Rodgers, "New Coal Liquefaction Techniques," presented at a conference of fossil energy contractors working on coal science and coal liquefaction projects managed by the Pittsburgh Energy Technology Center, Pittsburgh, Pa., Oct. 21-22, 1980.
28. Meyer, J. P.,⁶⁹ and M. S. Edwards,⁶⁵ "State of the Art of High-Temperature, High-Pressure Gas Filtration and Desulfurization," presented at the American Institute of Chemical Engineers Fuels and Petrochemicals Division Session, Houston, Apr. 1-5, 1979.
29. Meyer, J. P.,⁶⁹ J. W. Wells,³³ J. R. Cox,⁷⁰ J. P. Belk,³³ G. C. Frazier,⁷¹ and R. Salmon, "Mathematical Model of the Hygas Pilot Plant Reactor," presented at the American Institute of Chemical Engineers Fuels and Petrochemicals Division Session, Houston, Apr. 1-5, 1979.
30. Meyer, J. P.,⁶⁹ J. W. Wells,³³ J. R. Cox,⁷⁰ J. P. Belk,³³ G. C. Frazier,⁷¹ and R. M. Wham, *Mathematical Model of the Hygas Pilot Plant Reactor*, ORNL-5475 (November 1980).
31. Oswald, G. E., and E. L. Youngblood, "Physical Properties of Coal Liquids," presented at a conference of fossil energy contractors working on coal science and coal liquefaction projects managed by Pittsburgh Energy Technology Center, Pittsburgh, Oct. 21-22, 1980.
32. Oswald, G. E., E. L. Youngblood, J. R. Hightower, and H. D. Cochran, "Measurement of Physical Properties of Coal Liquids Under Process Conditions," presented at the Symposium on Instrumentation and Control for Fossil Energy Processes, Virginia Beach, Va., June 9-11, 1980; published in the *Proceedings*, Argonne National Laboratory, ANL-80-62, CONF-800602 (1980).
33. Oswald, G. E., E. L. Youngblood, and J. R. Thurgood,⁷² "Rheological Characterization of Coal-Solvent Slurry at High Temperature and Pressure," presented at the American Institute of Chemical Engineers Meeting on Coal Liquefaction—Properties of Coal Liquids Relevant to Design, Philadelphia, June 8-12, 1980.
34. Rodgers, B. R., "Stability of Coal-Derived Particles in Organic Media," presented at the Pacific Chemical Conference of the American Chemical Society, Honolulu, Apr. 1-5, 1979.
35. Rodgers, B. R., "Advanced Coal Conversion Research at ORNL," presented at Purdue University, Lafayette, Ind., May 4, 1979.
36. Rodgers, B. R., "Clean Energy from Coal," presented at the Southeastern Regional Meeting of the American Institute of Chemical Engineers, Atlanta, Apr. 12, 1980.
37. Rodgers, B. R., "New Coal Liquefaction Techniques," presented at the Institute for Mining and Minerals Research, Lexington, Ky., Apr. 18, 1980.
38. Rodgers, B. R., *Stability of Coal-Derived Particles in Organic Media*, ORNL-5631 (August 1980).

---

69. Production Research Center, Atlantic Richfield Co., Plano, Tex.; formerly of the Chemical Technology Division.

70. Co-op student from Clemson University, Clemson, S.C.

71. University of Tennessee, Knoxville; consultant to the Chemical Technology Division.

72. Utah Power and Light Co., Salt Lake City.

39. Rodgers, B. R., "Origin of the Charge on Coal-Derived Particles in Organic Media," presented at the Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
40. Rodgers, B. R., "Separation of Micron-Sized Particles from Coal Liquids: Verification of Surface Charge," *AIChE Symp. Ser.* 192, 68-73 (1980).
41. Rodgers, B. R., M. S. Edwards,⁶⁵ C. H. Brown, P. K. Carlson,³⁶ W. R. Gambill, T. M. Gilliam, J. M. Holmes,³⁶ R. P. Krishnan,³⁶ and L. F. Parsly, Jr.,³⁶ "Assessment of Current Research and Development in Support of the U.S.A. Coal Demonstration Plants Program," presented at the Intersociety Energy Conversion Engineering Conference, Seattle, Aug. 17-22, 1980.
42. Salmon, R., "Economic Evaluation of the Production of Methanol and Gasoline from Coal," presented at the University of Tennessee, Knoxville, Oct. 14, 1980.
43. Salmon, R., M. S. Edwards,⁶⁵ and R. M. Wham, *Production of Methanol and Methanol-Related Fuels from Coal*, ORNL-5564 (May 1980).
44. Salmon, R., H. F. Hartman, Jr.,³⁶ B. Niemann,³⁶ W. R. Gambill, M. S. Edwards,⁶⁵ J. R. Horton,³⁶ W. R. Reed,³⁶ J. F. Fisher, and D. A. Canonico,⁷ *A Review of the Badger Report FE-2416-24, "Conceptual Design of a Coal-to-Methanol Commercial Plant," February 1978*, ORNL-5558 (October 1979).
45. Sams, T. L., and J. W. Larsen,⁶ "Facile Internal Hydrogen Rearrangements in Coals," presented at the Chemical Technicians Symposium, National Meeting of the American Chemical Society, San Francisco, Aug. 25-26, 1980.
46. Singh, S. P. N., J. F. Fisher, and G. R. Peterson, "Potential Costs of Environmental Control Processes for Low-Btu Coal Gasification Plants," presented at the Annual Meeting of the American Institute of Chemical Engineers, San Francisco, Nov. 25-29, 1979; published in *Coal Processing Technology* 6, 66 (1980).
47. Singh, S. P. N., J. F. Fisher, and G. R. Peterson, *Evaluation of Eight Environmental Control Systems for Low-Btu Coal Gasification Plants*, ORNL-5481 (March 1980).
48. Singh, S. P. N., R. Salmon, J. F. Fisher, and G. R. Peterson, *Costs and Technical Characteristics of Environmental Control Processes for Low-Btu Coal Gasification Plants*, ORNL-5425 (June 1980).
49. Trevino-Lozano, R. A.,²³ D. M. Baars,²³ E. N. Keitelman,²³ G. E. Oswald, and E. L. Youngblood, *Characterization of Heat Transfer in Preheaters of Bench-Scale, Solvent-Refined Coal Apparatus*, ORNL/MIT-316 (December 1980).
50. Ulrich, W. C., M. S. Edwards,⁶⁵ and R. Salmon, *Process Designs and Economic Evaluations for the Linked Vertical Well In Situ Coal Gasification Process*, ORNL-5341 (August 1979).
51. Ulrich, W. C., M. S. Edwards,⁶⁵ and R. Salmon, *Evaluation of an In Situ Coal Gasification Facility for Producing M-Gasoline via Methanol*, ORNL-5439 (December 1979).
52. Westmoreland, P. R.,⁶⁸ "Pyrolysis of Blocks of Texas Lignite," presented at the National Meeting of the American Institute of Chemical Engineers, Houston, Apr. 1-5, 1979.
53. Westmoreland, P. R.,⁶⁸ "Measurement of Thermal Diffusivity and Application to In Situ Coal Gasification," presented at the Intersociety Energy Conversion Engineering Conference, Boston, Aug. 5-10, 1979; published in the *Proceedings*, American Chemical Society, 1979, pp. 1018-21.
54. Westmoreland, P. R.,⁶⁸ and L. S. Dickerson, "Pyrolysis of Blocks of Texas Lignite," presented at the National Meeting of the American Institute of Chemical Engineers, Houston, Apr. 1-5, 1979.
55. Westmoreland, P. R.,⁶⁸ and L. S. Dickerson, "A Review of Supporting Research at Oak Ridge National Laboratory for Underground Coal Conversion," presented at the Fifth Underground Coal Conversion Symposium on Laboratory Studies, Alexandria, Va., June 18-21, 1979.

56. Westmoreland, P. R.,⁶⁸ and L. S. Dickerson, "Pyrolysis of Blocks of Lignite," *In Situ* 4, 325-43 (1980).
57. Wham, R. M., J. F. Fisher, R. C. Forrester III,⁶⁶ A. R. Irvine, R. Salmon, S. P. N. Singh, and W. C. Ulrich, *Liquefaction Technology Assessment. Phase I. Indirect Liquefaction of Coal to Methanol and Gasoline Using Available Technology*, ORNL-5664 (February 1981).
58. Wham, R. M., and R. C. Forrester III,⁶⁶ "Available Technology for Indirect Conversion of Coal to Methanol and Gasoline: A Technology and Economics Assessment," presented at the Third Miami International Conference on Alternative Energy Sources, Miami, Dec. 15-18, 1980.
59. Wham, R. M., D. J. McCracken,⁷³ and R. C. Forrester III,⁶⁶ "Indirect Conversion of Coal to Methanol and Gasoline-Product Price vs Product Slate," presented at Coal Technology '80, Third International Coal Utilization Exhibition and Conference, Houston, Nov. 18-20, 1980.
60. Williams, W. R.,³³ T. M. Andress,³³ W. F. Boudreau,¹⁰ W. A. Bush,³³ D. A. Dyslin,³³ M. S. Edwards,⁶⁵ W. R. Gambill, D. W. Hatcher,³³ J. M. Holmes,³⁶ J. R. Horton,³³ J. P. Meyer,⁶⁹ W. R. Reed,³³ M. D. Silverman,³⁶ M. Siman-Tov,³³ E. C. Slade,³³ O. W. Thomas,³³ and C. B. Tolliver,³³ *Survey of Industrial Coal Conversion Equipment Capabilities: Executive Summary*, ORNL/TM-6810 (January 1980).
61. Youngblood, E. L., H. D. Cochran, P. R. Westmoreland,⁶⁸ C. H. Brown, Jr., and G. E. Oswald, "Hydrocarbonization of Coal in a Fluidized Bed," presented at the National Meeting of the American Institute of Chemical Engineers, Houston, Apr. 1-5, 1979.
62. Youngblood, E. L., H. D. Cochran, P. R. Westmoreland,⁶⁸ C. H. Brown, Jr., G. E. Oswald, and R. E. Barker, *Hydrocarbonization Research: Completion Report*, ORNL/TM-6693 (January 1981).
63. Youngblood, E. L., H. D. Cochran, P. R. Westmoreland,⁶⁸ C. H. Brown, Jr., G. E. Oswald, and C. T. Miller,⁷⁴ "Hydrocarbonization of Coal in a Fluidized Bed," *Ind. Eng. Chem. Prod. Res. Dev.* 19, 29-34 (1980).
64. Znaimer, S.,²³ P. F. Gubanc,²³ R. A. Hulseman,²³ and P. W. Fisher, *Characterization of Catalyst-Impregnated Coal Samples*, ORNL/MIT-317 (December 1980).

E. Miscellaneous Programs

1. Armento, W. J., "Safeguards in the Nuclear Fuel Cycle," presented at the Oak Ridge National Laboratory Proliferation Workshop, Feb. 21, 1980, and Feb. 11, 1981; also presented as part of the Health Physics and Radiation Protection Course, Oak Ridge Associated Universities, Oak Ridge, Tenn., Mar. 17, 1981.
2. Armento, W. J., W. D. Box, R. E. Brooksbank, F. G. Kitts, A. M. Krichinsky, and J. R. Parrott, Sr., "Implementation of the Engineering Safeguards Program (ESP) into Nuclear Fuel Recycle Facilities," presented at the Annual Meeting of the Institute of Nuclear Materials Management, Albuquerque, N.M., July 16-19, 1979; published in *J. Inst. Nucl. Mater. Manage.* 8, 295-300 (1979).
3. Armento, W. J., R. E. Brooksbank, and A. M. Krichinsky, "An Operational Facility-Integrated Computer System for Safeguards," presented at the American Nuclear Society National Topical Meeting on Fuel Cycles for the '80s, Gatlinburg, Tenn., Sept. 29-Oct. 2, 1980.
4. Armento, W. J., F. G. Kitts, and G. E. German,⁷⁵ "Routine and Postaccident Sampling in Nuclear Reactors," presented at the National Meeting of the American Institute of Chemical Engineers, Portland, Oreg., Aug. 17-20, 1980.

---

⁷³. Fluor Engineers and Constructors, Houston.

⁷⁴. Division of Fossil Fuel Processing, U.S. Department of Energy, Washington, D.C.

⁷⁵. Tennessee Valley Authority, Knoxville.

5. Besmann, T. M., "A National Energy Perspective," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 27-30, 1980; presented at Clemson University, Clemson, S.C., Feb. 3, 1981; presented at the Annual Southeast Regional Student Conference of the American Institute of Chemical Engineers, Myrtle Beach, S.C., Mar. 26-28, 1981; published in *Am. Ceram. Soc. Bull.* **59**, 325 (1980).
6. Besmann, T. M., and M. Olszewski,³⁶ "Letter to the Editor," *Science* **209**, 966 (1980).
7. Boyle, J. W.,⁷⁶ J. A. Carpenter,⁷ S. J. Cotter,⁶⁰ F. E. Harrington, N. E. Hinkle,⁷⁶ D. R. Johnson,⁷ R. L. Kroodsma,²⁵ and K. H. Lin, *Preliminary Draft. Environmental Impact Statement for Hot Fuels Engineering Laboratory*, ORNL/TM-7101 (March 1980).
8. Carter, W. L., and R. H. Rainey,⁵⁸ *Methodology for Estimating Reprocessing Costs for Nuclear Fuels*, ORNL/TM-6648 (February 1980).
9. Fisher, P. W., J. R. Coggins, Jr.,¹¹ S. E. Mitchell, and J. S. Watson, "Modeling Solid Hydrogen Storage Beds," pp. 413-16 in *Proceedings of the U.S. Department of Energy Chemical/Hydrogen Energy Systems Contractor Review*, CONF-781142, Brookhaven National Laboratory, May 1979.
10. Fisher, P. W., and D. W. Ramey, "Analysis of Hydrogen Isotope Separation in Aqueous Systems Using Bipolar Electrolysis with Hydrogen Permeable Electrodes," presented at the Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., Oct. 30-Nov. 2, 1979.
11. Fisher, P. W., and J. S. Watson, "Modeling Solid Hydrogen Storage Beds," presented at the U.S. Department of Energy Chemical Energy Storage and Hydrogen Energy Systems Contracts Review Meeting, Reston, Va., Nov. 12-14, 1979.
12. Fisher, P. W., and J. S. Watson, "Modeling and Evaluation of Transport in Solid Hydrogen Storage Beds," presented at the Annual Meeting of the American Institute of Chemical Engineers, San Francisco, Nov. 25-29, 1979.
13. Fisher, P. W., and J. S. Watson, "Modeling and Evaluation of Designs for Solid Hydrogen Storage Beds," presented at the Third World Hydrogen Energy Conference, Tokyo, June 23-26, 1980; published in *Hydrogen Energy Progress*, Pergamon Press, New York, 1980, pp. 839-47.
14. Fisher, P. W., and J. S. Watson, *Modeling Solid Hydrogen Storage Beds*, ORNL/TM-7561 (March 1981).
15. Goeller, H. E., "Longer-Term Domestic Supply Problems for Nonrenewable Materials with Special Emphasis on Energy-Related Applications," presented at a briefing for the Presidential Committee on Materials (COMAT), Washington, D.C., May 22, 1980.
16. Goeller, H. E., "A Potential Materials Crisis," presented at the American Institute of Chemical Engineers Fall Symposium on the Developing Manpower and Materials Crisis, Oak Ridge, Tenn., Sept. 8-9, 1980.
17. Goeller, H. E., "Comments on Long-Term Aspects of Renewable Versus Nonrenewable Resource Substitution," presented at the Interciencia Workshop on Materials for the Future, Kingston, Jamaica, Nov. 17-21, 1980.
18. Goeller, H. E., *Future U.S. Energy Supply: Constraints by Nonfuel Mineral Resources*, ORNL-5656 (December 1980).
19. Goeller, H. E., "Technological Solutions: Substitution, Recycling, Conservation, Resource Recovery," presented at the Workshop on Strategic Materials Supply: A Minerals Crisis?, Foreign Service Institute, U.S. Department of State, Arlington, Va., Mar. 4, 1981.

20. Hightower, J. R., Jr., "What the Federal Budget Means to Chemical Engineering," *Chem. Eng. Prog.* 75, 34-36 (1979).
21. Hightower, J. R., Jr., "Chemical Engineering in the Federal Budget," *Chem. Eng. Prog.* 76, 17-24 (1980).
22. Hone, R. W.,²³ M. Lamarchand,²³ W. Malaty,²³ J. E. Mrochek, W. W. Pitt, Jr., and M. S. Denton, *Separation of Water-Ethanol Mixtures by Sorption. Part 2*, ORNL/MIT-304 (February 1981).
23. Lindemer, T. B., and J. B. Wachtman, Jr.,⁷⁷ "Four Research Institutes in China," *Am. Ceram. Soc. Bull.* 59, 922 (1980).
24. McEvers, J. A.,⁷⁸ A. M. Krichinsky, L. R. Layman,⁴² T. H. Durigan, Jr.,⁴² R. M. Tuft,³¹ and W. P. Murray,⁷⁸ "Implementation of the Facility Integrated Inventory Computer System (FICS)," presented at the Annual Meeting of the Institute of Nuclear Materials Management, Palm Beach, Fla., June 30-July 2, 1980; published in *J. Inst. Nucl. Mater. Manage.* 9, 680-87 (1980).
25. McGuire, S. C., "A Look at Isomerism in ²³⁶U," presented at the Sixth Annual Day of Scientific Lectures, Knoxville College, Knoxville, Tenn., Apr. 27, 1979.
26. Perona, J. J., and J. S. Watson, *Sulfur Hexafluoride Purification from Mixtures with Air: A Process Feasibility Study*, ORNL/TM-6939 (October 1979).
27. Rauenzahn, R. M.,²³ Y. B. Lee,²³ J. H. Stewart, Jr.,¹³ F. A. Posey,²³ and T. M. Gilliam, *Recovery of Silver from Waste Liquids of Photoreproduction Equipment*, ORNL/MIT-314 (November 1980).
28. Reynolds, B. A.,²³ J. C. Metsa,²³ M. E. Mullins,²³ J. M. Begovich, R. M. Canon, and S. D. Clinton, *Distribution Ratios on Dowex 50W Resins of Metals Leached in the Caron Nickel Recovery Process*, ORNL/MIT-301 (May 1980).
29. Rhodes, W. H.,⁷⁹ T. B. Lindemer, J. C. Wurst,⁸⁰ and W. B. Shook,⁸¹ "Two Universities in China," *Am. Ceram. Soc. Bull.* 59, 925 (1980).
30. Saltmarsh, M. J.,⁸² W. R. Grimes, and R. T. Santoro,⁵⁴ *An Optimization of the Fission-Fusion Hybrid Concept*, ORNL/PPA-79/3 (April 1979).
31. Wymer, R. G., "An Overview of Oak Ridge National Laboratory Energy Research and Development Programs," presented at the Swiss Federal Research Establishment, Wurenlingen, Switzerland, May 28, 1979.
32. Wymer, R. G., "An Overview of Union Carbide Corporation Nuclear Division—Oak Ridge Operations," presented at the Energy Resources Workshop, Oak Ridge National Laboratory, Oak Ridge, Tenn., Sept. 24-26, 1979.
33. Wymer, R. G., "Resources, Recycle and Substitution," presented to the Graduate Students of the Chemical Engineering Department, University of Tennessee, Knoxville, Feb. 12, 1980.

F. Nuclear Regulatory Commission Programs

1. Box, W. D., B. B. Klima,⁸³ R. D. Seagren, L. B. Shappert, and G. A. Aramayo,³³ *Safety Analysis Report for Packaging (SARP) of the Oak Ridge National Laboratory TRU Curium Shipping Container*, ORNL-5147/R1 (June 1980).

---

77. Center for Materials Science, National Bureau of Standards, Washington, D.C.

78. Roane State Community College, Harriman, Tenn.; formerly of the Instrumentation and Controls Division.

79. GTE Laboratories, Inc., Waltham, Mass.

80. Research Institute, University of Dayton, Dayton, Ohio.

81. Department of Ceramic Engineering, Ohio State University, Columbus.

82. Fusion Energy Division.

83. Roane State Community College, Harriman, Tenn.

2. Box, W. D., B. B. Klima,⁸³ R. D. Seagren, L. B. Shappert, C. D. Watson, and G. A. Aramayo,³³ *Safety Analysis Report for Packaging (SARP) of the Oak Ridge National Laboratory Garden Carrier No. 2, Rev. 1*, ORNL-5408/R1 (August 1979).
3. Box, W. D., L. B. Shappert, R. D. Seagren, B. B. Klima,⁸³ M. C. Jurgensen, C. R. Hammond,³³ and C. D. Watson, *Safety Analysis Report for Packaging (SARP) of the Oak Ridge National Laboratory TRU Californium Shipping Container*, ORNL-5409/R1 (January 1980).
4. Box, W. D., L. B. Shappert, R. D. Seagren, C. D. Watson, C. R. Hammond,³³ and B. B. Klima,⁸³ *Safety Analysis Report for Packaging (SARP) of the Oak Ridge National Laboratory Shipping Cask D-38, Rev. 1*, ORNL-5406/R1 (September 1979).
5. Campbell, D. O., A. P. Malinauskas, and W. R. Stratton,⁸⁴ "Chemical Behavior of Fission Product Iodine Following LWR Accidents," presented at a Special Session on Realistic Estimates of the Consequences of Nuclear Accidents, Annual Meeting of the American Nuclear Society/ European Nuclear Society, Washington, D.C., Nov. 16-21, 1980.
6. Campbell, D. O., A. P. Malinauskas, and W. R. Stratton,⁸⁴ "The Chemical Behavior of Fission Product iodine in Light Water Reactor Accidents," *Nucl. Technol.* 53, 111 (1981).
7. Collins, J. L., R. A. Lorenz, M. F. Osborne, and A. P. Malinauskas, "Chemical Behavior of Fission Products Released from Highly Irradiated LWR Fuel," presented at the American Chemical Society Joint Fall Meeting of Basic Science and Nuclear Divisions, New Orleans, Oct. 14-17, 1979.
8. Davis, W., Jr., G. A. West, and R. G. Stacy, *Oxide Particle Size Distribution from Shearing Irradiated and Unirradiated LWR Fuels in Zircaloy and Stainless Steel Cladding: Significance for Risk Assessment (Interim Report)*, ORNL/NUREG-60 (NUREG/CR-0868) (May 1979).
9. Gieseke, J. A.,⁸⁵ and G. W. Parker, "Inertial Classification of Aerosols for Size Measurement," presented at the Containment Systems for Nuclear Installations (CSNI) Specialists Meeting on Nuclear Aerosols in Reactor Safety, Gatlinburg, Tenn., Apr. 15-17, 1980; published in the *Proceedings*, ORNL/NUREG/TM-404, NUREG/CR-1724, CSNI-45 (October 1980) pp. 232-48.
10. Kress, T. S.,³⁶ and G. W. Parker, "Comparative Review of Aerosol Instrumentation Used in U.S. LMFBR Safety Studies," presented at a meeting of Containment Systems for Nuclear Installations (CSNI) Experts on Nuclear Aerosols, Paris, Apr. 4, 1979.
11. Lorenz, R. A., "ANS-5.4 Fission Gas Release Model. III. Low Temperature Release," presented at the American Nuclear Society Topical Meeting on Light Water Reactor Fuel Performance, Portland, Ore., Apr. 28-May 2, 1979; published in the *Proceedings*, pp. 336-45.
12. Lorenz, R. A., "Fission Product Source Terms," pp. 9-14 in *Environmental Decontamination, Proceedings of the Workshop*, CONF-791234 (February 1981).
13. Lorenz, R. A., J. L. Collins, and A. P. Malinauskas, "Fission Product Source Terms for the Light Water Reactor Loss-of-Coolant Accident," *Nucl. Technol.* 46, 404-10 (1979).
14. Lorenz, R. A., J. L. Collins, and A. P. Malinauskas, *Fission Product Source Terms for the LWR Loss-of-Coolant Accident*, ORNL/NUREG/TM-321 (NUREG/CR-1288) (July 1980).
15. Lorenz, R. A., J. L. Collins, A. P. Malinauskas, O. L. Kirkland, and R. L. Towns, *Fission Product Release from Highly Irradiated LWR Fuel*, ORNL/NUREG/TM-287R2 (NUREG/CR-0722) (February 1980).

---

⁸⁴. Los Alamos National Laboratory, Los Alamos, N.M.

⁸⁵. Battelle Columbus Laboratories, Columbus, Ohio.

16. Lorenz, R. A., J. L. Collins, A. P. Malinauskas, M. F. Osborne, and R. L. Towns, *Fission Product Release from Highly Irradiated LWR Fuel Heated to 1300-1600°C in Steam*, ORNL/NUREG/TM-346 (NUREG/CR-1386) (November 1980).
17. Lorenz, R. A., J. L. Collins, M. F. Osborne, and A. P. Malinauskas, "Fission Product Release from LWR Fuel Defected in Steam in the Temperature Range 500 to 1600°C," presented at the International Atomic Energy Agency Specialists' Meeting on Behavior of Defected Zirconium Alloy Clad Ceramic Fuel in Water Cooled Reactors, Chalk River National Laboratories, Ontario, Canada, Sept. 17-21, 1979; published in the *Proceedings*, 1980, pp. 167-70.
18. Lorenz, R. A., J. L. Collins, M. F. Osborne, and A. P. Malinauskas, "Fission Product Release from High Gap-Inventory LWR Fuel Under LOCA Conditions," presented at the Summer Meeting of the American Nuclear Society, Las Vegas, June 8-13, 1980; published in *Trans. Am. Nucl. Soc.* 34, 462-63 (1980).
19. Malinauskas, A. P., "Iodine Release from Fuel," presented at the Nuclear Safety Analysis Center Workshop on Reactor Accident Iodine Release, Electric Power Research Institute, Palo Alto, Calif., July 1-2, 1980.
20. Malinauskas, A. P., "Fission Product Release Mechanisms and Pathways," presented at the Faculty Institute on Light Water Reactor Safety—Degraded Core Cooling, Argonne National Laboratory, Argonne, Ill., Mar. 16-20, 1981.
21. Malinauskas, A. P., R. A. Lorenz, H. Albrecht,⁸⁶ and H. Wild,⁸⁶ "LWR Source Terms for Loss-of-Coolant and Core Melt Accidents," presented at the Containment Systems for Nuclear Installations (CSNI) Specialists Meeting on Nuclear Aerosols in Reactor Safety, Gatlinburg, Tenn., Apr. 15-17, 1980; published in the *Proceedings*, ORNL/NUREG/TM-404, NUREG/CR-1724, CSNI-45 (October 1980), pp. 24-45.
22. Malinauskas, A. P., R. A. Lorenz, and J. L. Collins, "Fission Product Release During LWR Loss-of-Coolant Accidents," presented at the Annual Meeting of the American Nuclear Society, Atlanta, June 3-8, 1979; published in the *Proceedings*.
23. Malinauskas, A. P., R. A. Lorenz, and J. L. Collins, "Fission Product Release from Defected LWR Fuel Rods," presented at the Seventh Water Reactor Safety Research Information Meeting, Gaithersburg, Md., Nov. 5-9, 1979.
24. Malinauskas, A. P., and C. A. Proaps, *Proceedings of the American Nuclear Society/European Nuclear Society Topical Meeting—Thermal Reactor Safety*, vols. 1 and 2, CONF-800403 (1980).
25. Parker, G. W., "Experimental Techniques for the Characterization of Nuclear Aerosols," presented at the Containment Systems for Nuclear Installations (CSNI) Specialists Meeting on Nuclear Aerosols in Reactor Safety, Gatlinburg, Tenn., Apr. 15-17, 1980; published in the *Proceedings*, ORNL/NUREG/TM-404 (NUREG/CR-1724), CSNI-45 (October 1980), pp. 278-301.
26. Parker, G. W., and G. E. Creek,¹⁰ "Impact of Secondary Effects on the Reduction of Fission Product Source Terms in Class IX Reactor Accidents," presented at a Special Session of the Annual Conference of the American Nuclear Society/European Nuclear Society, Washington, D.C., Nov. 16-21, 1980; published in *Nucl. Technol.* 53, 135-40 (1981).
27. Parker, G. W., G. E. Creek,¹⁰ and A. L. Sutton, Jr., "Size Distribution Measurements of Chain Agglomerate Reactor Fuel Aerosols," presented at the Aerosol Technology Meeting, General Motors Research Laboratories, Warren, Mich., Aug. 27-29, 1979.

---

⁸⁶. GFK Karlsruhe, Federal Republic of Germany.

G. Nuclear Waste Management

1. Alexander, C. W., and A. G. Croff, "Miscellaneous Fuel Cycle Impacts of Actinide Partitioning and Transmutation," presented at the International Conference on Nuclear Waste Transmutation, University of Texas, Austin, July 22-24, 1980.
2. Alexander, C. W., and A. G. Croff, *Actinide Partitioning-Transmutation Program Final Report. IV. Miscellaneous Aspects*, ORNL/TM-6984 (September 1980).
3. Beyerlein, S. W.,⁸⁷ and H. C. Claiborne, *The Possibility of Multiple Temperature Maxima in Geologic Repositories for Spent Fuel from Nuclear Reactors*, ORNL/TM-7024 (January 1980); presented at the Annual Winter Meeting of the American Society of Mechanical Engineers, Chicago, Nov. 16-21, 1980, and published in *Heat Transfer in Nuclear Waste Disposal*, vol. 2, American Society of Mechanical Engineers, 1980, pp. 49-57.
4. Blomeke, J. O., "Management of Radioactive Wastes," presented at the Nuclear Power Safety Course, Georgia Institute of Technology, Atlanta, Apr. 2-6, 1979; at the Proliferation Information Workshop, Oak Ridge National Laboratory, Oak Ridge, Tenn., Spring 1979; and at the School of Nuclear Engineering, Texas A&M University, College Station, Nov. 5-9, 1979.
5. Blomeke, J. O., "An Overview of the Nuclear Fuel Cycle," presented at the School of Nuclear Engineering, Texas A&M University, College Station, Nov. 5-9, 1979.
6. Blomeke, J. O., "Disposal of Radioactive Wastes," presented at the School of Nuclear Engineering, Texas A&M University, College Station, Nov. 5-9, 1979.
7. Blomeke, J. O., "Origin, Magnitude, and Treatment of Radioactive Wastes," presented at the School of Nuclear Engineering, Texas A&M University, College Station, Nov. 5-9, 1979.
8. Blomeke, J. O., and A. G. Croff, "An Overall Assessment of Actinide Partitioning and Transmutation," presented at the Annual Meeting of the American Nuclear Society, Las Vegas, June 8-13, 1980; published in *Trans. Am. Nucl. Soc.* 34, 417-19 (1980).
9. Blomeke, J. O., and A. G. Croff, "An Assessment of Partitioning and Transmutation," presented at the International Conference on Nuclear Waste Transmutation, University of Texas, Austin, July 22-24, 1980; published in the *Proceedings*, 1981, pp. 240-66.
10. Blomeke, J. O., and A. G. Croff, "An Assessment of Actinide Partitioning-Transmutation as a Waste Management Concept," presented at the International Atomic Energy Agency Panel on Environmental Evaluation and Hazard Assessment of the Separation of Actinides from Nuclear Wastes Followed by Either Transmutation or Separate Disposal, Ispra (Varese), Italy, April 1980.
11. Blomeke, J. O., A. G. Croff, B. C. Finney, and D. W. Tedder,⁸⁸ "An Overall Assessment of Actinide Partitioning and Transmutation for Waste Management Purposes," presented at the Second Technical Meeting on the Nuclear Transmutation of Actinides, Ispra (Varese), Italy, Apr. 21-24, 1980; published in the *Proceedings*, EUR 6929 EN/FR, ECSC-EEC-EAEC, Brussels, 1980, pp. 451-69.
12. Bond, W. D., "Chemical Aspects of Nuclear Waste Treatment," presented at the Symposium on Chemistry in Energy Production, American Chemical Society Southeast/Southwest Regional Meeting, New Orleans, Dec. 10-12, 1980.
13. Bond, W. D., and R. E. Leuze, "Removal of Americium and Curium from High-Level Wastes," presented at the Actinide Separations Symposium, Pacific Chemical Conference of the American Chemical Society, Honolulu, Apr. 1-6, 1979; published in ACS Symposium Series 117, 1980, pp. 441-53.

---

⁸⁷. Summer research participant from Oak Ridge Associated Universities, Oak Ridge, Tenn.

⁸⁸. Georgia Institute of Technology, Atlanta; formerly of the Chemical Technology Division.

14. Bond, W. D., R. E. Leuze, and F. M. Scheitlin, "Recovery of Plutonium from HEPA Filters by Ce(IV)-Promoted Dissolution of PuO_2 and Recycle of the Cerium Promoter," presented at the International Conference on Nuclear Waste Transmutation, Austin, Tex., July 22-24, 1980.
15. Brooksbank, R. E., "Fuel Cycle Safety and Safeguards Aspects," presented at the Nuclear Power Safety Course, School of Nuclear Engineering, Georgia Institute of Technology, Atlanta, Apr. 2-6, 1979.
16. Brooksbank, R. E., "The Nuclear Fuel Cycle," presented at the Health Physics and Radiation Protection Course, Oak Ridge Associated Universities, Oak Ridge, Tenn., Apr. 9, 1979; also presented at the Energy Resources Workshop, Oak Ridge National Laboratory, Oak Ridge, Tenn., Sept. 24-26, 1979.
17. Brooksbank, R. E., "Plenary Lecture. A Special Radioclement Problem: ORNL Assistance to Three Mile Island in Handling Contaminated Air and Water," presented at the 23rd Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., Oct. 9, 1979.
18. Brooksbank, R. E., "Decontamination Experience at ORNL," presented at the Facility Decontamination Technology Workshop, Hershey, Pa., Nov. 27-29, 1979.
19. Brooksbank, R. E., "The Nuclear Fuel Cycle—Safeguards and Nonproliferation Issues," presented to the Health Physics and Radiation Protection Group of Oak Ridge Associated Universities, Oak Ridge, Tenn., Mar. 25, 1980.
20. Brunton, G. D.,⁵ "United States National Waste Terminal Storage Argillaceous Rock Studies," presented at the Workshop on the Use of Argillaceous Materials for the Isolation of Radioactive Waste, Paris, Sept. 10-12, 1979; published in the *Proceedings*, OECD NEA, 1980, pp. 15-19.
21. Brunton, G. D.,⁵ "Evaluation of Argillaceous Rock for Nuclear Waste Containment," presented at the Annual Information Meeting of the Office of Nuclear Waste Isolation, Columbus, Ohio, Oct. 31, 1979; published in the *Proceedings*.
22. Brunton, G. D.,⁵ "National Nuclear Waste Terminal Storage Argillaceous Rock Studies," presented at the Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Chicago, Feb. 22-26, 1981; and at the American Nuclear Society Topical Meeting on Waste Management, Tucson, Ariz., Feb. 23-26, 1981.
23. Carter, W. L., B. C. Finney, C. W. Alexander, and J. O. Blomeke (contributors), *Spent Fuel and Waste Inventories and Projections*, ORO-778 (August 1980).
24. Chilton, J. M., *An Evaluation of the Low-Level Waste Treatment Plant at Oak Ridge National Laboratory, and Suggested Changes in the Design and Operation*, ORNL-5618 (March 1980).
25. Claiborne, H. C., "Overview of Some Current U.S. Design Concepts for Nuclear Waste/Spent Fuel Repositories in Salt," presented at the United States/Federal Republic of Germany Bilateral Workshop on Waste Isolation Performance Assessment and In Situ Testing, Berlin, Oct. 1-5, 1979; published in the *Proceedings*.
26. Claiborne, H. C., "Waste Management in Perspective with Emphasis on Deep Geologic Disposal," presented at the Workshop on Nuclear Power and the Energy Crisis, Oak Ridge Associated Universities, Oak Ridge, Tenn., Oct. 21-26, 1979, and Apr. 18, 1980; also presented at the Energy Specialists Training Program for Education Personnel, Oak Ridge Associated Universities, Oak Ridge, Tenn., July 15, 1980.
27. Claiborne, H. C., and L. D. Rickertsen,⁸⁹ "Expected Repository Environment—Salt," presented at the National Waste Terminal Storage Program Information Meeting, Columbus, Ohio, Oct. 30-Nov. 1, 1979; published in the *Proceedings*.

---

⁸⁹. Science Applications, Inc., Oak Ridge, Tenn.

28. Claiborne, H. C., L. D. Rickertsen,⁸⁹ and R. F. Graham,⁸⁹ *Expected Environments in High-Level Nuclear Waste and Spent Fuel Repositories in Salt*, ORNL/TM-7597 (August 1980).
29. Claiborne, H. C., R. S. Wagner,³³ and R. A. Just,³³ *A Comparison of the Results of Several Heat Transfer Computer Codes When Applied to a Hypothetical Nuclear Waste Repository*, ORNL/TM-7112 (January 1980).
30. Clark, W. E.,¹⁰ and W. B. Howerton, "The Fixation of Radioiodine with Portland Cement. Part II. Radiation Stability Tests," *Nucl. Technol.* **49**(2), 209-13 (1980).
31. Compere, E. L., "Summary of the Report to the President by the Interagency Review Group on Nuclear Waste Management," *Nucl. Saf.* **20**(6), 706-21 (1979).
32. Compere, E. L., W. B. Cottrell,³⁶ and W. R. Casto,⁹⁰ "ICPP Criticality Event of October 17, 1978," *Nucl. Saf.* **21**(5), 648-53.
33. Compere, E. L., and H. W. Godbee, "The Interrelation of Short-Term Leach Tests and Long-Term Leaching," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11-16, 1979; published in *Trans. Am. Nucl. Soc.* **33**, 207-8 (1979).
34. Counce, R. M., W. S. Groenier, W. D. Holland, and J. J. Perona, "Nitrogen Oxide Removal from Gaseous Mixtures of Steam, Air, Nitrogen Oxides, and Iodine by Absorption into Dilute Nitric Acid in Packed Towers," presented at the 16th Nuclear Air Cleaning Conference, sponsored by the Department of Energy, San Diego, Oct. 20-23, 1980.
35. Croff, A. G., "ORIGEN2: A Revised and Updated Version of ORIGEN," presented at the Annual Meeting of the American Nuclear Society, Las Vegas, June 8-13, 1980; published in *Trans. Am. Nucl. Soc.* **34**, 349-50 (1980).
36. Croff, A. G., *A User's Manual for the ORIGEN2 Computer Code*, ORNL/TM-7175 (July 1980).
37. Croff, A. G., *ORIGEN2—A Revised and Updated Version of the Oak Ridge Isotope Generation and Depletion Code*, ORNL-5621 (July 1980).
38. Croff, A. G., "Radioactive Waste Management," Chap. 4 in *Light Water Reactor Nuclear Fuel Cycle*, R. G. Wymer and B. L. Vondra,⁵² Eds., CRC Press, Boca Raton, Fla., 1981.
39. Croff, A. G., and C. W. Alexander, *Decay Characteristics of Once-Through LWR and LMFBR Spent Fuels, High-Level Wastes, and Fuel-Assembly Structural Material Wastes*, ORNL/TM-7431 (November 1980).
40. Croff, A. G., C. W. Alexander, and J. W. Wachter, "Transmutation and Fuel Cycle Impacts," presented at the Annual Meeting of the American Nuclear Society, Las Vegas, June 8-13, 1980; published in *Trans. Am. Nucl. Soc.* **34**, 413-14 (1980).
41. Croff, A. G., and M. A. Bjerke,⁴² *Alternative Fuel Cycle PWR Models for the ORIGEN Computer Code*, ORNL/TM-7005 (February 1980).
42. Croff, A. G., and M. A. Bjerke,⁴² *Once-Through CANDU Reactor Models for the ORIGEN2 Computer Code*, ORNL/TM-7177 (November 1980).
43. Croff, A. G., J. O. Blomeke, and B. C. Finney, *Actinide Partitioning-Transmutation Program Final Report. I. Overall Assessment*, ORNL-5566 (June 1980).
44. Finney, B. C., and D. W. Tedder,⁸⁸ "Actinide Partitioning Processes for Fuel Cycle Wastes," presented at the Annual Meeting of the American Nuclear Society, Las Vegas, June 8-13, 1980; published in *Trans. Am. Nucl. Soc.* **34**, 412-13 (1980).

---

⁹⁰. Operations Division.

45. Finney, B. C., and D. W. Tedder,⁸⁸ "Actinide Partitioning Processes for Fuel Reprocessing and Refabrication Plant Wastes," presented at the International Conference on Nuclear Waste Transmutation, University of Texas, Austin, July 22-24, 1980.
46. Ford, W. E., III,⁸⁴ C. C. Webster,⁴² B. R. Diggs,⁴² R. E. Pevey,¹⁹ and A. G. Croff, *FCXSEC: Multigroup Cross-Section Libraries for Nuclear Fuel Cycle Shielding Calculations*, ORNL/TM-7038, ENDF-287 (May 1980).
47. Forsberg, C. W., *Cation Exchange Chromatography Studies: Elution Sequence of Plutonium and Neptunium with Diethylenetriaminepentaacetic Acid (DTPA) and the Effects of Bidentate Impurities on Cation Loading*, ORNL/TM-6737 (August 1979).
48. Forsberg, C. W., *Separation of Americium, Curium, and Rare Earths from High-Level Wastes by Oxalate Precipitation: Experiments with Synthetic Waste Solutions*, ORNL/TM-6445 (January 1980).
49. Forsberg, C. W., *Computer Simulation of Displacement Cation Exchange Chromatography: Separation of Trivalent Actinides and Lanthanides*, ORNL/TM-6738 (May 1980).
50. Forsberg, C. W., "Separation of Americium, Curium, and Trivalent Lanthanides from High-Level Wastes by Oxalate Precipitation: Experiments with Synthetic Waste Solutions," *Nucl. Technol.* **49**, 243-52 (1980).
51. Godbee, H. W., and E. L. Compere, "A Figure of Merit Determined from the ANS Leachability Standard," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11-16, 1979; published in *Trans. Am. Nucl. Soc.* **33**, 205-7 (1979).
52. Godbee, H. W., E. L. Compere, D. S. Joy, A. H. Kibbey, J. G. Moore, C. W. Nestor, Jr.,⁴² O. U. Anders,⁹¹ and R. M. Neilson, Jr.,⁹² "Application of Mass Transport Theory to the Leaching of Radionuclides from Waste Solids," *Nucl. Chem. Waste Manage.* **1**, 29 (1980).
53. Godbee, H. W., and E. J. Frederick, "Volume Reduction Workshop," presented at The State of Waste Disposal Technology, Mill Tailings and Risk Assessment Models, Waste Management '80, Tucson, Ariz., Mar. 10-14, 1980.
54. Godbee, H. W., and A. H. Kibbey, "Radioactive Waste: An Introductory Overview," presented at the American Society of Mechanical Engineers Short Course on Nuclear Waste Management, Alexandria, Va., May 21-25, 1979; also presented at Tucson, Ariz., May 19-25, 1980.
55. Godbee, H. W., and A. H. Kibbey, "Chemical Engineering Unit Operations Used to Treat Radioactive Waste," presented at the School of Chemical Engineering, Georgia Institute of Technology, Atlanta, July 28, 1980.
56. Godbee, H. W., and A. H. Kibbey, "Unit Operations Used to Treat Process and/or Waste Streams at Nuclear Power Plants," presented at the National Meeting of the American Institute of Chemical Engineers, Portland, Oreg., Aug. 17-20, 1980; published in *Nucl. Chem. Waste Manage.* **2**(1), 71-88 (1981).
57. Haag, G. L., "Carbon-14 Removal and Fixation from Off-gas Streams at Nuclear Facilities," presented at the Annual Meeting of the American Nuclear Society, Las Vegas, June 8-13, 1980; published in *Trans. Am. Nucl. Soc.* **34**, 394-95 (1980).
58. Haag, G. L., "Carbon-14 Immobilization via the $\text{CO}_2\text{-Ba(OH)}_2$ Hydrate Gas-Solid Reaction," presented at the 16th Nuclear Air Cleaning Conference, sponsored by the U.S. Department of Energy, San Diego, Oct. 20-23, 1980; published in the *Proceedings*.

---

91. Dow Chemical Company, Midland, Mich.

92. Brookhaven National Laboratory, Upton, N.Y.

59. Heiskell, M. M.,⁹³ "ORNL Nuclear Legislative Data Base Program," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11-16, 1979; published in *Trans. Am. Nucl. Soc.* 33, 451-52 (1979).
60. Heiskell, M. M.,⁹³ *Annotated Bibliography on the Transportation and Handling of Radioactive Materials—3*, ORNL/NUREG/NSIC-168 (NUREG/CF-1275) (September 1980).
61. Hillsman, E. L., P. E. Johnson, and B. E. Peterson, "Predicting Routes of Radioactive Wastes Moved on the U.S. Railroad System," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980.
62. Jenks, G. H. *Effects of Temperature, Temperature Gradients, Stress, and Irradiation on Migration of Brine Inclusions in a Salt Repository*, ORNL-5526 (July 1979).
63. Jenks, G. H., *Effects of Gaseous Radioactive Nuclides on the Design and Operation of Repositories for Spent LWR Fuel in Rock Salt*, ORNL-5578 (December 1979).
64. Jenks, G. H., *Review of Information on the Radiation Chemistry of Materials Around Waste Canisters in Salt and Assessment of the Need for Additional Experimental Information*, ORNL-5607 (March 1980).
65. Joy, D. S., "Spent Fuel Logistics Model and the Routing Models," presented at the National Academy of Sciences, Washington, D.C., June 13, 1980.
66. Joy, D. S., and B. J. Hudson,⁹⁴ *Transportation Analysis for the Concept of Regional Repositories*, ORNL/TM-7170 (June 1980).
67. Joy, D. S., and B. J. Hudson,⁹⁴ "The Oak Ridge Spent Fuel Logistics Model," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980; published in the *Proceedings*.
68. Joy, D. S., and B. J. Hudson,⁹⁴ "Transportation Analysis for the Concept of Regional Repositories," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980; published in the *Proceedings*.
69. Joy, D. S., B. J. Hudson,⁹⁴ and M. W. Anthony,⁹⁵ *Logistics Characterization for Regional Spent Fuel Repositories Concept. Technical Report*, ONWI-124, Office of Nuclear Waste Isolation, Battelle Columbus Laboratories, Columbus, Ohio (August 1980).
70. Joy, D. S., B. J. Hudson,⁹⁴ and R. D. Seagren, "Predicting Transportation Routes for Radioactive Wastes: U.S. Highway System," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980; published in the *Proceedings*.
71. Joy, D. S., P. E. Johnson, D. B. Clarke,⁹⁶ and S. C. McGuire, "Predicting Transportation Routes for Radioactive Wastes," presented at the American Nuclear Society Topical Meeting on Waste Management, Tucson, Ariz., Feb. 23-26, 1981.
72. Katz, S.,¹⁰ "The Reaction of Hydrogen and Oxygen in the Presence of Concretes Incorporating Simulated Radioactive Waste," presented at the Annual Meeting of the Materials Research Society, Boston, Mass., Nov. 26-30, 1979; published in *Scientific Basis for Nuclear Waste Management*, vol. 2, C. J. M. Northrup, Jr., Ed., Plenum Press, New York, 1980, pp. 577-84.

---

93. U.S. Department of Energy, Oak Ridge Operations Office; formerly of the Chemical Technology Division.

94. System Development Corp., Oak Ridge, Tenn.; formerly of the Chemical Technology Division.

95. Battelle Memorial Institute, Columbus, Ohio.

96. Graduate consultant from University of Tennessee, Knoxville.

73. Kibbey, A. H., and H. W. Godbee, "Physicochemical Characterization of Solidification Agents Used and Products Formed with Radioactive Wastes at LWR Nuclear Power Plants," pp. 495-98 in *Scientific Basis for Nuclear Waste Management*, vol. 1, Plenum, New York, 1979.
74. Kibbey, A. H., and H. W. Godbee, "Sources, Amounts, and Characteristics of Low-Level Radioactive Solid Wastes," pp. 11-15 in *Radioactive Waste Management*, EPA 520/3-79-002 (May 1979).
75. Kibbey, A. H., and H. W. Godbee, *A State-of-the-Art Report on Low-Level Radioactive Waste Treatment*, ORNL/TM-7427 (September 1980).
76. Kibbey, A. H., H. W. Godbee, and E. L. Compere, "A Review of Solid Radioactive Waste Practices in Light-Water-Cooled Nuclear Reactor Power Plants," *Nucl. Saf.* 21, 193-205 (1980).
77. Lackey, W. J.,⁷ P. Angelini,⁷ F. L. Layton,¹³ D. P. Stinton,⁷ and J. S. Vavruska,⁵⁶ "Sol-Gel Technology Applied to Glass and Crystalline Ceramics," presented at the Waste Management Symposium, Tucson, Ariz., Mar. 10-14, 1980; published in *Waste Management '80, The State of Waste Disposal Technology, Mill Tailings, and Risk Analysis*, University of Arizona, Tucson, 1980, pp. 391-417.
78. Lackey, W. J.,⁷ R. E. Blanco, and A. L. Lotts,²⁰ "Application of Sol-Gel Technology to Fixation of Nuclear Reactor Waste," *Nucl. Technol.* 49, 321-24 (1980).
79. Lin, K. H., W. E. Clark, and W. B. H. Horton, "Processes for Immobilization of High-Level Solid Wastes by Glass and Ceramic Matrices," presented at the International Symposium on Ceramics in Nuclear Waste Management, Cincinnati, Apr. 30-May 2, 1979; published in the *Proceedings*, U.S. Department of Energy Technical Information Center, 1979, pp. 354-58.
80. Lomenick, T. F., and R. B. Laughon,⁹⁵ "An Investigation of the Regional Characteristics of the Devonian Shales for the Storage/Disposal of Radioactive Wastes," presented at the Workshop on the Use of Argillaceous Materials for the Isolation of Radioactive Waste, Paris, Sept. 10-12, 1979; published in the *Proceedings*, Nuclear Energy Agency, 1979, pp. 121-27.
81. Los Alamos Technical Associates, Inc., *Appendix. Actinide Partitioning-Transmutation Program Final Report. VII. Long-Term Risk Analysis of the Geologic Repository*, ORNL/Sub-80/31,038/1 (January 1980).
82. Los Alamos Technical Associates, Inc., *Actinide Partitioning-Transmutation Program Final Report. V. Preconceptual Designs and Costs of Partitioning Facilities and Shipping Casks (Summary Report)*, ORNL/TM-6985 (June 1980).
83. Los Alamos Technical Associates, Inc., *Actinide Partitioning-Transmutation Program Final Report. VII. Long-Term Risk Analysis of the Geologic Repository*, ORNL/TM-6987 (September 1980).
84. Los Alamos Technical Associates, Inc., *Appendix. Actinide Partitioning-Transmutation Program Final Report. VII. Long-Term Risk Analysis of the Geologic Repository*, ORNL/Sub-80/31038/1 (September 1980).
85. Marshall, J. R.,⁹⁷ D. S. Joy, and B. J. Hudson,⁹⁴ "ORNL Interface and Logistics Studies," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11-16, 1979; published in *Trans. Am. Nucl. Soc.* 33, 452-53 (1979).
86. McDaniel, E. W., *Cement Technology for Borehole Plugging: An Interim Report on Permeability Measurements of Cementitious Solids*, ORNL/TM-7092 (January 1980).
87. McDaniel, E. W., *Rheology of Sludge-Slurry Grouts*, ORNL/TM-7497 (October 1980).

---

⁹⁷. Guest consultant.

88. McDaniel, E. W., J. G. Moore, and H. B. Greene, "Saltcretes as Possible Borehole Plugs—Physical Characteristics," presented at the International Symposium on Ceramics in Nuclear Waste Management, Annual Meeting of the American Ceramic Society, Cincinnati, Apr. 30–May 2, 1979.
89. McDaniel, E. W., and H. O. Weeren, *Flowability of Bulk Solids Used in Shale Fracturing Grouts as Determined by the Jenike and Jonanson Method*, ORNL/TM-6882 (September 1979).
90. McDaniel, E. W., H. O. Weeren, and J. G. Moore, "Disposal of Intermediate-Level Radioactive Sludge by Hydrofracturing at ORNL," presented at the Annual Meeting of the Materials Research Society, Boston, Nov. 16–20, 1980.
91. Moore, J. G., "A Review of ORNL Programs on the Use of Cementitious Materials in Radioactive Waste Management," presented at Savannah River Laboratory, Aiken, S.C., June 12, 1979.
92. Moore, J. G., "Testing Procedures and Initial Results from Studies on the Effect of Fly Ash and Salt in Mortars," presented at the First Annual Information Meeting of the Office of Nuclear Waste Isolation, Columbus, Ohio, Oct. 30–Nov. 1, 1979.
93. Moore, J. G., "A Survey of Concrete Waste Forms," presented at the Conference on Alternate Nuclear Waste Forms and Interactions in Geologic Media, Gatlinburg, Tenn., May 13–15, 1980; published in the *Proceedings*.
94. Moore, J. G., M. T. Morgan, E. W. McDaniel, H. B. Greene, and G. A. West, *Cement Technology for Borehole Plugging: Interim Report on the Effects of Fly Ash and Salt on the Physical Properties of Cementitious Solids*, ORNL/TM-7106 (March 1980).
95. Moore, J. G., G. C. Rogers, S. Katz, M. T. Morgan, and E. Newman, "FUETAP Concretes—Tailored Autoclaved Concretes for the Fixation of Radioactive Wastes," presented at the American Nuclear Society Topical Meeting on Waste Management, Tucson, Ariz., Feb. 23–26, 1981.
96. Moore, J. G., G. C. Rogers, E. W. McDaniel, E. Newman, and H. E. Devaney, "Current ORNL Studies on Cementitious Hosts for Radioactive Wastes," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 27–30, 1980.
97. Moore, J. G., G. C. Rogers, J. H. Paehler, and H. E. Devaney, "FUETAP (Formed Under Elevated Temperatures and Pressures) Concretes as Hosts for Radioactive Wastes," presented at the International Symposium on Ceramics in Nuclear Waste Management, Annual Meeting of the American Ceramic Society, Cincinnati, Apr. 30–May 2, 1979; published in *Ceramics in Nuclear Waste Management*, CONF-790420 (1979), pp. 132–35.
98. Morgan, M. T., *Thermal Conductivity of Rock Salt from Louisiana Salt Domes*, ORNL/TM-6809 (June 1979).
99. Morgan, M. T., and G. A. West, "The Thermal Conductivity of the Rocks in the Bureau of Mines Standard Rock Suite," presented at the International Thermal Conductivity Conference, Illinois Institute of Technology Research Institute, Chicago, Nov. 7–9, 1979; published in the *Proceedings*.
100. Morgan, M. T., and G. A. West, *Thermal Conductivity of the Rocks in the Bureau of Mines Standard Rock Suite*, ORNL/TM-7052 (January 1980).
101. Newman, E., "Radioactive Waste Fixation and Isolation Using Concrete," presented at the University of Arkansas, Pine Bluff, Dec. 5, 1979.
102. Parrott, J. R., Sr., "Cleanup of Building 3019 and Surroundings," presented at the Environmental Decontamination Workshop, Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec. 4, 1979.
103. Parrott, J. R., Sr., "The Decontamination of Concrete Surfaces in Building 3019, Oak Ridge National Laboratory," presented at the Concrete Decontamination Workshop, Battelle Conference Center, Seattle, May 28–29, 1980; published in the *Proceedings*, PNL-SA-8855, CONF-800542 (1980), pp. 151–68.

104. Parrott, J. R., Sr., "Preparation of $^{233}\text{UO}_2$ for the Light Water Breeder Reactor Demonstration Program," presented at the Annual Meeting of the American Nuclear Society, Las Vegas, June 8-13, 1980; published in *Trans. Am. Nucl. Soc.* **34**, 434-35 (1980).
105. Parsons Company, The Ralph M., *Actinide Partitioning-Transmutation Program Final Report. V. Preconceptual Designs and Costs of Partitioning Facilities and Shipping Casks (Summary Report)*, ORNL/TM-6985 (January 1980).
106. Parsons Company, The Ralph M., *Actinide Partitioning-Transmutation Program Final Report. V. Preconceptual Designs and Costs of Partitioning Facilities and Shipping Casks, Appendix 1*, ORNL/Sub-79/31056/1/A1; *Appendix 2*, ORNL/Sub-79/31056/1/A2; *Appendix 3*, ORNL/Sub-79/31056/1/A3; *Appendix 4*, ORNL/Sub-79/31056/1/A4 (all appendixes to ORNL/TM-6985) (June 1980).
107. Patch, K. D.,²³ R. P. Hart,²³ W. A. Schumacher,²³ G. L. Haag, D. W. Holladay, and D. F. Green, *Analysis of Barium Hydroxide and Calcium Hydroxide Slurry Carbonation Reactors*, ORNL/MIT-300 (May 1980).
108. Peterson, B. E.,⁴² D. S. Joy, P. E. Johnson,⁴² and E. L. Hillsman,⁴² "Predicting Transportation Routes for Radioactive Wastes: U.S. Railroad System," presented at the American Nuclear Society Topical Meeting on Waste Management, Tucson, Ariz., Feb. 23-26, 1981.
109. Pope, R. B.,⁹⁸ G. C. Allen,⁹⁸ S. H. Sutherland,⁹⁸ D. S. Joy, and L. B. Shappert, "Projected Spent Fuel and Waste Shipping Cask Requirements in the United States," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980.
110. Pope, R. B.,⁹⁸ R. D. Seagren, L. B. Shappert, and H. R. Yoshimura,⁹⁸ "Relative Response of Type B Packages to Regulatory and Other Impact Test Environments," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980.
111. Raines, G. E.,⁹⁹ L. D. Rickertsen,⁹⁹ H. C. Claiborne, J. L. McElroy,²⁸ and R. W. Lynch,⁹⁸ "Development of Reference Conditions for Geologic Repositories for Nuclear Waste in the U.S.A.," presented at the Annual Meeting of the Materials Research Society, Boston, Nov. 16-20, 1980.
112. Rickertsen, L. D.,⁹⁹ and H. C. Claiborne, *Expected Environments for a Defense High-Level Waste Repository in Salt*, ORNL/TM-7597 (March 1981).
113. Rogers, G. C., J. G. Moore, and M. T. Morgan, *Scrubbing of Iodine from Gas Streams with Mercuric Nitrate—Conversion of Mercuric Iodate Product to Barium Iodate for Fixation in Concrete*, ORNL/TM-7102 (June 1980).
114. Scheitlin, F. M., and W. D. Bond, *Recovery of Plutonium from HEPA Filters by Ce(IV)-Promoted Dissolution of PuO_2 and Recycle of the Cerium Promoter*, ORNL/TM-6802 (May 1980).
115. Science Applications, Inc., *Actinide Partitioning-Transmutation Program Final Report. VI. Short-Term Risk Analysis of Reprocessing, Refabrication, and Transportation (Summary)*, ORNL/TM-6986 (June 1980).
116. Science Applications, Inc., *Appendix. Actinide Partitioning-Transmutation Program Final Report. VI. Short-Term Risk Analysis of Reprocessing, Refabrication, and Transportation*, ORNL/Sub-80/31048/1 (June 1980).

---

⁹⁸. Sandia Laboratories, Albuquerque, N.M.

⁹⁹. Office of Nuclear Waste Isolation, Battelle Columbus Laboratories, Columbus, Ohio.

117. Seagren, R. D., B. J. Hudson,⁹⁴ and D. S. Joy, "Motor Carrier Routing Using the Compu.Map Program," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980.
118. Seagren, R. D., L. B. Shappert, H. R. Yeshimura,⁹⁸ R. M. Jefferson,⁹⁸ and R. B. Pope,⁹⁸ "Relative Response of Type-B Packagings to Regulatory and Other Impact Test Environments," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980.
119. Seagren, R. D., C. D. Watson, and W. D. Box, *The Chemical Technology Division Quality Assurance Program for Radioactive Material Packagings*, ORNL/TM-6471 (September 1979).
120. Shaffer, J. H., and J. O. Blomeke, *Hydraulic Fracturing as a Method for the Disposal of Volatile Radioactive Wastes*, ORNL/TM-6931 (August 1979).
121. Shaffer, J. H., W. E. Shockley, and C. W. Greene, *The Solubilities of Krypton and Xenon at Infinite Dilution in Dichlorodifluoromethane*, ORNL/TM-6652 (January 1980).
122. Shappert, L. B., and D. S. Joy, "The Effects of AFR Storage Location on Spent-Fuel Transportation," presented at the Annual Meeting of the American Nuclear Society, Atlanta, June 3-8, 1979; published in *Trans. Am. Nucl. Soc.* 32, 415-16 (1979).
123. Stinton, D. P.,⁷ J. S. Vavruska,⁵⁶ P. Angelini,⁷ and W. J. Lackey,⁷ "Sintering Behavior and Characterization of Sol-Gel Produced Synroc," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 26-30, 1980.
124. Tedder, D. W.,⁸⁸ "GENEX - A Generalized Solvent Extraction Code," presented at the Actinide Separations Symposium, Pacific Chemical Conference of the American Chemical Society, Honolulu, Apr. 1-6, 1979.
125. Tedder, D. W.,⁸⁸ "Partitioning and Transmutation," Sect. 3.9 of *Draft Environmental Impact Statement for the Management of Commercially Generated Radioactive Wastes*, DOE/EIS 0046-D (April 1979).
126. Tedder, D. W.,⁸⁸ B. C. Finney, and J. O. Blomeke, "Actinide Partitioning Flowsheets," presented at the Actinide Separations Symposium, Pacific Chemical Conference of the American Chemical Society, Honolulu, Apr. 1-6, 1979; published in ACS Symposium Series 117, 1980.
127. Tedder, D. W.,⁸⁸ B. C. Finney, and J. O. Blomeke, "Methods for Separating Actinides from Reprocessing and Refabrication Plant Wastes," presented at the Annual Meeting of the Materials Research Society, Boston, Nov. 27-30, 1979; published in *Scientific Basis for Nuclear Waste Management*, vol. 2, C. J. M. Northrup, Jr., Ed., Plenum Press, New York, 1980, pp. 893-900.
128. Tedder, D. W.,⁸⁸ B. C. Finney, and J. O. Blomeke, *Actinide Partitioning-Transmutation Program Final Report. II. Partitioning Processes for LWR Fuel Reprocessing and Refabrication Plant Wastes*, ORNL/TM-6982 (June 1980).
129. Tennery, V. J.,⁷ E. S. Bomar,⁷ W. D. Bond, L. E. Morse, H. R. Meyer,⁶⁰ J. E. Till,⁶¹ and M. G. Yalcintas,⁶⁰ *Summary of the Radiological Assessment of the Fuel Cycle for a Thorium-Uranium Carbide Fueled Fast Breeder Reactor*, ORNL/TM-6953 (January 1980).
130. Tennery, V. J.,⁷ E. S. Bomar,⁷ W. D. Bond, L. E. Morse, H. R. Meyer,⁶⁰ J. E. Till,⁶¹ and M. G. Yalcintas,⁶⁰ "Environmental Impact of Radioactive Releases from Recycle of Thorium-Based Fuel Using Current Containment Technology," presented at the Second U.S. Department of Energy Symposium on Environmental Control, Reston, Va., March 1980; published in the *Proceedings*, CONF-800334/2, pp. 1-18.
131. Vavruska, J. S.,⁵⁶ "Gel Sphere Technology Applied to Synroc Waste Forms," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 26-30, 1980.

132. Wachter, J. W., and A. G. Croff, *Actinide Partitioning-Transmutation Program Final Report. III. Transmutation Studies*, ORNL/TM-6983 (July 1980).
133. Watson, C. D., B. J. Hudson,⁹⁴ D. A. Keith,³³ M. K. Preston, Jr.,³³ P. N. McCreery,¹⁰⁰ W. Knox,¹⁰⁰ E. M. Easterling,¹⁰⁰ A. S. Lamprey,¹⁰⁰ and G. Wiedemann,¹⁰⁰ *Fleet Servicing Facilities for Servicing, Maintaining and Testing Rail and Truck Radioactive Waste Transport Systems: Functional Requirements, Technical Design Concepts and Options, Cost Estimates, and Comparisons*, ORNL/Sub-79/13866/1 (May 1980).
134. Watson, C. D., B. J. Hudson,⁹⁴ D. A. Keith,³³ M. K. Preston, Jr.,³³ P. N. McCreery,¹⁰⁰ W. Knox,¹⁰⁰ E. M. Easterling,¹⁰⁰ A. S. Lamprey,¹⁰⁰ and G. Wiedemann,¹⁰⁰ "Fleet Servicing Facilities for Testing and Maintaining Radioactive Waste Rail and Truck Transport Systems," presented at the Sixth International Symposium on Packaging and Transportation of Radioactive Materials (PATRAM '80), Berlin, Federal Republic of Germany, Nov. 10-14, 1980.
135. Weeren, H. O., "Waste Disposal by Shale Fracturing at ORNL," presented at the International Symposium on the Underground Disposal of Radioactive Wastes sponsored by the International Atomic Energy Agency/Nuclear Energy Agency, Otaniemi (Helsinki), Finland, July 2-6, 1979.
136. Weeren, H. O., *Shale Fracturing Injections at Oak Ridge National Laboratory—1977-1979 Series*, ORNL/TM-7421 (September 1980).
137. Weeren, H. O., and T. S. Mackey,⁹⁰ *Waste Sludge Resuspension and Transfer--Development Program*, ORNL/TM-7125 (February 1980).
138. Weeren, H. O., and J. J. Perona, *A Preliminary Engineering and Economic Analysis of the Fixation of High-Level Radioactive Wastes in Concrete*, ORNL/TM-6863 (July 1979).

H. Patents

1. Holladay, D. W., and G. L. Haag, "Methods of Immobilizing Carbon Dioxide from Gas Streams," U.S. Patent 4,162,298 (July 24, 1979).
2. McDowell, W. J., "Process for Removal of Particulates from Coal-Derived Liquids," U.S. Patent 4,191,628 (1980).
3. Seeley, F. G., and W. J. McDowell, "Process for Recovery of Metal Values from Fly Ash," U.S. Patent 4,252,777 (Feb. 24, 1981).
4. Seeley, F. G., and W. J. McDowell, "Salt-Soda-Sinter Process for Recovery of Metal Values from Fly Ash," U.S. Patent 4,254,088 (Mar. 3, 1981).

I. Progress Reports

1. Bianco, R. E., and A. L. Lotts,²⁰ *High-Level Waste Program Progress Report for October 1, 1978, through March 31, 1979*, ORNL/TM-6866 (May 1979).
2. Bianco, R. E., and A. L. Lotts,²⁰ *High-Level Waste Program Progress Report for July 1, 1979, through September 30, 1979*, ORNL/TM-7118 (November 1979).
3. Bianco, R. E., and A. L. Lotts,²⁰ *High-Level Waste Program Progress Report for October 1, 1979, through December 31, 1979*, ORNL/TM-7253 (March 1980).
4. Bianco, R. E., and A. L. Lotts,²⁰ *High-Level Waste Program Progress Report for January 1, 1980, through March 31, 1980*, ORNL/TM-7371 (May 1980).

---

¹⁰⁰. Allied-General Nuclear Services, Barnwell, S.C.

5. Blanco, R. E., and A. L. Lotts,²⁰ *High-Level Waste Program Progress Report for April 1, 1980, through June 30, 1980*, ORNL/TM-7476 (August 1980).
6. Malinauskas, A. P., R. A. Lorenz, J. L. Collins, M. F. Osborne, and R. L. Towns, *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period October-December 1978*, ORNL/NUREG/TM-308 (NUREG/CR-0682) (April 1979).
7. Malinauskas, A. P., R. A. Lorenz, J. L. Collins, M. F. Osborne, and R. L. Towns, *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period January-March 1979*, ORNL/NUREG/TM-332 (August 1979).
8. Malinauskas, A. P., R. A. Lorenz, J. L. Collins, M. F. Osborne, and R. L. Towns, *Quarterly Progress Report on Fission Product Behavior in LWRs for the Period April-June 1979*, ORNL/NUREG/TM-348 (October 1979).
9. Moore, J. G., M. T. Morgan, E. W. McDaniel, H. B. Greene, and G. A. West, *Cement Technology for Plugging Boreholes in Radioactive Waste Repository Sites: Progress Report for the Period October 1, 1977, to September 30, 1978*, ORNL-5524 (August 1979).
10. Moore, J. G., M. T. Morgan, E. W. McDaniel, H. B. Greene, and G. A. West, *Cement Technology for Plugging Boreholes in Radioactive Waste Repository Sites: Progress Report for the Period October 1, 1978, to September 30, 1979*, ORNL-5610 (August 1980).
11. Pitt, W. W., Jr., and J. E. Mrochek, *Advanced Technology Section Semiannual Progress Report for the Period September 1, 1976, to March 31, 1977. Volume 1: Biotechnology and Environmental Programs*, ORNL/TM-6012/V1 (July 1979).
12. Pitt, W. W., Jr., and J. E. Mrochek, *Advanced Technology Section Semiannual Progress Report for the Period April 1, 1977, to September 30, 1977. Volume 1: Biotechnology and Environmental Programs*, ORNL/TM-6328/V1 (June 1980).
13. Scheitlin, F. M., and W. D. Bond, *Removal of Hazardous Radionuclides from Uranium Ore and/or Mill Tailings: Progress Report for the Period October 1, 1978, to September 30, 1979*, ORNL/TM-7065 (January 1980).
14. Watson, J. S., and S. D. Clinton, *Advanced Technology Section Semiannual Progress Report for the Period April 1, 1977, to September 30, 1977. Vol. 2. Engineering Science Programs*, ORNL/TM-6328/V2 (November 1979).
15. Watson, J. S., and S. D. Clinton, *Advanced Technology Section Semiannual Progress Report for the Period October 1, 1977, to March 31, 1978. Vol. 2. Engineering Science Programs*, ORNL/TM-6377/V2 (July 1980).
16. Watson, J. S., and S. D. Clinton, *Advanced Technology Section Semiannual Progress Report for the Period April 1, 1978, to September 30, 1978. Vol. 2. Engineering Science Programs*, ORNL/TM-6647/V2 (July 1980).

J. Special Isotope Production and Separations

1. Bigelow, J. E., B. L. Corbett, L. J. King, S. C. McGuire, and T. M. Sims, "Production of Transplutonium Elements in the High-Flux Isotope Reactor (HFIR)," presented at the Symposium on Industrial-Scale Production-Separation-Recovery of Transplutonium Elements, Second Chemical Congress of the North American Continent, Las Vegas, Aug. 24-29, 1980.
2. Caudill, H. H., H. R. Gwinn, and L. E. McBride, "Anodic Oxidation--An Improved Technique in the Chemical Recovery and Refinement of Isotopic Thallium," presented at the Ninth World Conference of the International Nuclear Target Development Society, Gatlinburg, Tenn., Oct. 12-16, 1980.

3. Davis, W. C., *Stable Isotope Customer List and Summary of Shipments—FY 1978*, ORNL/TM-6710 (May 1979).
4. Davis, W. C., *Stable Isotope Customer List and Summary of Shipments—FY 1979*, ORNL/TM-7214 (April 1980).
5. Ferguson, D. E., "Production of Einsteinium and Fermium in Reactors," pp. 35–38 in *Proceedings of the Symposium Commemorating the 25th Anniversary of Elements 99 and 100*, LBL-7701, CONF-780134 (April 1979).
6. Howell, G. D., Jr., W. A. Bell, Jr., A. M. Veach, H. H. Caudill, and E. Newman, "Technique for the Collection of EM-Enriched Rare Gases," presented at the Tenth International Conference on Electromagnetic Isotope Separators and Techniques Related to Their Applications, Zinal, Valais, Switzerland, Sept. 1–6, 1980.
7. McGuire, S. C., "Influence of Nuclide Cross Sections and Decay Data on Heavy Element Evolution in the High Flux Isotope Reactor (HFIR)," presented at the Weekly Department of Physics Seminar, Atlanta University, Atlanta, Nov. 14, 1980.
8. Newman, E., "The Electromagnetic Isotope Separation Program at the Oak Ridge National Laboratory," *Nucl. Instrum. Methods* 167, 81–84 (1979).
9. Newman, E., "The Oak Ridge Isotope Enrichment Program—A Status Report," presented at the Ninth World Conference of the International Nuclear Target Development Society, Gatlinburg, Tenn., Oct. 12–16, 1980.
10. Tracy, J. G., "Targets Produced in Mass Separators," presented at the Sixth Conference on the Application of Accelerators in Research and Industry, North Texas State University, Denton, Nov. 3–5, 1980; published in the *Proceedings*.
11. Tracy, J. G., and E. Newman, "Research Samples of the Titanium Isotopes," *International Nuclear Target Development Society Newsletter*, J. Van Audenhove, Ed., CBNM, Geel, Belgium, issue 2 (1980).
12. Young, J. P.,¹³ R. G. Haïre,⁶ J. R. Peterson,⁶ D. D. Ensor,¹⁰¹ and R. L. Fellows, "Chemical Consequences of Radioactive Decay. I. Study of Californium-249 Ingrowth into Crystalline Berkelium-249 Tribromide: A New Crystalline Phase of Californium Tribromide," *Inorg. Chem.* 19, 2209–12 (1980).

K. Theses

1. Krichinsky, A. M., "NUMATH: A Nuclear Material Holdup Estimator for Unit Operations and Chemical Processes," M. S. Thesis, The University of Tennessee, Knoxville, March 1981.

L. Three Mile Island Support Studies

1. Brooksbank, R. E., "Postaccident Cleanup of Radioactivity at Three Mile Island," presented at Oglethorpe University Science Seminar, Atlanta, Dec. 3, 1979; also to the Health Physics and Radiation Protection Group of Oak Ridge Associated Universities, Oak Ridge, Tenn., Apr. 3, 1980.
2. Brooksbank, R. E., "Cleanup Problems at TMI," presented to the National Academy of Sciences Committee on Radioactive Waste Management, Washington, D.C., May 20, 1980.

---

¹⁰¹. University guest from Tennessee Technological University, Cookeville.

3. Brooksbank, R. E., "Recent Chemical Engineering Requirements as the Result of TMI Onsite Experience," presented at the National Meeting of the American Institute of Chemical Engineers, Portland, Oreg., Aug. 17-20, 1980.
4. Brooksbank, R. E., "Cleanup Problems at TMI—What Has Been Learned," presented at the Annual Meeting of the Materials Research Society, Boston, Nov. 16-20, 1980.
5. Brooksbank, R. E., W. J. Armento, D. O. Campbell, E. D. Collins, F. E. Harrington, L. J. King, J. R. Parrott, Sr., W. A. Shannon, and J. W. Snider, *Postaccident Cleanup of Radioactivity at the Three Mile Island Nuclear Power Station*, ORNL/TM-7081 (February 1980).
6. Brooksbank, R. E., D. O. Campbell, J. W. Snider, and O. O. Yarbrow, "Emergency Actions Concerned with Effluent Control at TMI," presented at the Annual Meeting of the American Nuclear Society, Las Vegas, June 8-13, 1980.
7. Brooksbank, R. E., and L. J. King (compilers), *Involvement of the ORNL Chemical Technology Division in Contaminated Air and Water Handling at the Three Mile Island Nuclear Power Station*, ORNL/TM-7044 (August 1979).
8. Campbell, D. O., E. D. Collins, L. J. King, and J. B. Knauer, *Evaluation of the Submerged Demineralizer System and Flowsheet for Decontamination of High-Activity-Level Water at the Three Mile Island Unit 2 Nuclear Power Station*, ORNL/TM-7448 (July 1980).
9. Collins, E. D., J. E. Bigelow, D. O. Campbell, L. J. King, and J. B. Knauer, "Flowsheet Development Studies for the Decontamination of High-Activity-Level Water at Three Mile Island Unit 2," presented at the National Meeting of the American Institute of Chemical Engineers, Portland, Oreg., Aug. 17-20, 1980.
10. Snider, J. W., "Evaporators for High-Level Waste," presented at the Reactor Operations Workshop sponsored by the American Nuclear Society, Arlington Heights, Ill., July 10-11, 1979.
11. Snider, J. W., R. W. Glass, and T. J. Burns,⁵⁴ "Transportable Equipment for Treating Liquid Radwaste Streams Generated from a Damaged Light Water Reactor," presented at the National Meeting of the American Institute of Chemical Engineers, Portland, Oreg., Aug. 17-20, 1980.

SEMINARS

1979

April 4	<i>Gel Sphere Process Development</i>	
	Status of Process for UO_2 Spheres	J. M. Begovich
	Engineering-Scale Preparation of UO_2	J. S. Vavruska
April 11	Status of Process for $(Th,U)O_2$ Spheres	R. D. Spence
	Solvent Extraction Kinetics: Thorium	D. E. Horner
	Solvent Extraction Kinetics: Zirconium	J. C. Mailen
April 18	<i>Preliminary Results from the Solvent Extraction Test Facility</i>	
	Description of Flowsheets Being Tested	D. J. Crouse
	Equipment Operation and Test Results	E. D. Collins
April 25	Waste Treatment for Coal Conversion Processes	J. A. Klein
	Ozonation of Aqueous Wastes	J. I. Brand
	Catalytic Oxidation of Tail Gas	C. H. Brown
May 2	A Portable Fluorescence Monitor for PNA Contamination on Work Surfaces	D. D. Schuresko
	Characterization of Liquids from Coal Conversion Processes	M. S. Denton
	Deashing Solvent Refined Coal with Molten Salts	W. F. Kinard
May 9	Chemistry of the Recovery of Minerals from Fly Ash	F. G. Seeley
	Engineering Aspects of Resource Recovery from Fly Ash	R. M. Canon
	HTGR Head-End Studies	C. L. Fitzgerald
May 16	Thorex Solvent Extraction Studies	C. E. Lamb
	SEPHIS-MOD4: Solvent Extraction Process Modeling	A. D. Mitchell
	<i>Status of Developments on Voloxidation</i>	
May 23	Hot-Cell Test Results	V. C. A. Vaughen
	Operation of the Pilot-Scale Voloxidizer	T. D. Welch
	Heat Transfer Studies in Rotary Kilns	B. B. Spencer

May 30	<i>Radioactive Materials Transport Program</i>	
	Spent Fuel Receiving and Cask Handling Facility Simulation	J. R. Marshall
	Radioactive Transport Regulations and Information Retrieval	M. M. Heiskell
June 6	Spent Fuel Logistics Program Update	D. S. Joy
	Thermodynamics of the (ThC + UC) Stainless Steel Interface	E. C. Beahm
	Fission Product Release from LWR Fuel under Accident Conditions	J. L. Collins
June 13	Physical Properties of Reactor Fuel Aerosols	G. W. Parker
	Energy Conservation with Anaerobic Bioreactors in Wastewater Treatment	R. K. Genung
	Microbial Cells: Biosorbents for Removal of Uranium from Aqueous Process Streams	G. W. Strandberg
June 27	Tritium Removal by Voloxidation	R. G. Stacy
	Tritium Removal by Nonoxidative Heating	D. O. Campbell
	Engineering Aspects of Voloxidation	M. E. Whatley
July 11	Removal of $^{14}\text{CO}_2$ from Off-Gas with Packed Columns or Fluidized Beds of Hydrated Barium Hydroxide	G. L. Haag
	Removal and Recovery of ^{230}Th and ^{226}Ra from Uranium Mill Tailings	F. M. Scheitlin
	Coal Liquids Flow System	E. L. Youngblood
July 18	Physical Properties of Coal Liquids	G. E. Oswald
	Coal Slurry Preheater	J. R. Thurgood
July 25	<i>Status of the Conceptual Design of the Hot Experimental Facility</i>	
	Overview	M. J. Feldman
	Facility Options Studies	J. R. White
August 1	Detailed Concepts	J. N. Herndon
	Thermal Conductivity of Coal	P. R. Westmoreland
	Partial Dissolution of Coal	T. M. Gilliam
August 8	Engineering Safeguards Program	W. J. Armento
August 29	Removal of Hazardous Radionuclides from Uranium Ore and/or Tailings	F. M. Scheitlin
	Removal of $^{14}\text{CO}_2$ from Reprocessing Off-Gases with the Hydrated Barium Hydroxide Sorption System	G. L. Haag

September 26	Activities and Systems in Buildings 3541 and 3503	D. F. Williams C. C. Haws
October 3	Fuel-Grade Methanol Synthesis	M. S. Edwards
October 10	Chemical Behavior of Fission Products Released from Highly Irradiated LWR Fuel (under Accident Conditions)	J. L. Collins
	Status of Experiments on Characterizing Sodium Oxide Aerosols	G. W. Parker
October 24	Iodine Adsorption on Low Alloy Steel	M. F. Osborne
	Fuel, Silicon Carbide, and Fission Product Interactions in HTGR Particles	R. L. Pearson
October 31	Potential Costs of Environmental Control Processes for Low-Btu Coal Gasification Plants	S. P. N. Singh

**DIVISIONAL PERSON-POWER AND FINANCIAL SUMMARY
FY 1981**

	Funding (in thousands)	Person-years
DOE PROGRAMS		
Coal and Petroleum	\$ 1,750	8.0
Breeder	2,440	16.0
Converter	3,103	26.0
Remedial Action	1,323	7.0
Commercial Waste Management	1,146	11.5
Defense Waste Management	2,168	17.5
Spent Fuel Storage	197	1.5
Solar Energy	175	1.5
ANFLOW	552	4.0
CEUSP and ²³⁵ U Dispensing Facility	6,120	15.0
Fuel Cycle Workshop	20	
Environmental R&D	1,293	12.0
Basic Energy Sciences	7,638	78.0
TOTAL DOE PROGRAMS	\$27,925	198.0
WORK FOR OTHERS PROGRAMS		
Nuclear Regulatory Commission	\$ 1,777	11.5
SRC and H-Coal	1,115	6.5
National Lead Company of Ohio	559	0.5
Office of Nuclear Waste Isolation	365	2.0
Lawrence Livermore Laboratory	148	1.0
Tennessee Valley Authority	142	1.0
Miscellaneous	862	6.5
TOTAL WORK FOR OTHERS	\$ 4,968	29.0
TOTAL FINANCIAL PLANS	\$32,893	227.0

CHEMICAL TECHNOLOGY DIVISION AUTHOR INDEX

- Alexander, C. W., G.1, G.2, G.23, G.39, G.40
 Andrews, R. L., D.18
 Arcuri, E. J., B.2, B.3, B.4, B.5, B.91, B.93, B.96
 Armento, W. J., E.1, E.2, E.3, E.4, L.5
 Arnold, S. L., B.103, B.104
 Bahner, C. T., A.1
 Barker, P. E., A.2, D.62
 Beahm, E. C., A.3, A.4, A.9, C.51
 Begovich, J. M., A.5, A.6, A.16, A.21, A.22, C.23, C.53, E.28
 Bell, J. T., A.101
 Bell, W. A., J.6
 Benker, D. E., A.7, A.26, A.29, A.30, C.7
 Besmann, T. M., A.8, A.9, A.10, A.11, A.12, A.13, A.14, A.65, E.5, E.6
 Bigelow, J. E., A.15, A.60, A.61, A.62, C.7, J.1, L.9
 Blanco, R. E., G.78, I.1, I.2, I.3, I.4, I.5
 Blomeke, J. O., G.4, G.5, G.6, G.7, G.8, G.9, G.10, G.11, G.23, G.43, G.120, G.126, G.127, G.128
 Bond, W. D., C.25, C.26, C.37, C.44, C.64, G.12, G.13, G.14, G.114, G.129, G.130, I.13
 Bostick, W. D., B.6, B.7, B.8, B.9, B.10, B.11, B.12, B.13, B.18, B.21
 Box, W. D., E.2, F.1, F.2, F.3, F.4, G.119
 Brand, J. I., B.14, B.15, B.28, B.66, D.19, D.20, D.21
 Brooksbank, R. E., E.2, E.3, G.15, G.16, G.17, G.18, G.19, L.1, L.2, L.3, L.4, L.5, L.6, L.7
 Brown, C. H., A.17, D.10, D.41, D.61, D.62, D.63
 Brunton, G. D., A.18, G.20, G.21, G.22
 Burtis, C. A., B.9, B.13, B.16, B.17, B.18, B.19
 Buxton, S. R., C.58
 Campbell, D. O., A.19, C.2, C.3, C.4, C.58, F.5, F.6, L.5, L.6, L.8, L.9
 Campbell, G. D., A.54, A.56
 Canon, R. M., A.20, A.21, A.22, A.23, A.24, A.25, A.46, A.51, E.28
 Carter, W. L., C.5, C.24, E.8, G.23
 Case, G. N., A.73, A.74
 Caudill, H. H., J.2, J.6
 Chattin, F. R., A.7, A.26, A.30, C.7
 Chilton, J. M., G.24
 Claiborne, H. C., G.3, G.25, G.26, G.27, G.28, G.29, G.111, G.112
 Clark, W. E., G.30, G.79
 Clinton, S. D., A.27, A.28, A.44, A.98, A.99, E.28, I.14, I.15, I.16
 Cochran, H. D., A.18, D.1, D.2, D.3, D.4, D.5, D.6, D.7, D.8, D.24, D.32, D.61, D.62, D.63
 Collins, E. D., A.7, A.15, A.29, A.30, A.60, A.61, A.62, C.7, L.5, L.8, L.9
 Collins, J. L., F.7, F.13, F.14, F.15, F.16, F.17, F.18, F.22, F.23, I.6, I.7, I.8
 Compere, E. L., G.31, G.32, G.33, G.51, G.52, G.76
 Creek, G. E., F.26, F.27
 Croff, A. G., G.1, G.2, G.8, G.9, G.10, G.11, G.35, G.36, G.37, G.38, G.39, G.40, G.41, G.42, G.43, G.46, G.132
 Davis, W., Jr., C.8, C.13, C.27, F.8
 Davis, W. C., J.3, J.4
 Denton, M. S., B.10, B.11, B.23, B.24, B.25, B.26, B.27, B.28, B.71, E.22
 Devaney, H. E., G.96, G.97
 Dickerson, L. S., D.9, D.18, D.54, D.55, D.56
 Dinsmore, S. R., B.10, B.11, B.25, B.26, B.27, B.28, B.71
 Dyer, F. F., C.10
 Egan, B. Z., A.34, A.35, A.54, A.56, A.89, B.29, B.30
 Eubanks, J. P., B.48
 Felker, L. K., A.36, A.87, A.89
 Fellows, R. L., A.37, A.38, A.83, J.12
 Ferguson, D. E., J.5
 Finney, B. C., G.11, G.23, G.43, G.44, G.45, G.126, G.127, G.128
 Fisher, J. F., D.44, D.46, D.47, D.48, D.57
 Fisher, P. W., A.39, A.104, D.64, E.9, E.10, E.11, E.12, E.13, E.14
 Fitzgerald, C. L., C.14, C.29
 Forsberg, C. W., C.47, G.47, G.48, G.49, G.50
 Frederick, E. J., G.53

- Friedman, H. A., A.40, A.41, A.42, A.43, A.101, A.102, C.65
 Gambill, W. R., D.10, D.17, D.41, D.44, D.60
 Genung, R. K., B.1, B.21, B.31, B.32, B.33, B.34, B.50, B.54, B.56, B.73, B.74, B.80
 Gibson, M. R., D.18
 Gibson, S. M., B.3
 Gilliam, T. M., A.45, A.46, D.10, D.19, D.20, D.21, D.41, E.27
 Godbee, H. W., G.33, G.51, G.52, G.53, G.54, G.55, G.73, G.74, G.75, G.76
 Goeller, H. E., A.55, E.15, E.16, E.17, E.18, E.19
 Goode, J. H., C.15, C.16, C.17, C.18, C.19, C.67
 Green, D. F., G.107
 Greenbaum, E., B.35, B.36, B.37, B.38, B.39, B.40, B.41, B.42, B.43, B.44, B.45, B.46, B.47, B.48
 Greene, C. W., G.121
 Greene, H. B., G.88, G.94, I.9, I.10
 Grimes, W. R., A.18, A.52, C.12, E.30
 Gwinn, H. R., J.2
 Haag, G. L., C.47, G.57, G.58, G.107, H.1
 Haas, P. A., C.22, C.23, C.53, C.55, C.56, C.60, C.61, C.68
 Hamner, R. L., C.63
 Hancher, C. W., B.50, B.51, B.52, B.53, B.69, B.75, B.76, B.80, B.91
 Harrington, F. E., E.7, L.5
 Haws, C. C., C.73
 Hewitt, J. D., J.22
 Hightower, J. I., A.18, D.23, D.32, E.20, E.21
 Holladay, D. W., C.47, G.107, H.1
 Horner, D. E., A.47, A.48, A.49, A.50, A.67, A.68, C.40, C.41, C.42
 Howell, G. D., J.6
 Howerton, W. B., C.6, C.59, G.30, G.79
 Irvine, A. R., D.57
 Jenks, G. H., G.62, G.63, G.64
 Jennings, H. L., B.56
 Johnson, P. J., D.25
 Jolley, R. L., B.20, B.22, B.57, B.58, B.59, B.60, B.61, B.62, B.63, B.64, B.65, B.70, B.71, B.77, B.81
 Jones, G., Jr., A.51, B.77, B.78
 Joy, D. S., G.52, G.65, G.66, G.67, G.68, G.69, G.70, G.71, G.85, G.108, G.109, G.117, G.122
 Jurgensen, M. C., F.3
 Katz, S., C.25, C.26, G.72, G.95
 Kelmers, A. D., A.23, A.34, A.35, A.53, A.54, A.55, A.56, A.87, A.89, C.8, C.27, D.26
 Kibbey, A. H., G.52, G.54, G.55, G.73, G.74, G.75, G.76
 King, L. J., A.15, A.59, A.60, A.61, A.62, C.7, J.1, L.5, L.7, L.8, L.9
 Kirkland, O. L., F.15
 Kitts, F. G., E.2, E.4
 Klein, J. A., B.14, B.15, B.66, B.67, B.68, B.72
 Knauer, J. B., A.7, C.28, L.8, L.9
 Krichinsky, A. M., E.2, E.3, E.24, K.1
 Lamb, C. E., C.29, C.30
 Lee, D. D., B.69, B.79
 Lee, N. E., B.21, B.22, B.63, B.64, B.65, B.70, B.71, B.81
 Leuze, R. E., C.31, C.32, C.33, C.34, C.35, C.36, C.37, G.13, G.14
 Lin, K. H., E.7, G.79
 Lindemer, T. B., A.11, A.12, A.13, A.14, A.63, A.64, A.65, A.95, C.38, C.49, C.50, C.51, C.63, E.23, E.29
 Lloyd, M. H., A.26, A.37, A.38, C.7, C.28, C.39, C.62
 Lomenick, T. F., G.80
 Lorenz, R. A., F.7, F.11, F.12, F.13, F.14, F.15, F.16, F.17, F.18, F.21, F.22, F.23, I.6, I.7, I.8
 Mailen, J. C., A.47, A.48, A.49, A.50, A.66, A.67, A.68, C.40, C.41, C.42, C.43, C.57, C.58, C.59
 Malinauskas, A. P., F.5, F.6, F.7, F.13, F.14, F.15, F.16, F.17, F.18, F.19, F.20, F.21, F.22, F.23, F.24, I.6, I.7, I.8
 McBride, L. E., J.2
 McDaniel, E. W., G.56, G.87, G.88, G.89, G.90, G.94, G.96, I.9, I.10
 McDowell, W. J., A.1, A.23, A.24, A.57, A.58, A.69, A.70, A.71, A.72, A.73, A.74, A.75, A.76, A.77, A.78, A.85, A.88, A.89, A.91, A.92, A.105, H.2, H.3, H.4
 McGuire, S. C., E.25, G.71, J.1, J.7
 McTaggart, D. R., C.54
 McWhirter, D. A., B.48, B.94, B.101
 Mitchell, A. D., C.21, C.30, C.45, C.46
 Moore, J. G., G.52, G.88, G.90, G.91, G.92, G.93, G.94, G.95, G.96, G.97, G.113, I.9, I.10
 Morgan, M. T., G.94, G.95, G.98, G.99, G.100, G.113, I.9, I.10
 Morse, L. E., C.44, C.64, G.129, G.130
 Mrochek, J. E., B.8, B.18, B.19, B.21, E.22, I.11, I.12
 Newman, E., G.95, G.96, G.101, J.6, J.8, J.9, J.11
 Norman, R. E., C.1
 Notz, K. J., C.1, C.47
 Osborne, M. F., C.48, C.72, F.7, F.16, F.17, F.18, I.6, I.7, I.8
 Osborne, M. M., A.43, C.65

- Oswald, G. E., D.31, D.32, D.33, D.49, D.61,
 D.62, D.63
 Overton, J. B., B.12, B.13
 Pachler, J. H., C.28, G.97
 Parker, G. W., F.9, F.10, F.25, F.26, F.27
 Parrott, J. R., Jr., B.94, B.95, B.100, B.101
 Parrott, J. R., Sr., E.2, G.102, G.103, G.104, L.5
 Pattison, W. L., C.4
 Patton, B. D., B.53, B.75, B.76
 Pearson, R. L., A.79, A.80, C.49, C.50, C.51
 Perona, J. J., A.27, A.31, A.32, A.33, A.44, E.26,
 G.34, G.138
 Pitt, W. W., Jr., B.32, B.33, B.34, B.52, B.53,
 B.64, B.65, B.71, B.73, B.74, B.75, B.76, B.77,
 d.78, B.79, E.22, I.11, I.12
 Proops, C. A., F.24
 Pruett, D. J., A.81, A.82
 Rivera, A. L., B.1, B.56
 Robinson, S. M., A.68, C.40
 Roddy, J. W., A.84, A.85
 Rodgers, B. R., D.10, D.20, D.21, D.22, D.27,
 D.34, D.35, D.36, D.37, D.38, D.39, D.40, D.41
 Rogers, G. C., G.95, G.96, G.97, G.113
 Ross, R. G., A.7, A.26, A.30, C.7
 Ryon, A. D., C.73, C.52, C.53
 Salmon, R., D.11, D.14, D.29, D.42, D.43, D.44,
 D.48, D.50, D.51, D.57
 Sams, T. L., D.45
 Savage, H. C., C.7
 Scheitlin, F. M., C.37, G.14, G.114, I.13
 Scott, C. D., A.86, B.30, B.55, B.69, B.86, B.87,
 B.88, B.89, B.90, B.91, B.92, B.93, B.96
 Seagren, R. D., F.1, F.2, F.3, F.4, G.70, G.110,
 G.117, G.118, G.119
 Secley, F. G., A.23, A.24, A.25, A.34, A.35, A.36,
 A.54, A.56, A.87, A.88, A.89, H.3, H.4
 Shannon, R. J., C.30
 Shannon, W. A., L.5
 Shappert, L. B., F.1, F.2, F.3, F.4, G.109, G.110,
 G.118, G.122
 Shockley, W. E., G.121
 Shoun, R. R., A.1, A.58, A.75, A.76, A.77, A.90,
 A.91, A.92
 Shumate, S. E., II, E.3, B.4, B.5, B.76, B.93, B.94,
 B.95, B.96, B.99, B.100, B.101
 Singh, S. P. N., D.25, D.46, D.47, D.48, D.57
 Sisson, W. G., A.5, A.6, A.22
 Snider, J. W., L.5, L.6, L.10, L.11
 Spence, R. D., A.93, A.94, C.55, C.56, C.61
 Stacy, R. G., C.15, C.16, C.17, C.18, C.19, F.8
 Stewart, M. G., C.28
 Strandberg, G. W., B.94, B.95, B.97, B.98, B.99,
 B.100, B.101
 Sutton, A. L., C.13, F.27
 Talbot, J. B., A.96, A.97, A.98, A.99, A.104
 Tallent, O. K., C.42, C.57, C.58, C.59
 Thompson, J. E., B.22, B.63, B.64, B.65, B.71,
 B.81
 Toth, L. M., A.41, A.42, A.43, A.100, A.101,
 A.102, C.43, C.65
 Towns, R. L., F.15, F.16, I.6, I.7, I.8
 Tracy, J. G., J.10, J.11
 Ulrich, W. C., D.11, D.12, D.24, D.50, D.51, D.57
 Vaughn, V. C. A., C.14, C.17, C.18, C.19, C.29,
 C.30, C.66, C.67
 Veach, A. M., J.6
 Vondra, B. L., C.24, C.69, C.76
 Walker, J. F., B.50, B.80
 Watson, C. D., F.2, F.3, F.4, G.119, G.133, G.134
 Watson, J. S., A.18, A.23, A.24, A.25, A.28, A.39,
 A.44, A.52, A.103, A.104, E.9, E.11, E.12, E.13,
 E.14, E.26, I.14, I.15, I.16
 Weaver, B., A.92
 Weeren, H. O., G.89, G.90, G.135, G.136, G.137,
 G.138
 West, G. A., F.8, G.94, G.99, G.100, I.9, I.10
 Westmoreland, P. R., D.16, D.52, D.53, D.54,
 D.55, D.56, D.61, D.62, D.63
 Wham, R. M., D.30, D.43, D.57, D.58, D.59
 Whatley, S. K., C.59
 Wichner, R. P., C.10, C.11, C.70, C.71, C.72
 Wiggins, J. T., A.7, A.26
 Williams, D. F., C.73
 Woodward, J., B.48, B.102, B.103, B.104
 Wymer, R. G., C.24, C.74, C.75, C.76, E.31, E.32,
 E.33
 Youngblood, E. L., D.31, D.32, D.33, D.49, D.61,
 D.62, D.63

JUL 1, 1981