MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0383096 9

ORNL-5295
cy. 3

Chemical Technology DIVISION

Annual Progress Report

PERIOD ENDING MARCH 31, 1977

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.
UCN-7969
(3 3-67)

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy $5.00; Microfiche $3.00

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Energy Research and Development Administration/United States Nuclear Regulatory Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL-5295
Dist. Category UC-10

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION
ANNUAL PROGRESS REPORT
for Period Ending March 31, 1977

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

Date Published: October 1977

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0383096 9

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-3314	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

Preface

This progress report is a summary of the research and development efforts conducted in the Chemical Technology Division during the period April 1, 1976–March 31, 1977. Further information regarding work in the various programs can be obtained from the topical reports and journal articles cited in the references.

Contents

1. ADVANCED FUEL RECYCLE AND ALTERNATE FUEL CYCLE PROGRAMS 1

2. HTGR FUEL RECYCLE DEVELOPMENT PROGRAM 2

3. MOLTEN-SALT REACTOR PROGRAM 3

4. HTGR TECHNOLOGY PROGRAM 4

5. WASTE MANAGEMENT 5
   - 5.1 Partitioning and Transmutation 5
   - 5.2 Removal and Segregation of Radioactive Nuclides and Nitrate from Liquid Waste Streams 6
   - 5.3 Removal of Organic Contaminants and Tritium from Fuel Reprocessing Effluent Streams 6
   - 5.4 Fixation of Wastes in Concretes 7
   - 5.5 Updating of the ORIGEN Computer Code 8
   - 5.6 Projections of Radioactive Wastes from the Nuclear Fuel Cycle 8

6. TRANSURANIUM-ELEMENT PROCESSING 10
   - 6.1 TRU Operations 10
   - 6.2 Special Projects 11

7. ISOTOPIC SEPARATIONS 13
   - 7.1 Stable Isotope Separations 13
   - 7.2 Separator Research and Development 14

8. COAL CONVERSION PROCESS DEVELOPMENT 15
   - 8.1 Coal Hydrocarbonization and Residue Carbonization 15
   - 8.2 Engineering Support for In Situ Gasification Process Development 17
   - 8.3 Solid-Liquid Separations Technology 18
   - 8.4 Coal-Solvent-Hydrogen Mixing 19
   - 8.5 Pressurized Carbonization of Consol Synthetic Fuel Residue 20

9. COAL CONVERSION ENGINEERING STUDIES AND PROGRAM ANALYSIS 22
   - 9.1 Technical and Economic Evaluation of the Synthoil Process 22
   - 9.2 Engineering Evaluation of a Commercial-Scale Hydrocarbonization Process 23
   - 9.3 Survey of Coal Conversion Industrial Equipment Capabilities 24

9.4 Process Modeling 25
9.5 Technical Support Activities 25
9.6 Program Analysis Studies 26
9.7 In Situ Coal Gasification Studies 27

10. SEPARATIONS CHEMISTRY 30
10.1 New Separations Agents 30
10.2 Separation of Radium and Other Radionuclides from Uranium Ores and Leached Tailings 31
10.3 Separation of Alpha Emitters from Fuel Reprocessing Waste 31
10.4 Resource Recovery 32
10.5 Waste Stream Processing Studies 33
10.6 Ash Removal from Solvent Refined Coal 33
10.7 Physical Separations 34
10.8 Distribution Equilibria 35

11. BIOMEDICAL TECHNOLOGY 36
11.1 Advanced Analytical Techniques 36
11.2 Development of the Centrifugal Fast Analyzer 37

12. ENVIRONMENTAL STUDIES 40
12.1 Environmental Monitoring 40
12.2 Pollutant Identification 40
12.3 Environmental Effects of Antifoulants 43
12.4 Chemical Effects of Disinfectants 43
12.5 Assessment of Environmental Control Technology for Coal Conversion Processes 45

13. BIOENGINEERING TECHNOLOGY 47
13.1 Bioengineering Research 47
13.2 Bioprocess Development and Demonstration 47

14. PREPARATION OF UO_2 49
14.1 Recovery of ^{233}U from Waste UO_2 and Scrap UO_2-ThO_2 Pellets 49
14.2 ^{233}U Purification Systems 49
14.3 Conversion of ^{233}U from Nitrate Solution to Ceramic-Grade Dioxide Powder 49

15. ACTINIDE OXIDES, NITRIDES, AND CARBIDES 50
15.1 Thermodynamics of the U-C-O System 50
15.2 Transition Metal–U-C Phase Equilibria 50

16. CHEMICAL ENGINEERING RESEARCH 52
16.1 Three-Phase Fluidized-Bed Reacting System 52
16.2 Continuous Chromatography 53
16.3 Hydraulic Cyclone Studies 54

16.4 Mass Transfer Studies Using Stirred, Nondispersing Water-Mercury Contactors 55
16.5 Adiabatic Combustion of Graphite 55
16.6 Packed Columns for Cryogenic Sorption Systems 57
16.7 Agglomeration Studies 57
16.8 Hydrogen Permeation-Oxidation Studies 58

17. FUSION ENERGY STUDIES 60
17.1 Cryosorption Vacuum Pumping for Fusion Reactors 60
17.2 Tritium Sorption Studies 61
17.3 Tritium Recovery from Irradiated Lithium-Aluminum and Sintered Aluminum Product Alloys 63
17.4 Sorption Pumping of Gases by Deep Beds of Sorbents 64
17.5 TNS Support Studies 64

18. IODINE STUDIES 66

19. REACTOR SAFETY RESEARCH 67
19.1 Fission Product Release from LWR Fuel 67
19.2 Fission Product Transport Tests 68
19.3 Transient Release from LMFBR Fuel 69

20. NUCLEAR REGULATORY COMMISSION PROGRAMS 73
20.1 Development of "As Low As Reasonably Achievable" (ALARA) Guides for the Nuclear Fuel Cycle . . 73
20.2 Safety Review of Nuclear Facilities 73
20.3 Safeguards Studies 73
20.4 Environmental Statement on Plutonium Utilization (GESMO) 74
20.5 Waste Management Parametric Studies 74
20.6 Waste Management Generic Studies 75

21. MISCELLANEOUS PROGRAMS 76
21.1 Studies Involving Tests of Obsolete Casks 76
21.2 Cement and Concrete Technology 76
21.3 Conversion of Consolidated Edison Uranium from a Nitrate Solution to UO_3 77
21.4 Nuclear Safety Assistance 77
21.5 Assistance to the Office of Waste Isolation 78

PUBLICATIONS, SPEECHES, AND SEMINARS 79

1. Advanced Fuel Recycle and Alternate Fuel Cycle Programs

The work concerned with the development of aqueous processes for LMFBR fuels is not reported here, in compliance with regulations which stipulate that such information must be distributed solely under the category UC-79 – Liquid-Metal Fast Breeder Reactors. Recently, this program was renamed the Advanced Fuel Recycle Program. The results of our studies have been summarized in a series of quarterly progress reports, the most recent of which is the *LMFBR Fuel Reprocessing Program Progress Report for Period January 1 to March 31, 1977,* ORNL/TM-5879 (May 1977). Work is also documented in topical reports.

The associated efforts in LWR fuel reprocessing are being reported in a separate series of quarterly progress reports, the most recent of which is the *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period January 1 to March 31, 1977,* ORNL/TM-5864 (May 1977). Some major new emphasis in this program has recently been given to examination of reprocessing by other than conventional Purex flowsheets. In this context, the program name has been changed to the Alternate Fuel Cycle Program.

2. HTGR Fuel Recycle Development Program

The Chemical Technology Division's activities under the HTGR Fuel Recycle Development Program, which is under the Thorium Utilization Program, include development work in head-end reprocessing and fuel fabrication, off-gas cleanup, waste treatment, and cost studies. This work is not reported here this year, in compliance with regulations which stipulate that such information must be distributed solely under the category UC-77 – Gas-Cooled Reactor Technology. The work has been reported separately in monthly GCR documents and in annual reports, the most recent of which is the *Gas-Cooled Reactor Programs, Thorium Utilization Program Progress Report for the Period July 1, 1975, through September 30, 1976,* ORNL-5266 (in press).

3. Molten-Salt Reactor Program

The Chemical Technology Division's activities under the Molten-Salt Reactor Program were concerned with the development of on-site fuel processing methods for molten-salt breeder reactors and with the production of the various molten-salt mixtures required for the MSR Program's research and development activities. These activities are not discussed here this year, in compliance with regulations which stipulate that such information be distributed solely under the category UC-76 – Molten-Salt Reactor Technology. Although the MSR Program was terminated by ERDA on September 30, 1976, several topical reports describing MSR fuel processing development have been issued.[1–3]

1. R. B. Lindauer and J. R. Hightower, Jr., *Conceptual Design of a Continuous Fluorinator Experimental Facility (CFEF)*, ORNL/TM-5253 (July 1976).
2. C. H. Brown, Jr., J. R. Hightower, Jr., and J. A. Klein, *Measurement of Mass Transfer Coefficients in a Mechanically Agitated, Nondispersing Contactor Operating with a Molten Mixture of LiF-BeF_2-ThF_4 and Molten Bismuth*, ORNL-5143 (November 1976).
3. H. C. Savage and J. R. Hightower, Jr., *Engineering Tests of the Metal Transfer Process for Extraction of Rare-Earth Fission Products from a Molten-Salt Breeder Reactor Fuel Salt*, ORNL-5176 (February 1977).

4. HTGR Technology Program

The work relative to HTGR technology studies is not reported here this year, in compliance with regulations which stipulate that such information must be distributed solely under the category UC-77 – Gas-Cooled Reactor Technology. The results of our investigations have been reported in monthly GCR documents and in annual reports, the most recent of which is the *Gas-Cooled Reactor Programs, HTGR Base Technology Program Progress Report for the Period July 1, 1975, through December 31, 1976*, ORNL-5274 (in press).

5. Waste Management

5.1 PARTITIONING AND TRANSMUTATION

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

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

The experimental tasks that have been undertaken to verify partitioning flowsheets and the installations that have responsibility for each are: (1) Purex process modifications (ORNL); (2) actinide recovery from solids, for example, HEPA filters (Mound Laboratory); (3) americium and curium recovery with oxalate precipitation and ion exchange (OPIX), Talspeak, and cation exchange chromatography (ORNL); (4) americium and curium recovery using bidentate extractants (Allied Chemical Corporation, Idaho Chemical Programs); (5) americium and curium recovery using inorganic ion exchange media (Sandia Laboratories); (6) recovery alternatives applicable to waste streams (Argonne National Laboratory); (7) actinide recovery from combustible wastes (Rocky Flats Plant); (8) secondary waste processing and recycle studies (Rocky Flats Plant); and (9) radiation effects on reagents (Brookhaven National Laboratory).

The computational tasks undertaken as a part of this program include: (1) fabrication studies for fuels containing waste actinides (ORNL); (2) LMFBR transmutation studies (ORNL); (3) thermal reactor transmutation studies (Savannah River Laboratory); (4) analysis of the fuel cycle impacts of P-T (ORNL); (5) risk/benefit analysis of P-T (not presently active); (6) detailed analysis of the costs of P-T (not presently active); and (7) programmatic analysis, coordination, and evaluation (ORNL).

During this report period, experimental work was initiated at the various sites. Tentative partitioning flowsheets have been developed for LWR fuel reprocessing and mixed-oxide fuel fabrication plants. These flowsheets will form the basis for the experimental studies. Computer simulations of transmutation in fuel cycles with constant or variable waste actinide generation rates were completed. Preparation of reports containing the partitioning flowsheets and the results of the computer simulations of P-T fuel cycles was initiated.[1,2]

One of the ORNL staff members attended the First Technical Meeting on the Nuclear Transmutation of

1. J. O. Blomeke and D. W. Tedder (compilers), *Actinide Partitioning and Transmutation Program Progress Report for the Period Oct. 1, 1976, to Mar. 31, 1977,* ORNL/TM-5888 (May 1977).

2. A. G. Croff, D. W. Tedder, J. P. Drago, and J. O. Blomeke, *On the Evaluation of Partitioning-Transmutation as a Waste Management Concept,* ORNL/TM-5808 (to be published).

Actinides and presented papers on the fuel cycle impacts of P-T and on actinide partitioning problems.[3,4] Most western European countries and Japan are actively studying P-T as a waste management alternative. The most comprehensive study is the combined European effort at the EURATOM Joint Research Center in Ispra, Italy.[5] The scope of this program is commensurate with that of the ERDA-ORNL program.

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

A three-task study, which began in FY 1977, is concerned with the removal of certain radionuclides and other chemicals (e.g., NH_4^+, NO_3^-) from aqueous process and effluent streams associated with the nuclear fuel cycle and with special situations in ERDA facilities.

Task I: Iodine Removal from Waste Vapor or Condensate Streams

The goal of this work is the development of a practicable process for removing the small amount of residual iodine from the vapor and/or condensate streams produced from the evaporation of solvent extraction waste streams. Major emphasis is on the utilization of activated charcoal, macroreticular resins, or Iodox technology. Several types of activated charcoal and macroreticular resin were tested for iodine sorption efficiency. A feed solution with an iodine concentration of 200 μg/liter (^{131}I tracer) was pumped through a parallel array of 25-mm-diam by 250-mm-deep beds of candidate sorbents, and breakthrough curves were determined for each sorbent. Of the sorbents tested, the activated carbons have been more effective than the resins.

Task II: Biological Denitrification

Nitrate-bearing aqueous waste streams emanate from many operations in the nuclear fuel cycle and in special ERDA facilities. In situations where recovery is not feasible, reduction of nitrate to nitrogen gas appears to be the only acceptable long-range solution. In cooperation with the Environmental Sciences Division at ORNL and the Development Division at the Y-12 Plant, efforts have been focused on the development of microbiological denitrification processes using either a continuous-flow stirred tank reactor (CSTR) or a tapered fluidized-bed bioreactor (TFBBR). Applied microbiological studies have determined that the bacteria are highly tolerant to radiation (10^4 R/hr) and reasonably tolerant to high sodium (1.5 *N*) and nitrate (8.0 g/liter) concentrations. Process development studies have shown that a TFBBR with bacteria adhering to fluidized coal particles and operating at a space time (reactor volume/volumetric feed rate) of 9 min can achieve much higher nitrate conversion rates [40 g of N (NO_3^-) per day per liter] than a CSTR [0.7 g of N (NO_3^-) per day per liter] operating at its minimum space time of four days.

Task III: Isolation of Radioactive Metals, Using Microorganisms

Many operations in the nuclear fuel cycle and in special ERDA facilities produce aqueous waste streams that contain dissolved radioactive metals. One possible method for removing such metals would utilize the capability which certain microorganisms possess for isolation and concentration of metal species. Strontium isolation from solution by *Chlorella pyrenoidosa* (alga) in an illuminated columnar bioreactor has been studied for the case of a relatively high strontium concentration in the feed stream (10 mg/liter). Up to 70% of the strontium was isolated by the cells that attained strontium distribution coefficients as high as 2500. The distribution coefficient is defined as (Sr/g dry cells)/(Sr/g liquid).

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

This two-task study, which also began in FY 1977, is concerned with the removal of organic contaminants and tritium from aqueous process and effluent streams associated with the nuclear fuel cycle and with special situations in ERDA facilities.

Task I: Biological Removal of Organics

In all nuclear fuel cycle operations that utilize solvent extraction, aqueous process and effluent streams can be

3. A. G. Croff, "The Technological Impacts of Partitioning-Transmutation on the Nuclear Fuel Cycle," presented at the First Technical Meeting on the Nuclear Transmutation of Actinides, Ispra, Italy, Mar. 16–18, 1977.

4. R. E. Leuze, W. D. Bond, D. O. Campbell, and D. W. Tedder, "Conceptual Methods for Actinide Partitioning," presented at the First Technical Meeting on the Nuclear Transmutation of Actinides, Ispra, Italy, Mar. 16–18, 1977.

5. M. Bresesti and F. Girardi, "Research Programme of the EURATOM Joint Research Centre in the Field of Chemical Separation and Nuclear Transmutation of Actinides," presented at the First Technical Meeting on the Nuclear Transmutation of Actinides, Ispra, Italy, Mar. 16–18, 1977.

contaminated with dissolved and dispersed-phase organic compounds such as 2-, 3-, and 4-carbon alcohols; carboxylic acids; tri-, di-, and monobutyl phosphates; kerosene; and even vacuum-pump oil. Commercially available mixed cultures of organic degrading bacteria, Polybac and Petrobac, have been studied to determine their capability for degrading such organic species in CSTRs and TFBBRs. The CSTR studies serve as a baseline comparison for evaluation of other reactor types such as the TFBBR. Thus far, removal of 2-, 3-, and 4-carbon alcohols and carboxylic acids has been demonstrated; removal rates of 9 g day^{-1} $liter^{-1}$ have been achieved using the TFBBR operating at a space time of 7.5 min. These cultures have also attained total organic carbon reduction from 420 mg/liter to 15 mg/liter.

Task II. Biological Concentration of Tritium

Tritium contamination of aqueous streams is a problem encountered in nuclear reactor operation, fuel reprocessing, and fusion reactor technology. Investigation of possible microbial methods for hydrogen isotope fractionation was prompted by reports of a marine bacterium that evolved hydrogen gas depleted in deuterium. Isotope fractionation experiments have been carried out using the marine bacterium (Sisler's G4A strain) and a hydrogen-evolving, blue-green alga *Anabaena flos-aquae.* The cultures were grown in a medium containing tritiated water (2 mCi/liter), and the cellular uptake of tritium was determined. An isotopic differentiation was detected with both cultures, but an economic differentiation was not seen; that is, the cells discriminated against the heavier isotope, tritium. Typical distribution coefficents between the cell and the tritium-containing liquid medium on a total hydrogen basis were 0.12 for the G4A bacteria and 0.28 for the blue-green alga. The distribution coefficient is defined as (^{3}H/g of hydrogen dry cells)/(^{3}H/g of hydrogen medium).

5.4 FIXATION OF WASTES IN CONCRETES

The purpose of this program is to develop processes for solidifying all low-heat-generating liquid and solid wastes with cementitious mixtures. Laboratory studies are directed toward developing durable solids with specific properties and a maximum content of wastes. In general, the final product characteristics are low leachability, high thermal conductivity, high chemical and radiation stability, good mechanical properties, noncorrosiveness to the container, minimum volume, and minimum cost.

Current emphasis continues to be directed toward formulations and procedures for fixing the radioactive iodine (^{129}I, $t_{1/2}$ = 1.7 × 10^7 years) from concentrated nitric acid (the Iodox process) and mercuric nitrate scrubber solutions in concrete. Since the iodine products from these processes may be easily converted to the iodate,[6] the investigation has centered on incorporating the more insoluble iodates in type I portland cement. Leach studies are in progress using the modified IAEA leach method[7] to determine the rate of iodine release from these concretes as a function of several variables (e.g., curing time, iodine concentration, compound or cation used, admixtures, and irradiation).

As shown in Fig. 5.1, iodine leach rates are essentially diffusion controlled. The linear relationship indicates diffusion-type behavior. In this particular case, the specimen was type I portland cement containing 9.05 wt % iodine as barium iodate. The specimen was cured for 56 days before it was leached for 93 days with carbon dioxide–free distilled water. Using these values and an expression developed previously,[8] the modified effective diffusion coefficient for the iodine was 8 × 10^{-10} cm^2/sec.

Although many of the leach tests were not continued for sufficient time to calculate precise effective diffusivities, a number of trends were apparent:

1. There was no significant effect of curing time, at least up to 56 days (the extent of the tests), on the amount of iodine released.
2. Iodine concentrations up to 18 wt % appeared to have little effect on the leach rate. Higher concentrations (21 wt %) caused difficulty during sample preparation.
3. The release rate of iodine from concrete was greater when using mercury or calcium iodate than when using barium iodate.
4. The addition of 0.5 wt % fluosilicic acid or butyl stearate (0.9 wt % plus surface treatment with poly-

6. W. Davis, Jr., R. E. Blanco, B. C. Finney, G. S. Hill, R. E. Moore, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle – Reprocessing of High-Temperature Gas-Cooled Reactor Fuel Containing U-233 and Thorium,* ORNL/NUREG/TM-4 (May 1976).

7. J. G. Moore, *Development of Cementitious Grouts for the Incorporation of Radioactive Wastes. Part 2: Continuation of Cesium and Strontium Leach Studies,* ORNL-5142 (September 1976), pp. 6–7.

8. 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), pp. 41–49.

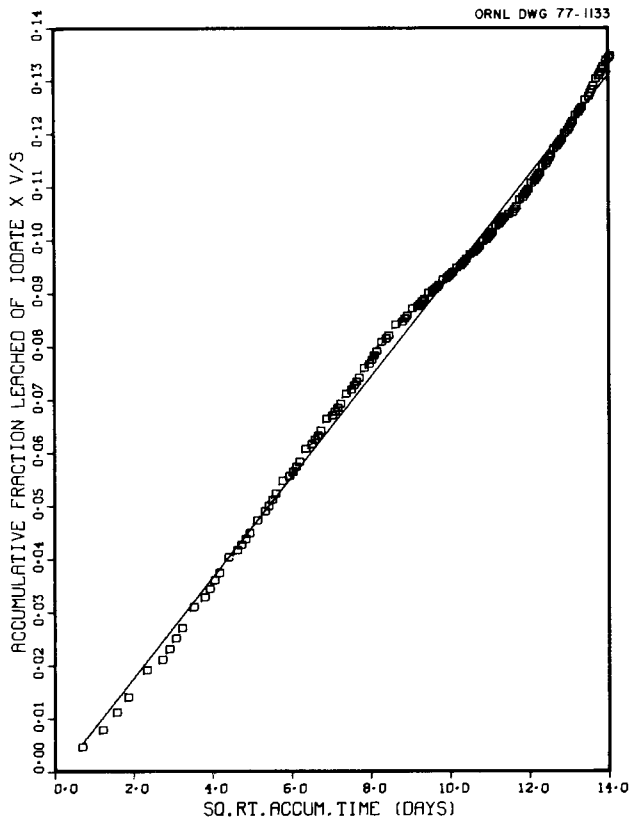

Fig. 5.1. Leachability of iodine into CO_2-free distilled water from type I portland cement containing 9.05 wt % iodine as barium iodate (water/cement ratio = 0.89; cured 56 days).

butene) to waterproof the specimens was not effective in controlling iodine release.

5. The addition of fly ash to the cement reduced the iodine leach rate.
6. Exposures up to 1.2×10^9 rads in a ^{60}Co source, equivalent to 4×10^4 years of self-exposure for a specimen containing 15 wt % ^{129}I, had little, if any, effect on the leachability of iodine from concrete. Test results also indicated that the amount of iodide formed from the iodate by self-irradiation would be insignificant.

5.5 UPDATING OF THE ORIGEN COMPUTER CODE

The effort to update the ORIGEN computer code and its associated data bases, which began during FY 1976, continued during this report period. The principal goal is to place the ORIGEN code and data bases on as firm a theoretical basis as possible. This involves modification of the original ORIGEN code to more accurately reflect the neutronic behavior of the actinides during irradiation. The result will be a program that can directly incorporate cross sections calculated by more sophisticated reactor physics codes. Traditionally, these cross sections were determined by arbitrarily adjusting cross sections so that the fuel discharge compositions calculated by ORIGEN agreed with a discharge composition calculated by a more sophisticated neutron physics code.

During this report period, (1) multigroup cross-section libraries were generated using existing cross-section compilations;[9–11] (2) one-dimensional neutron spectrum calculations and point depletion calculations for uranium-enriched PWRs and BWRs were completed; (3) decay and photon data were processed into an intermediate form for over 400 nuclides; and (4) the ORIGEN code was modified to correctly account for the effective, one-group cross sections generated by the spectrum and depletion calculations.

A by-product of the updated decay library will be a compilation of beta-particle end-point energies, intensities, and transition types for use in calculating bremmstrahlung radiation.

Future ORIGEN updating activities will include: (1) one-dimensional neutron spectrum and point-depletion calculations for plutonium-enriched PWRs and BWRs, one or more thorium cycle LWRs, one or more uranium-plutonium cycle LMFBRs, one or more uranium-thorium cycle LMFBRs, and other reactor types that may be required for future fuel cycle studies; (2) completion of the updated decay and photon libraries; (3) completion of a bremmstrahlung photon library; (4) calculation of radionuclide concentration guide values similar to those in 10 CFR 20 for certain ^{237}Np daughters to replace the default values used previously; and (5) documentation of the calculations and results of the ORIGEN update activities.

5.6 PROJECTIONS OF RADIOACTIVE WASTES FROM THE NUCLEAR FUEL CYCLE

To obtain waste management data based on more current power forecasts, new projections were made of the volumes and characteristics of wastes to be shipped and

9. ENDF/B-IV Fission Product Library Tapes 414–419 (December 1974); available from National Neutron Cross-Section Center, Brookhaven National Laboratory, Upton, N.Y.
10. R. W. Benjamin, V. D. Vandervelde, T. C. Gorrell, and F. J. McCrosson, *A Consistent Set of Transplutonium Multigroup Cross Sections*, DP-MS-74-61 (March 1975).
11. R. J. Howerton, *The Lawrence Livermore Laboratory Evaluated Nuclear Data Library (ENDL) Translated into the ENDF/B Format*, UCID-16727 (March 1975).

stored through the year 2000.[12] A recent forecast ("Mid-Case," August 1976) of nuclear power growth in the United States, developed by the ERDA Office of Assistant Administrator for Planning and Analysis, was used. Installed nuclear power capacities of 68.1, 251.8, and 510 GW(e) in the years 1980, 1990, and 2000, respectively, are forecast. In this plan, reprocessing is assumed to begin in 1981, and recycle of plutonium in LWR fuels starts in 1983. The ratio of PWRs to BWRs is 2:1. The fast breeder reactor is introduced commercially in 1995 and achieves 6% of the installed capacity in the year 2000.

A summary of the projections of 11 types of waste for the year 2000 is given in Table 5.1. Lower installed capacities and minor revisions in the waste generation rates account for the generally lower volumes and activity levels. Work is in progress on studies that include a "throwaway" fuel cycle, a fuel cycle based on recycling only uranium, and several proposed fast and thermal fuel cycles that may reduce the risk of nuclear weapons proliferation.

12. C. W. Kee, A. G. Croff, and J. O. Blomeke, *Updated Projections of Radioactive Wastes to Be Generated by the U.S. Nuclear Power Industry*, ORNL/TM-5427 (December 1976).

Table 5.1. Fuel cycle waste projected for the year 2000 (Mid-Case, August 1976)

Category	Annual generation (10^3 m^3)	Annual shipments[a]	Total inventory in the United States			
			Volume (10^3 m^3)	Activity (MCi)	Metric tons of actinides	Toxicity[b] (m^3 water)
High-level solidified waste	0.88	200[c]	10	72,000	700	2.4×10^{16}
Transuranium wastes						
Cladding hulls	0.8	450[c]	8.5	1,300	57	2.7×10^{13}
Intermediate-level solids	4	1,300[d]	38	22	0.3	6.7×10^{12}
Low-level wastes	12	410[c]	110	90	9.2	1.1×10^{12}
Nontransuranium wastes						
Noble gases	0.03	100[c,e]	0.32	620		
Iodine	0.013	47[d]	0.14	0.0036		6.0×10^{10}
Carbon-14				0.059		7.4×10^{7}
LWR tritium	65	4,100[d]	790	2.7		8.9×10^{8}
Fission product tritium	0.09	340[d]	1.0	41		1.4×10^{10}
Low-level solid	260	19,000[d]	2,900	4.6		5.5×10^{10}
Ore tailings	20,000		300,000	3.4	48,000	1.4×10^{13}

[a]High-level waste is solidified immediately and shipped ten years later; other wastes are shipped after one year.

[b]Volume required for dilution to RCG valves (Appendix B, Table II, of 10 CFR 20).

[c]Rail shipments.

[d]Truck shipments.

[e]Pressurized at 2000 psi (1.4×10^7 Pa).

6. Transuranium-Element Processing

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

6.1 TRU OPERATIONS

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

The purposes of this section are to report the production of transuranium materials and to describe recent changes in the processes and equipment that are being used in TRU. More detailed information is presented in a series of semiannual reports on production, status, and plans.[1,2]

Status

The primary role of TRU as a supplier of research materials is expected to remain at the present level. This involves the fabrication and irradiation of 20 to 25 HFIR targets per year containing a total of about 200 g of curium, and two chemical processing campaigns to recover transuranium elements from the irradiated targets. Each year, approximately 60 mg of ^{249}Bk, 600 mg of ^{252}Cf, 2 mg of ^{253}Es, and 1 pg of ^{257}Fm are produced, and about 75 product shipments are made. This level of production is considered to be about one-half of TRU's capacity for fabricating and processing HFIR targets. The present supply of curium feed material, all of which is contained in 55 HFIR targets, is sufficient to sustain operation at the present level for three to four years.

Production, Shipment, and Fabrication

During this report period, Campaigns 51 and 52 were made to process a total of 23 HFIR targets. The amounts of key isotopes in the campaign products are compared in Table 6.1 with the total amounts produced at TRU in previous operation (ten years).

Product finishing operations include: (1) final purification and packaging of the transcurium elements; (2) separation, purification, and packaging of daughter products (^{248}Cm, ^{249}Cf, and ^{253}Es); and (3) final purification of the americium-curium product followed by conversion of the actinide elements to the oxide form for use in HFIR targets. This year we purified the products from Campaigns 51 and 52, some of the products from previous campaigns, and various rework materials. The amounts of materials undergoing product finishing operations included 105 g of curium, 57 mg of ^{249}Bk, 781 mg of ^{252}Cf, 2.6 mg of ^{253}Es (mixed isotopes), and about 1 pg of ^{257}Fm. We also recovered and purified 336 μg of ^{253}Es (the daughter product of ^{253}Cf), 5.9 mg of ^{249}Cf (the daughter product of

1. L. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June 30, 1976,* ORNL-5216 (February 1977).

2. L. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1976,* ORNL-5305 (in press).

Table 6.1. Amounts of materials recovered in the Transuranium Processing Plant

Time period	April 1976 to March 1977	August 1966 to March 1976
Number of years	1	10
Number of target campaigns	2	34
Number of targets processed	23	405[a]
Amounts of key isotopes recovered		
^{242}Pu	0	141
^{243}Am	0.4	248
^{244}Cm	38	1745
^{249}Bk	52	305
^{252}Cf	499	2678
^{253}Es	2.6	10.3
^{257}Fm	0.9	6.7

[a]Number of targets includes 215 HFIR targets, 175 SRP slugs, and 21 SRP Pu-Al tubes.

^{249}Bk), and 180 mg of ^{248}Cm (the daughter product of ^{252}Cf).

Seventy-two product shipments were made this year to researchers throughout the country. Twenty-four targets were fabricated in order to recycle curium to the HFIR.

Processes and Equipment

The sequence of steps used to purify the californium products was modified this year to increase the yield of high-purity ^{253}Es. Previously, the high-purity ^{253}Es had been recovered at the same time that the californium was purified from ^{244}Cm. We added two ion exchange runs specifically to recover high-purity ^{253}Es. The yield was increased 50% because of a shorter recovery time for the short-lived ^{253}Es (half-life = 20 days).

No equipment changes were made this year. The condition of processing equipment at TRU is generally good and is continually maintained.

6.2 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 irradiation in the HFIR, and fabrication of neutron sources from ^{252}Cf.

Fabrication of Neutron Sources from ^{252}Cf

Some of the californium recovered at TRU is incorporated into neutron sources, which are loaned to researchers. Eight sources containing from 0.26 to 22 mg of ^{252}Cf were fabricated this year; seven of these were doubly encapsulated in type 304L stainless steel in a standard TRU configuration (NSD).[3] One source was prepared for the National Bureau of Standards in a special "point-source" configuration.[4]

Sources Returned

Neutron sources are returned to TRU when the projects for which they were requested are completed or when replacement sources are ordered to make up for decay of the ^{252}Cf. These sources are available for reassignment until the appropriate time for reprocessing to recover the ^{248}Cm daughter. During the report period, one source was returned and seven were reassigned. Seventy-nine sources are now on loan, and one source containing 500 μg of ^{252}Cf is available for reassignment.

Production of ^{250}Cf

Argonne National Laboratory requested that 0.5 mg of ^{250}Cf be produced from a portion of their share of the ^{249}Bk from Campaign 50. The calculated amount

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

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

of ^{249}Bk required for this project was 3.0 mg (about 53% of ANL's share). Nine aluminum pellets, each containing 0.33 mg of ^{249}Bk, were prepared by means of the resin-loading–magnesium-diluent technique.[5] Three HFIR rabbits, each containing three pellets, were fabricated and transferred to the HFIR for a 16-hr irradiation at a thermal flux of 3×10^{15} neutrons cm^{-2} sec^{-1}. After the irradiation, the rabbits were transferred to TRU for chemical processing. Approximately 0.54 mg of ^{250}Cf and 2.3 mg of residual ^{249}Bk were obtained. Isotopic composition of the ^{250}Cf product was: ^{249}Cf, 6.68%; ^{250}Cf, 87.18%; ^{251}Cf, 5.57%; and ^{252}Cf, 0.566%.

Production of ^{254}Cf

A special sample of californium enriched in the isotope ^{254}Cf was prepared at the request of Los Alamos Scientific Laboratory. The technique involved was to make use of the electron-capture decay (0.078% branching) of 39-hr ^{254m}Es produced by irradiation of ^{253}Es. Calculations showed that the optimum procedure was to irradiate the ^{253}Es for 32 hr in the HFIR hydraulic rabbit facility at a flux of 3×10^{15} neutrons cm^{-2} sec^{-1} and to process the rabbits as soon as possible to purify the mixed einsteinium isotopes. Subsequent milking of einsteinium daughters should yield a mixture of ^{250}Cf and ^{254}Cf. This procedure was tried first on an experimental basis to confirm the calculations and work out the optimum process scheduling.

A rabbit containing 5 μg of ^{253}Es was fabricated (by the resin-loading process) and irradiated. After a cooling time of 2 hr, the rabbit was chemically processed in the junior cave at TRU to isolate the irradiated einsteinium ($^{253-254m}$Es) from other actinide, fission product, and activation product elements. The isolated einsteinium was transferred to a glove box and processed at a micro level by means of ion exchange runs to separate the californium daughters. One run was made as soon as possible after the einsteinium was isolated, and a second run was made after a five-day interval. The isotopic compositions of the californium products, listed in the first two columns of Table 6.2, are similar to those predicted by calculation except that there was somewhat more ^{252}Cf than expected.

After this favorable experience, a new irradiation was scheduled so that the customer would be ready to handle the product when it became available. This time the isolated einsteinium was left in the junior cave five days until most of the ^{254m}Es had decayed. A similar series of microscale ion exchange runs produced a single californium product that contained 1.24 μg of ^{250}Cf and 245 pg of ^{254}Cf. The isotopic analysis of the californium product, Table 6.2, showed an unexplained contamination by ^{249}Cf.

5. L. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1973,* ORNL-4965 (November 1974).

Table 6.2. Isotopic composition of californium separated from irradiated ^{253}Es

	First separation (at. %)	Second separation (at. %)	Production run (at. %)
^{249}Cf	$\leq 6.0^a$	$\leq 6.4^a$	71.80
^{250}Cf	83.33	88.60	23.30
^{251}Cf	8.38	3.95	3.41
^{252}Cf	2.25	1.03	1.44
^{253}Cf	$\leq 0.05^b$	$<0.45^b$	0.037^b
^{254}Cf	0.032^c	0.054^c	0.0046^c
Total ^{254}Cf recovered	113 pg	79 pg	245 pg

[a]Determination is difficult due to residue of ^{249}Bk.

[b]Determination is difficult due to residue of ^{253}Es.

[c]These values were derived from the results of neutron counting, alpha counting, and mass spectrographic analyses.

7. 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 commercial applications such as analytical instrumentation, atomic clocks, lasers, and nuclear medicine. One hundred twenty-five new loans, amounting to approximately 5 kg of enriched stable isotopes, were made from the RMC during the past fiscal year. During the same period, 2954 sales of material were made whose value was more than $2 million.

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

7.1 Stable Isotope Separations

The separation facility has three basic types of electromagnetic separators available for the enrichment of the isotopes of stable elements. The 180° beta calutron is the primary production unit. The 255° inhomogeneous magnetic-field separator has approximately 50% greater dispersion than the beta calutron but slightly less ion output. The 180° sector separator is a high-resolution machine with only about one-tenth the output of the beta unit. At the beginning of the period covered by this report, 24 separators were in operation, but only eight are being utilized for isotopic separations. The machines are run on a 5-day, 24-hr basis. The majority of the work has been scheduled in the 180° beta calutrons.

Isotopic separations of eight elements were accomplished in either the beta calutron or the 255° inhomogeneous magnetic-field separator. Table 7.1 lists these elements along with the approximate percentage of total annual effort that was expended for each separation, the isotope of primary interest, the estimated quantity collected (based on monitored ion current), and the isotopic purity of the isotope of major interest. The listed nuclides are used for both basic physics research and as source material for the production of radiopharmaceuticals in nuclear medicine. The other isotopes that were collected concurrently are available for potential sales or RMC inventories. In addition to the production separations, a special effort was made to obtain greater than 1 g of both ^{107}Ag and ^{109}Ag with an isotopic purity of >99.9%. The best assays attained previously were 98.54% and 99.26% for ^{107}Ag and ^{109}Ag respectively. The special effort resulted in isotopic purities of 99.92% and 99.98% in a single pass, which is a decrease in the "other" isotope contamination level by more than a factor of 20.

The continuing efforts to improve operating techniques have been successful for some specific elements. Typical examples are the increased isotopic purities obtained in both the zinc and germanium series, which are the highest of any production separations to date.

During the year, 25 new lots of isotopes of seven elements were added to the inventory to fill sales or loan requirements. In addition, 52 samples that had

Table 7.1. Summary of stable isotope production

Element	Annual effort (%)	Major isotope	Quantity (mg)	Assay (%)
Chlorine	4.5	37	22,661	98
Tin	6.7	112	4,702	80
Germanium	7.3	73	25,008	94
Nickel	9.5	62	48,246	98
Selenium	18.7	74	5,205	75
Zinc	14.4	68	271,137	99
Iron	25.4	57	39,208	90
Calcium	13.5	46	36	*a*

[a]Separation incomplete.

been returned from RMC loans were reprocessed and returned to inventory.

Seventeen isotopically enriched, surface-deposited thin targets were prepared in the 180° sector separator. Typically, these targets were line-shape depositions that measured 1.5 mm by 1 cm on carbon substrates with thicknesses of 50 to 100 $\mu g/cm^2$. Deposition thicknesses, which ranged from 25 to 75 $\mu g/cm^2$, were produced by decelerating the ion beam to less than 200 eV. The surface-deposited targets have been prepared primarily from the rare-earth and platinum-metal groups. In addition to the surface-deposited targets, four ion implantation targets were made using the sector separator. These targets were made from the noble-gas group, and the host material was polycrystalline aluminum.

In an effort to further improve the quality of targets, the receiver for the 180° sector separator was modified to include an electrostatic beam deflection system. The deflection is such that the ions strike the target 1 cm above the normal straight-line path. This technique separates the desired ions from neutral particles which are sputtered from the tank walls and are then carried with the beam and deposited on the target. Although the contamination is very small, it can be extremely troublesome in some experiments.

7.2 Separator Research and Development

The temperature capability of the ion source used in rare-earth and heavy-element separations has been increased from 1000°C to >1500°C as part of an effort to improve source performance. In the past, chlorination of the oxide charge in situ with carbon tetrachloride appeared limited by temperature, since the ion output was still increasing at maximum temperature. The temperature of ~1000°C was limited by both the failure of heater insulators at >2 kW power input and by the heat lost from the massive system due to a minimal amount of thermal shielding. The changes that were made included substituting BN_3 for MgO as heater insulators, reducing the mass to be heated, and installing increased thermal shielding. Doubling the power input from 2 kW to 4 kW resulted in no heater failures during 100 hr of operation. Up to an applied power of 3.6 kW, ion output continued to increase. At this power input, the ion current for the $Dy_2O_3 + CCl_4$ feed maximized, principally because of the increase in system pressure generated by further heating. Attempts to directly vaporize elemental dysprosium to provide feed vapor failed. At a maximum heater power of 4 kW, the $^{164}Dy^+$ current was ~30 μA for the elemental charge as compared with 1.0 to 1.3 mA from the $Dy_2O_3 + CCl_4$ feed system. The charge container for the elemental dysprosium experiments showed that the dysprosium was evenly coated on the interior surfaces of the container as a glossy black deposit which oxidized on standing. Virtually no material vaporized out of the container.

These results, obtained thus far only with dysprosium, indicate the desirability of continuing to use the in situ chlorination method of introducing feed vapor into the arc region, and for this system an optimum temperature can now be achieved routinely.

A program to enhance the isotopic assay of the tellurium isotopes is virtually complete. Medical needs for ≥97% ^{122}Te containing ≤0.35% ^{123}Te prompted efforts to reduce the adverse effects of three major separation problems: high-voltage sparking, failure to attain adequate beam focus as determined by peak-to-valley current ratios, and cross-contamination by tellurium solids as flakes which fall into collector pockets. Sparking was largely a tellurium condensation problem, which was decreased by reduction in the surface area of the extraction electrodes. Beam focus was found to be closely correlated with system pressure and arc conditions. An increase in gas conductance to the pumps and the addition of calcium vapor pumping yielded adequate improvement in pressure. However, adjustment of arc conditions still remains a variable. The control of tellurium flakes has improved, but results are not always reproducible. The flakes are generated by that portion of the ion beam sputtered from the collector faceplate and pockets. The sputtered tellurium condenses on cooled metallic surfaces and then loosens and falls back onto the faceplate or into a collector pocket. The adopted solutions included the use of visors, screens, shutters, and special pocket designs.

The tellurium now collected and assayed shows >97% ^{122}Te and <0.3 ^{123}Te, which compares very favorably with material previously collected and assayed at 95% ^{122}Te and 0.41 to 0.48% ^{123}Te. These developmental results are adequate to meet current medical requirements, and steps are being taken to adapt developmental equipment and procedures into a forthcoming tellurium separation.

8. Coal Conversion Process Development

During this report period, the activities relative to coal conversion process development encompassed six areas: (1) continuing effort on the hydrocarbonization of coal, (2) a brief study of carbonization of H-Coal vacuum still residues in an atmospheric-pressure fluidized bed, (3) continuing effort on the pyrolysis of coal blocks to provide supporting data for in situ gasification, (4) the conclusion of research on improved methods of solid-liquid separations, (5) fundamental studies of mixing characteristics in models of hydroliquefaction reactors aimed at enhanced reactor performance, and (6) a brief investigation of the effects of elevated pressure on carbonization of Consol Synthetic Fuel (CSF) residues in a fluidized bed.

8.1 COAL HYDROCARBONIZATION AND RESIDUE CARBONIZATION

Fluidized-bed pyrolysis processes constitute an important part of coal conversion technology. In the hydrocarbonization process, coal is pyrolyzed under hydrogen pressure in a fluidized bed to produce hydrocarbon liquids, substitute natural gas, and solid char. The relative yields and the quality of these products may be controlled by adjustment of the operating conditions. Carbonization of residues from the vacuum distillation of H-Coal product may be carried out in a fluidized-bed reactor to recover volatile values. Significant progress in the experimental investigation of these two fluidized-bed pyrolysis processes is reported in this section. Related work on the pyrolysis of coal blocks and on the effect of pressure on the fluidized-bed pyrolysis of another coal liquefaction residue is reported in subsequent sections.

Bench-Scale Hydrocarbonization Experiment

Fourteen experiments have been completed in the 4-in.-ID fluidized-bed hydrocarbonization reactor. These experiments provided data on the hydrocarbonization of Wyodak coal, which is a low-sulfur, western, subbituminous C coal. Table 8.1 summarizes the operating conditions and most significant results from these experiments. Additional details on these results have been reported elsewhere.[1-4]

These results support three significant conclusions about the hydrocarbonization of this type of coal at a hydrogen pressure of 315 psia (2170 kPa), as summarized in Fig. 8.1:

1. The use of a recirculating fluidized bed containing an axial draft tube leads to generally higher oil yields than would be predicted from a published correlation[5] of yields from hydrocarbonization of subbituminous C coals. This probably results from the reduced vapor residence time in the reactor, which minimizes the loss of oil due to thermal cracking.
2. Oil yields generally increase with increasing temperature up to a point between 1000 and 1100°F (540 and 590°C), where the effects of thermal cracking begin to predominate. This result is in agreement with the predicted results.[5]
3. Oil yields are significantly reduced when coal has been exposed to the atmosphere during preparation. (In this study, oil yields were improved by the installation of a facility for the preparation of feed coal under an inert gas atmosphere.)

In addition to these results, the single experiment (run HC-6) conducted at 165 psia (1140 kPa) indicated, as

1. H. D. Cochran et al., p. 28 in *Coal Technology Program Annual Interim Report for Fiscal Year Ending June 30, 1976*, ORNL-5208 (October 1976).
2. H. D. Cochran et al., p. 7 in *Coal Technology Program Quarterly Progress Report for the Period Ending September 30, 1976*, ORNL-5224 (January 1977).
3. H. D. Cochran et al., p. 17 in *Coal Technology Program Quarterly Progress Report for the Period Ending December 31, 1976*, ORNL-5252 (April 1977).
4. H. D. Cochran et al., in *Coal Technology Program Quarterly Progress Report for the Period Ending March 31, 1977*, ORNL-5282 (in press).

Table 8.1. Summary of hydrocarbonization experiments with Wyoming subbituminous C coal (Wyodak coal)

	Hydrocarbonization run													
	HC-1[a]	HC-2[a]	HC-3[a]	HC-4[a]	HC-5[a]	HC-6[a]	HC-7[a]	HC-8	HC-9	HC-10	HC-11	HC-12	HC-13	HC-14
Uniformly or recirculating fluidized-bed reactor (UFB or RFB)	UFB	UFB	UFB	UFB	UFB	UFB	RFB	RFB	RFB	RFB	RFB	RFB	RFB	RFB
Bed temperature, °F	1075	1030	910	1000	965	1030	820	790	955	1050	1035	1025	905[b]	1070[c]
°C	580	555	490	540	520	555	440	420	515	565	555	550	485[b]	570[c]
Reactor pressure, psia	315	315	315	315	315	165	315	315	315	315	315	315	315	315
kPa	2170	2170	2170	2170	2170	1140	2170	2170	2170	2170	2170	2170	2170	2170
Coal feed														
Rate, as received, lb/hr	1.3	8.3	13.2	14.0	15.5	16.3	14.8	13.6	6.8	4.4	8.9	10.2	11.1	9.2
kg/hr	0.59	3.76	5.99	6.35	7.03	7.39	6.71	6.17	3.08	2.00	4.04	4.63	5.04	4.17
Elapsed time, hr	9.6	13.2	8.1	7.3	7.7	5.1	6.9	6.2	4.8	10.6	2.3	10.5	10.3	6.0
Hydrogen feed rate, scfm	6.48	4.86	4.42	4.71	4.55	2.28	6.90	10.04	10.34	10.28	10.21	10.21	10.23	10.23
10^{-4} std m^3/sec	30.58	22.94	20.86	22.23	21.47	10.76	32.56	47.29	48.80	48.52	48.18	48.18	48.28	48.28
Oil yield,[d] wt % of maf coal	8.7	10.3	11.2[e]	8.7	6.7	8.0	5.4	6.1	3.1[e]	15.3[e]	*f*	18.1	15.4	21.0
Carbon recovery, %														
In char[d]	51.5	51.3	69.9	65.1	63.2	66.2	73.3	71.4	68.6	56.4	*f*	61.3	70.3	58.4
In liquid[d]	11.7	14.3	14.4	12.8	8.4	10.1	6.7	6.0	5.5	15.6	*f*	17.8	13.4	18.5
In gas[d]	29	23.5	13.7	23.4	21.1	19.2	11.5	7.1	10.2	15.6	*f*	12.6	10.4	18.4
Overall[d]	92	89.0	98.0	101.2	92.6	95.5	91.5	84.5	84.3	87.6	*f*	91.7	94.1	95.3

[a]Coal used in runs HC-1 through HC-7 was exposed to air during grinding and sizing. Coal for subsequent runs was prepared in an inert atmosphere.

[b]Time-averaged temperature. Operated at 950°F (510°C) for 4.6 hr; lost bed during shutdown; restarted at 950°F (510°C) for 1.8 hr, temperature dropped to 900°F (480°C) for 0.8 hr, then 810°F (430°C) for 3.1 hr.

[c]Time-averaged temperature. Operated at 1100°F (595°C) for 6.0 hr; temperature dropped to ~1065°F (~575°C) for 1.1 hr, then 1010°F (545°C) for 1.5 hr.

[d]Preliminary calculations pending comprehensive evaluation of data.

[e]Oil yields in runs HC-3, HC-9, and HC-10 are questionable because of operational sampling and analysis problems. These data are omitted from Fig. 8.1.

[f]Steady-state period was too short to produce yield data.

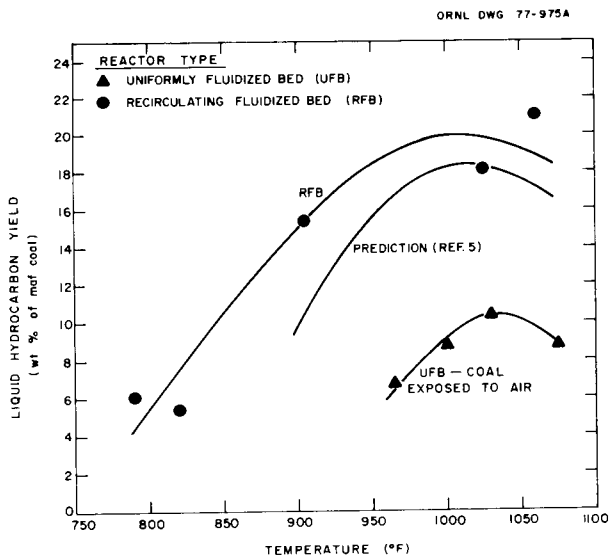

Fig. 8.1. Hydrocarbonization oil yields as a function of temperature and reactor type at 300 psig.

predicted,[5] that oil yields increase with increasing hydrogen partial pressure. These 14 experiments complete the campaign to establish baseline hydrocarbonization performance with subbituminous C coal. During the coming year, the bench-scale system will be used to establish operability and yield data with an agglomerating bituminous coal (Illinois No. 6).

Residue carbonization. A short study was conducted on the carbonization of vacuum distillation residues of H-Coal product in an atmospheric-pressure, fluidized-bed reactor. The emphasis in the first part of this study was centered on a review and an evaluation of the design and operation of the low-temperature carbonizer at the Consolidation Coal Company's pilot plant in Cresap, West Virginia. The results of this review[6] were used as the design basis for modification of an existing carbonizer to permit continuous operation with a recirculating fluidized bed containing an axial draft tube. Additional details have been presented elsewhere.[1–4]

Initial experiments focused on establishing technology for feeding and carbonizing the residue without excessive agglomeration or plugging. A total of 21 runs was performed, culminating in several satisfactory runs of more than 1-hr duration with minimal agglomeration. The project was terminated in late February by ERDA–Fossil Energy.

8.2 ENGINEERING SUPPORT FOR IN SITU GASIFICATION PROCESS DEVELOPMENT

It has been estimated that 6.3% of the U.S. coal reserves may be recovered by conventional deep-mining or strip-mining techniques. The approximately 2.8 trillion tons (~2.5 trillion metric tons) remaining comprise deposits that are either too thin or too deep to be obtained by these methods.[7,8] The energy contained in many such deposits, however, may be recovered by in situ gasification processes currently under development. The objective of the ORNL program supporting in situ or underground coal gasification development is the generation of data describing the pyrolysis of large coal blocks under expected process conditions. Such data will be used in the development of mathematical models which describe process reactions and help to interpret field test results.

Two-dimensional pyrolysis studies – western subbituminous coal. Two-dimensional effects during the pyrolysis of 16-cm cylindrical blocks of Wyodak subbituminous coal have been observed as functions of maximum pyrolysis temperature and heating rate. Details of block preparation, instrumentation, and product analysis have been described elsewhere;[9–13] however, the

5. J. M. Holmes et al., "Evaluation of Coal Carbonization Processes," pp. 40–46 in *Coal Processing Technology*, vol. 3, American Institute of Chemical Engineers, New York, 1977.

6. J. B. Gibson and F. T. Endelman, *Review and Evaluation of Residue Carbonization in the Consol Synthetic Fuel Process*, ORNL/TM-5346 (May 1976).

7. V. E. McKelvey, "Testimony at Hearings before Subcommittees of the Committee on Appropriations of the House of Representatives, Special Energy Research and Development Appropriation Bill for 1975," pp. 373–75 (Mar. 5, 1974).

8. R. C. Forrester III, "Recovery of Inaccessible Coal Reserves by In Situ Gasification," presented at the 11th Intersociety Energy Conversion Engineering Conference, Sahara Tahoe, State Line, Nev., Sept. 12–17, 1976.

9. R. C. Forrester III, "Comparison of One- and Two-dimensional Pyrolysis Results," presented at the Third Technical Working Group for UCG Laboratory Research, MERC, Morgantown, W.Va., June 3, 1976.

10. R. C. Forrester III, "Two-dimensional Studies of Coal Pyrolysis: Preliminary Results," in *Proceedings of the Second Annual Underground Coal Gasification Symposium, Morgantown, W.Va., Aug. 10–12, 1976*, MERC/SP-76/3.

11. R. C. Forrester III and P. R. Westmoreland, "Two-Dimensional Pyrolysis Effects During In Situ Coal Gasification: Preliminary Results," presented at the 51st Annual Fall Meeting of the SPE/AIME, New Orleans, La., Oct. 3–6, 1976.

12. R. C. Forrester III, "Status of 2-D Pyrolysis Studies at ORNL," presented at the Fourth Combined Technical Working Group for UCG Modeling and Laboratory Research, MERC, Morgantown, W.Va., Mar. 15, 1977.

13. P. R. Westmoreland and R. C. Forrester III, "Pyrolysis of Large Coal Blocks: Implications of Heat and Mass Transport Effects for In Situ Gasification," presented at the American Chemical Society Spring Meeting, New Orleans, La., Mar. 20–25, 1977.

essence of the experimental procedure consists in heating a test specimen at one of two heating rates chosen for these studies (3.0 or 0.3 C°/min). The temperature is permitted to increase to a specified maximum, T_m, where it is held constant until the thermocouples within the coal block have reached T_m and gas evolution has ceased. Most experiments have utilized as-received blocks and an argon cover gas at atmospheric pressure.

Results obtained thus far provide some qualitatively predictable information about two-dimensional pyrolysis (e.g., see ref. 11). Three distinct regions of gas production are observed: loss of adsorbed or loosely bound volatiles, the so-called[14] primary pyrolysis stage, and a secondary stage. As volatiles are evolved from within the block, reactions of tar and steam with the outer shell of hot char tend to increase gas production at higher temperatures beyond that observed when using powders. This is shown in Fig. 8.2, which describes total gas production per kilogram of coal as a function of pyrolysis temperature and heating rate. Determinations made by the Lawrence Livermore Laboratory using traditional powder pyrolysis techniques are included for comparison.[15–17]

Following the change in the composition of pyrolysis gases with time for a typical experiment, one observes that there is considerable evolution of methane and light hydrocarbons during the primary pyrolysis stage, but this diminishes rapidly as the temperature increases beyond 600°C. Production of CO and H_2 increases rapidly to account for nearly 90% of the total gas produced in latter stages of pyrolysis. Further tests utilizing dried coal blocks have shown that gas production from as-received blocks is two to three times greater than that observed from dried coal. These data support the conclusion that enhanced gas production is a result of the extensive steam-char reactions which take place as steam generated at the core of the block diffuses through a high-temperature char bank to the block surface.

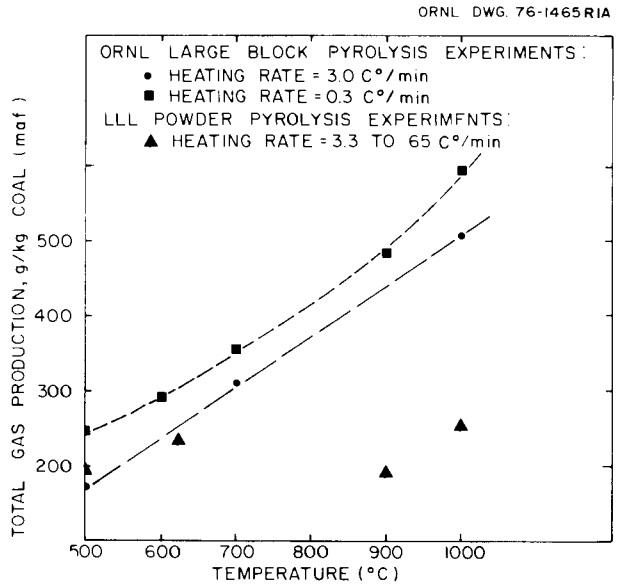

Fig. 8.2. Total gas production as a function of maximum pyrolysis temperature and heating rate.

Eastern bituminous coal. More recent tests have examined an eastern bituminous coal taken from the Pittsburgh seam near Pricetown, West Virginia. The chars produced in each of these tests have been singularly unreactive and have possessed considerable crushing strength, in direct contrast with the pyrophoric and extremely friable material produced by pyrolysis of western subbituminous coals. Large variations in the density and porosity of the chars are believed to be the result of tar cracking and subsequent carbon deposition which take place as tars evolved near the center of the block diffuse outward and encounter the hot char bank.

8.3 SOLID-LIQUID SEPARATIONS TECHNOLOGY

The first phase of this two-year project consisted in a review of the available literature and an evaluation of the current state of the art in solid-liquid separations for coal liquefaction processes. These results were summarized in a brief topical report[18] which also designated those techniques that would most likely meet the needs of commercial coal liquefaction processes for effective, economical separations.

14. B. K. Mazumdar and N. N. Chatterjee, "Mechanism of Coal Pyrolysis. III. Relation to Industrial Practice," *Fuel* **52**, 11 (January 1973).

15. A. B. Macknick, *Pyrolysis of Wyoming Subbituminous Coal,* Lawrence Livermore Laboratory, UCID-16710 (Mar. 10, 1975).

16. D. R. Stephens (ed.), *LLL In Situ Coal Gasification Program Quarterly Progress Report July through September 1975,* UCRL-50026-75-3 (Oct. 31, 1975).

17. J. H. Campbell, *Pyrolysis of Subbituminous Coal as It Relates to In Situ Gasification,* Lawrence Livermore Laboratory, UCRL-52035 (Mar. 11, 1976).

18. M. S. Edwards, B. R. Rodgers, and R. Salmon, *Coal Technology Program Supporting Research and Development on Separations Technology Phase I Report,* ORNL/TM-4801 (March 1975).

The second phase of the project consisted in a series of laboratory scouting experiments[19] that characterized the separations parameters of solids-containing streams produced by several coal conversion processes under development by ERDA. The purpose of these tests was to determine the separations techniques with the most potential and to supplement existing data that would help define the range of potentially viable separations processes.

The third phase, beginning in October 1975, has consisted in bench-scale development of a solvent agglomeration technique for improved solid-liquid separations.[20] The bench-scale unit, which was designed and fabricated on the basis of the previous studies, has been used to demonstrate the technical viability, limits of operability, preferred operating conditions, and preliminary economics of two proposed separations processes under realistic (filtration and settling) conditions.

This project has made the following significant contributions to coal conversion technology:[21–25]

1. Laboratory precoat filtrations have shown that the use of crushed char and/or coal as a precoat and body feed can improve filtration rates and can significantly increase the fuel value of collected solids. Preliminary economic evaluation shows a savings over conventional precoats of approximately $16 million per year for a 30,000-ton/day (26,700-metric ton/day) plant.

2. Thermal agglomeration has been shown to increase settling rates at high temperatures. Solvent agglomeration, coupled with thermal agglomeration and followed by settling at elevated temperatures and pressures, has been shown to be a viable alternative to filtration. A preliminary economic evaluation shows that this process has the potential to reduce current filtration costs by as much as 75%. A bench-scale evaluation of the process should be made.

3. Certain additives produce a clarified upper fraction after a settling time of 1 hr or less. In some cases the clarified fraction will meet EPA guidelines for direct combustion as a boiler fuel. Preliminary economics has not yet been determined, but it is possible that additive agglomeration at low concentrations (<1000 ppm) will be the least expensive of the proposed separations techniques.

4. Studies of both Solvent Refined Coal (SRC) and Char Oil Energy Development process stream characteristics have added significantly to the coal liquefaction data base. The electron microscope was used to characterize process solids by particle size distributions. The accumulation of physical and chemical property data, petrographic analyses, neutron activation analyses, and photon emission spectroscopy data also contributed to the data base. Aging tests have determined the effects of sampling and storing SRC unfiltered oil under various conditions.

8.4 COAL-SOLVENT-HYDROGEN MIXING

Improvements in hydrodesulfurization and hydroliquefaction of coal in hydrogen-donor solvent systems may possibly be achieved by inducing strong turbulence in the reactor in which the hydrogenation is carried out. Results obtained in the development of the Synthoil process[26,27] at the Pittsburgh Energy Research Center (PERC) suggest that, under conditions of high turbulence and plug flow in a reactor, adequate desulfurization and liquefaction may be achieved utilizing only the catalytic activity of the ash minerals.

Simulated contactor studies with water-coal slurries and air, which have the objective of identifying suitable reactor configurations, are being conducted to evaluate this hypothesis. Parameters being studied include pressure drop across the contactor, liquid holdup in the contactor, and the degree of axial dispersion present in the liquid phase. Baseline contactor data have been

19. B. R. Rodgers and S. Katz, *Supporting Research and Development on Separations Technology Phase II Report: Scouting Experiments,* ORNL/TM-4968 (October 1975).

20. B. R. Rodgers and S. Katz, *Supporting Research and Development on Separations Technology: Final Report,* ORNL/TM-5843 (in preparation).

21. B. R. Rodgers, "The Effects of Solvents on Separation of Micron-Sized Particles from Coal Liquefaction Process Streams," *Hydrocarbon Process.*, p. 191 (May 1976).

22. B. R. Rodgers and P. R. Westmoreland, "Agglomeration and Separation of Micron-Sized Particles from Liquid Streams," paper No. 19C presented at the 81st National American Institute of Chemical Engineers Meeting, Kansas City, April 1976.

23. S. Katz and B. R. Rodgers, "A Laboratory Evaluation of Precoat Filtration Parameters for the Solvent Refined Coal Process," *Ind. Eng. Chem., Process Des. Dev.* **15**(3), 407 (1976).

24. B. R. Rodgers and P. R. Westmoreland, "Removing Micron-Size Particles from Coal Liquids," pp. 28–38 in *Coal Processing Technology: Vol. 3,* a CEP Technical Manual (1977).

25. S. Katz and B. R. Rodgers, "Reformation of Inorganic Particles Suspended in Coal-Derived Liquids and Improved Separation," pp. 173–81 in *Liquid Fuels from Coal,* Academic Press, New York, 1977.

26. I. Wender, *Internal Quarterly Technical Progress Report, October–December 1975,* PERC/Qtr.-75/4, p. 22 (January 1976).

27. I. Wender, *Internal Quarterly Technical Progress Report, January–March 1976,* PERC/Qtr.-76/1, p. 48 (April 1976).

obtained using cocurrent upflow of air and water through a 1-in.-ID by 10-ft-long (2.5-cm-ID by 3.0-m-long) column packed with 4.6-mm-diam glass beads. The same packed column has also been used with the cocurrent upflow of air and a slurry of 35 wt % coal in water over a similar range of flow rates. The liquid hold-up and axial dispersion coefficient are being determined using the axially dispersed, piston flow model[28] to analyze data generated by the imperfect tracer pulse method.[29,30]

Figure 8.3 shows the pressure drop due to gas and liquid flow across the packed column, plotted as the energy dissipation per unit volume vs the liquid flow rate for the cocurrent upflow of air and coal slurry. The energy dissipation per unit volume has been correlated with mass transfer coefficients in the literature.[31,32] The pressure drop and, hence, the energy dissipation increase with both increasing liquid and gas flow rates.

Similar data will be obtained for two more contactors: (1) the packed column using ⅛-by ⅛-in. (3- by 3-mm) right circular cylinders to simulate the inert packing used for one run at PERC, and (2) a 1-in.-ID by 5-ft-long (2.5-cm-ID by 1.5-m-long) contactor filled with six Kenics mixing elements.[33] These in-line static mixers consist of a series of right- and left-hand helical elements. For fluids in turbulent flow, this geometry is claimed to cause complete stream inversion, create microscale turbulence, and produce radial mixing. For coal conversion applications, its low restriction of cross-sectional area should be conducive to low erosion rates and plug-free operation.

8.5 PRESSURIZED CARBONIZATION OF CONSOL SYNTHETIC FUEL RESIDUE

The CSF process, a type of hydrogen-donor process, is being evaluated by an ERDA contractor.[34] The process will produce a liquefaction residue stream that has a

28. O. Levenspiel, *Chemical Reaction Engineering*, 2d ed., chap. 9, Wiley, New York, 1972.

29. K. Ostergaard and M. L. Michelsen, *Can. J. Chem. Eng.* **47**, 104 (1969).

30. J. R. Hightower, Jr., and R. C. Lovelace, pp. 52–57 in *Coal Technology Program Quarterly Progress Report for the Period Ending September 30, 1976*, ORNL-5224 (January 1977).

31. L. P. Reiss, *Ind. Eng. Chem., Process Des. Dev.* **6**(4), 486 (1967).

32. T. Hirose et al., *J. Chem. Eng. Jpn.* 7(3), 187 (1974).

33. Manufactured by Kenics Corp., North Andover, Mass.

34. Fluor Engineers and Constructors, Inc., *Conceptual Design for Advanced Coal Liquefaction Commercial Plant*, FE-2251-TQ-1 (August 1976).

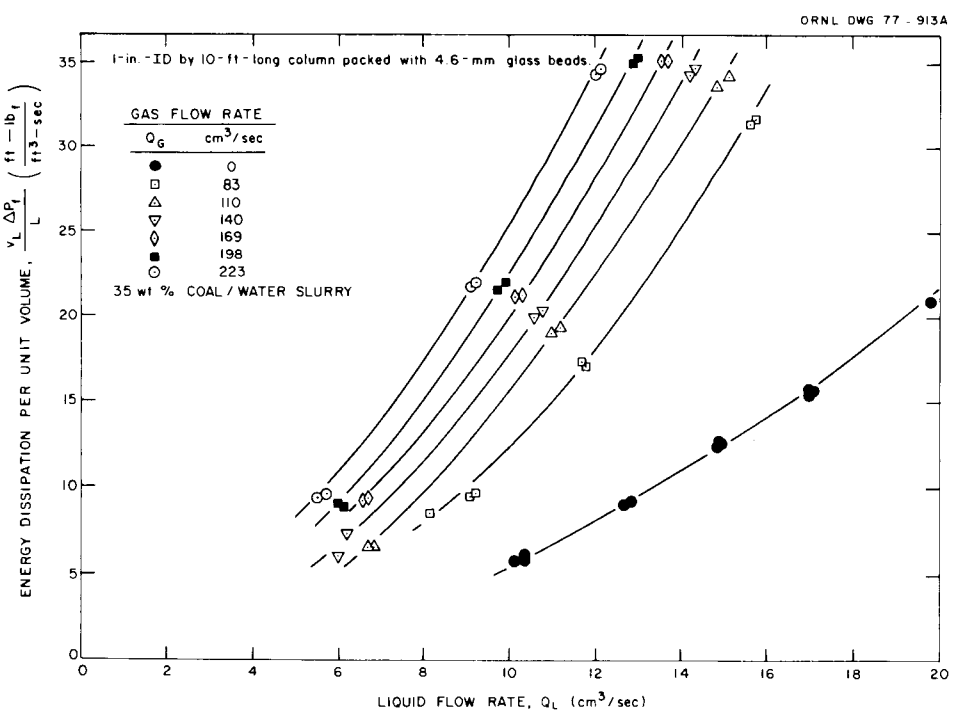

Fig. 8.3. Effect of fluid flow rates on the energy dissipation per unit volume.

high solids content (~40% solids) and contains valuable liquid products. The Chemical Technology Division is conducting experiments to simulate a low-temperature carbonization of CSF residue and to obtain information on coke formation and liquid recovery. The conditions to be investigated are temperature [900 to 1050°F (480 to 565°C)], pressure [65 and 415 psia (448 and 2860 kPa)], and fluidizing gas composition (argon is being used now, but a reducing gas will be used later in the project).

A system has been assembled to provide gas preheating, spraying of residue into a pressurized fluidized-bed carbonizer, condensation and collection of liquid product, and sampling and metering of gaseous effluent. The apparatus shown in Fig. 8.4 is being used to meet the objectives mentioned above.

Of the ten pressurized carbonization runs completed to date, the first six were made using a methyl naphthalene feed (simulating CSF residue) to shake down the system and to test procedures for closing the material balance. The latest four runs, two using the CSF residue and two using solvent [<700°F (<370°C) distillate from CSF residue], have been completed with two runs at each pressure [65 and 415 psia (448 and 2860 kPa)] at a temperature of 900°F (480°C). Preliminary results indicate that approximately 7% of the solvent decomposes at each pressure. However, the two runs using the residue indicated that more coke is formed at the higher pressure. These early results indicate that higher pressure increases coking of the heavier fraction but has little effect on the degradation of the lighter, more valuable solvent.

ORNL DWG 77-213R1B

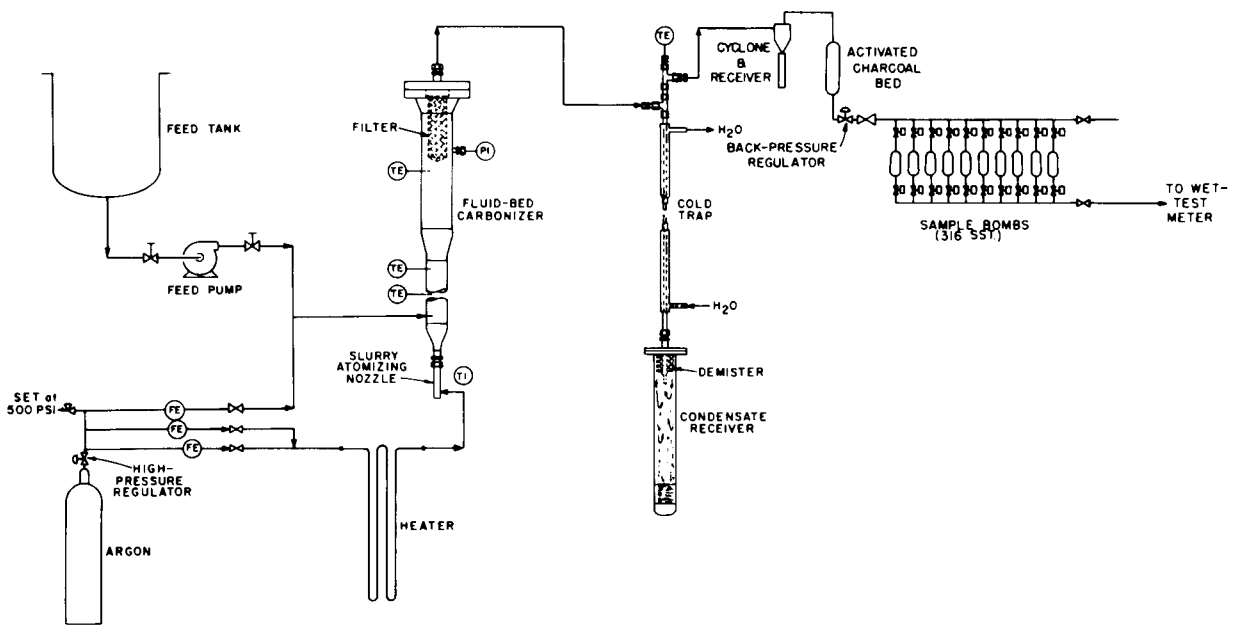

Fig. 8.4. Flow diagram of the pressurized carbonization experiment.

9. Coal Conversion Engineering Studies and Program Analysis

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

Process and program analysis studies, which involve most of the coal conversion processes, are being conducted for the ERDA–Fossil Energy, Office of Program Planning and Analysis (OPPA). The objective of the project is to consistently provide technical and economic evaluations of competing processes and systems for coal conversion and utilization. The subprograms included in the studies are low-Btu gasification, high-Btu gasification, direct combustion, advanced power-combined cycle, liquefaction, and in situ coal gasification.

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

9.1 TECHNICAL AND ECONOMIC EVALUATION OF THE SYNTHOIL PROCESS

A conceptual process design was prepared for a 100,000-bbl/day (0.184-m^3/sec) "grass-roots" Synthoil facility, and an economic evaluation of the process was made based on this design. This work was done for the ERDA–Fossil Energy, MFPM Division. The principal objectives of the evaluation were to estimate the cost of the product under various financing conditions and to assess the status of development of the process as a possible candidate for demonstration.

The report of the evaluation includes process flow diagrams, mass and energy balances, equipment sizes, cost estimates, and an economic and technical analysis.[1]

The Synthoil process, developed at the Pittsburgh Energy Research Center (PERC), is a fixed-bed catalytic hydrogenation process for producing liquid fuels from coal. Figure 9.1 shows the general flow scheme used in the 100,000-bbl/day facility. The process design basis was developed from experimental results obtained at PERC. Western Kentucky coal was used as the design feed, and estimated Synthoil reactor yields were based on the PERC data.[2] Net production of desulfurized liquid fuels was 97,216 bbl/day (0.179 m^3/sec). Total coal consumption was 50,133 tons/day (526.4 kg/sec), based on a moisture content of 9.2%. Coal consumption in the various parts of the facility was as follows: Synthoil reaction section, 32,069 tons/day (64.8 kg/sec); hydrogen production, 11,894 tons/day (124.9 kg/sec); steam and power requirements, 6170 tons/day (64.8 kg/sec). All utilities were generated on site, and there was no net export of fuel gas, steam, or electricity.

The calculated overall thermal efficiency was 59.6%, where efficiency is defined as the total heating value of the fuel products divided by the heating value of the total coal consumed in the facility.

Economic analysis. The estimated overall capital investment was $1900 million, consisting of $1670 million of depreciable and $230 million of nondepreciable capital, not including the cost of the coal mine. Coal delivered to the plant was considered as an oper-

1. R. Salmon, M. S. Edwards, W. C. Ulrich et al., *Evaluation of the Synthoil Process: Vol. I. Process Design and Economic Evaluation of a 100,000 Barrel/Stream Day Facility; Vol. II. Status of Development; Vol. III. Unit Block Flow Diagrams for a 100,000 Barrel/Stream Day Facility,* ORNL-5209, -5210, -5211 (in preparation).

2. S. Akhtar, J. J. Lacey, M. Weintraub, A. A. Reznik, and P. M. Yavorsky, "The Synthoil Process – Material Balance and Thermal Efficiency," presented at the 67th Annual Meeting of the A.I.Ch.E., Washington, D.C., Dec. 1–5, 1974.

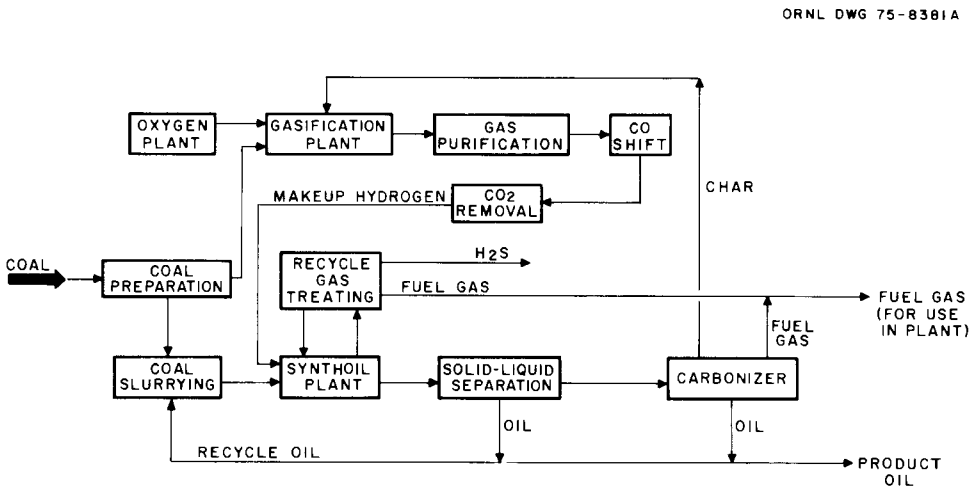

Fig. 9.1. Overall block flow diagram of the Synthoil facility.

ating expense, and its cost was treated as a variable. Interest during construction was not included in the capital investment but was accounted for in the calculation of the product price. All costs were on a first-quarter 1976 basis.

Using the discounted cash flow procedure, the price of the product oil was calculated as a function of coal cost and annual after-tax rate of return on equity capital. This was done for four capital structures ranging from 100% equity to 95% debt, using an annual interest rate of 9%. Results for the 100%-equity case are shown in Fig. 9.2. Calculations were based on a 5-year construction period followed by a 20-year operation period. Total on-stream efficiency of the plant was assumed to be 50% in the first year, 70% in the second year, and 90% thereafter. Taxes were based on a federal income tax rate of 48%, a state income tax rate of 3%, and a federal investment tax credit of 7%. Depreciation for tax purposes was calculated by the sum-of-the-years'-digits method, using a life of 16 years.

By-product credits were included for sulfur at \$60/long ton (\$0.0591/kg) and for anhydrous ammonia at \$160/ton (\$0.1764/kg). Reducing the sulfur credit to \$25/long ton (\$0.0246/kg) would increase the price of the product oil by \$0.70/bbl (\$4.40/m^3). A change of \$10/ton (\$0.011/kg) in the price of ammonia changes the product price by \$0.02/bbl (\$0.1258/m^3).

9.2 ENGINEERING EVALUATION OF A COMMERCIAL-SCALE HYDROCARBONIZATION PROCESS

A preliminary design and an economic evaluation of a hydrocarbonization facility based on the U.S. Steel Corporation clean coke process have been completed.[3] Volume I of the two-volume study includes the conceptual design and cost estimate of a commercial

3. J. M. Holmes et al., *Hydrocarbonization Process Evaluation Report. Vol. I, Conceptual Design and Cost Estimate of a Commercial-Scale Facility,* ORNL-5212; *Vol. II, Evaluation of Process Feasibility,* ORNL-5213 (to be issued).

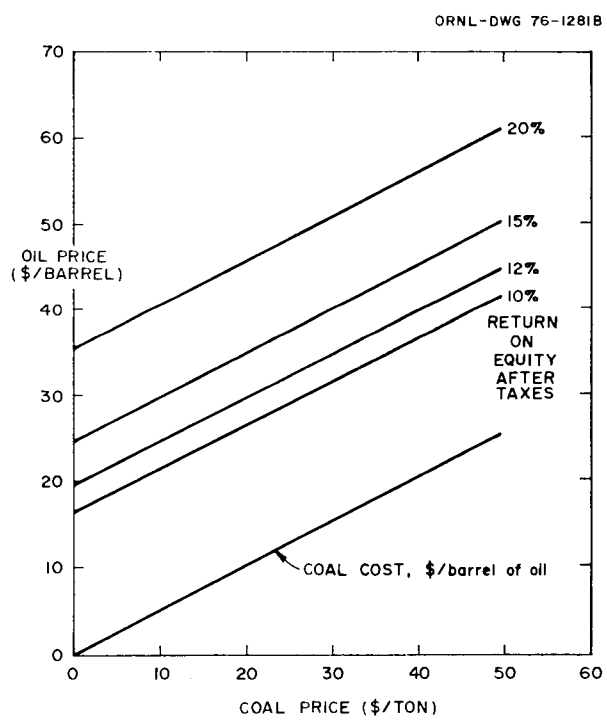

Fig. 9.2. Price of product oil at 100% equity and 7% investment tax credit.

facility for producing clean char, oil, and pipeline gas fuels having a heating value comparable to 100,000 bbl (15,900 m^3) of fuel oil per day. Volume II presents an evaluation of the process feasibility. The conceptual design includes a complete facility that will (1) prepare the coal for hydrocarbonization in a beneficiation system; (2) hydrocarbonize a fraction of the beneficiated coal to solid, liquid, and gaseous fuel products; (3) provide energy to the facility by burning the remainder of the beneficiated coal in a fluidized-bed combustor; (4) hydrotreat the liquid products, using hydrogen produced internally; and (5) treat the plant effluents to comply with regulations concerning disposal.

The total capital investment, including initial working capital, initial raw materials, catalysts and chemicals, and land, is about $1019 million. A discounted cash flow analysis [assuming 100%-equity financing, 12% return on equity, and coal priced at $20/ton ($22.05/10^3 kg)] resulted in a product fuel price of $3.15/million Btu ($2.99/10^9 J). This fuel price is equivalent to $19.85 per barrel ($124.86/m^3) of fuel oil, at a heating value of 6.3 million Btu per barrel (4.18 $\times 10^{10}$ J/m^3). Reduction of the debt/equity ratio from 0/100 to 70/30 will reduce the fuel price to $2.40/million Btu ($2.28/10^9 J), which is equivalent to $15.12 per barrel ($95.11/m^3) of fuel oil.

An alternative system was also considered in which the char produced by the hydrocarbonization facility is utilized as fuel for a power plant and a coal mine is included as the coal source. The addition of the coal mine and power plant increases the total capital cost to about $2280 million. Results demonstrated that, for an average bus-bar power price of 30 mills/kWhr ($8.33/$10^9$ J) and a pipeline gas price of $3.50/$10^3$ scf ($2.92/K · g-mole), the oil price would be $12.50/bbl ($78.62/m^3), using utility financing (debt/equity ratio of 70/30).

Results of the study emphasize the need for testing the evaluated process in a continuous pilot plant using a wide variety of highly caking bituminous coals as the feed material. A program suggested for the pilot plant would encompass (1) development of improved methods for the prevention of agglomeration of highly caking coals during hydrocarbonization, (2) optimization of the yields of coal liquids, (3) investigation of a single-stage high-temperature hydrocarbonizer optimized for char production, and (4) optimization of beneficiation ratios employed during coal preparation.

9.3 SURVEY OF COAL CONVERSION INDUSTRIAL EQUIPMENT CAPABILITIES

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

The current study is separated into four divisions:

1. **Rotating components.** Investigation of rotating machinery necessary for the various coal conversion processes includes (1) centrifugal and axial compressors, (2) liquid and slurry pumps (includes reciprocating types), (3) drives such as motors and turbines (includes couplings such as belts and gears), and (4) energy recovery devices such as expanders.

2. **Valves and other pressure letdown devices.** Investigation of valves and pressure letdown devices that are considered critical to successful operation of the various processes for the coal conversion plants includes factors such as process stream phase (solid, liquid, gas, or mixed phase); function and application (on-off, throttling, control, pressure letdown); operators (manual, hydraulic, pneumatic, electric); operating conditions (temperature, pressure, flow); and materials of construction.

3. **Hot-gas cleanup devices.** Investigations of equipment and methods to be used in hot-gas purificiation include cyclones, bag filters, absorbers, centrifuges, electrostatic precipitators, molten media (metals and salts), high-temperature scrubbers, and both solid- and moving-bed systems. The level of particulate loading is being considered. Operating temperatures of interest for gases leaving fluid-bed combustors range from 600 to 1500°F (316 to 816°C) and, for gasifiers, from 600 to 2400°F (316 to 1316°C).

4. **Heat recovery.** An evaluation is being made of equipment potentially suitable for the recovery and utilization of heat in process streams (gas, liquid, solid, and mixed phase) from primary exothermic coal conver-

sion process steps. Such process steps may include direct hydrogasification, solution hydrocracking, shift conversion, methanation, methanol synthesis, and Fischer-Tropsch synthesis. Hot-stream temperatures being considered are in the range 300 to 2700°F (149 to 1482°C). Information is being collected and evaluated regarding descriptions, sizes, costs, and commercial applicability of regenerators, fluid-bed contactors, heat pipes, related equipment, and, to a limited degree, conventional heat exchangers.

9.4 PROCESS MODELING

This project, which is funded by ERDA–Fossil Energy, is a joint effort involving Purdue University, Lehigh University, and ORNL. The overall objective is to develop computer programs for the design and cost estimation of coal conversion processes and facilities. Purdue is concentrating on the development of steady-state mass- and energy-balance process design models; Lehigh is concentrating on unsteady-state models. Since Purdue and Lehigh issue their own reports, details of their work are not covered here. The computer facilities at ORNL will be used for implementing the Purdue and Lehigh programs. ORNL will also help to develop, augment, and update the programs, especially in the areas of equipment design and cost estimation. A discussion of some of this work follows.

Computer program for product price calculation. The PRP (product price) program[4] was initially developed in July 1976; it has since been expanded and modified to include various options in the handling of taxes and interest during construction. This program was used to calculate the product price in the Synthoil and hydrocarbonization evaluations conducted at ORNL in 1976. The program uses the discounted cash flow procedure and provides for the parametric study of product price as a function of coal cost and rate of return on equity. Any desired values can be used for debt/equity ratio, interest rate on debt, construction time, operating life, tax rates, and depreciation methods. The plant operating factor (on-stream factor) can be varied in any desired way. Either private- or utility-type financing can be used at the user's option.

Piping layout and cost. Work has begun on a computer program (PPL) that calculates a piping layout, determines process piping diameters and lengths, and makes an overall piping cost estimate for a process plant. The user inputs the grid coordinate locations of the major process equipment, the rates of flow through the various process lines, and the routing of the process lines in terms of the process equipment items. Desired pressure drops are specified in terms of allowable pounds per square inch per 100 ft. The program calculates line sizes, pressure drops, line routings, lengths, and costs. Factors will be applied to account for small miscellaneous lines. It is believed that a cost estimate made in this way will be a considerable improvement over one made by conventional procedures in which factors are directly applied to process equipment costs. Also, the program will permit more direct estimation of the costs of insulation, painting, and pipe supports.

Heat exchanger design and cost estimation. In June 1976, work was initiated on a computer program that calculates the mechanical design and dimensions of a heat exchanger and estimates its cost. This does not include thermal rating (i.e., the calculation of heat transfer coefficients), which has to be done separately. Using the results of the thermal design as a starting point, the program calculates the mechanical design, the weights of all parts, and the estimated cost.

The inputs required by the program are as follows: total surface area; tube diameter, length, pitch, and type of layout (square, triangular); tube gage (thickness); number of tube passes; materials of construction; design pressures and temperatures; type of construction (floating head, U-tube, etc.); size of nozzles; and baffle spacing.

The cost estimating procedure used in the program will simulate that used by equipment manufacturers. The cost estimate is based on materials, labor, overhead, and profit. The output of the program shows the detailed mechanical design and the cost breakdown for each exchanger. The program is now operational and prints out a complete materials and labor summary for a shell-and-tube exchanger in any of the Tubular Exchanger Manufacturers Association categories. However, further testing and calibration are necessary before the program can be considered ready for release.

9.5 TECHNICAL SUPPORT ACTIVITIES

The technical support work ranges from engineering calculations to the publication of a digest on synthetic fuels process research. One of the projects was concerned with the survey of processes for hot-gas cleanup and another with processes for heat recovery.

4. R. Salmon, *PRP – A Discounted Cash Flow Program for Calculating the Production Cost (Product Price) of the Product from a Process Plant,* ORNL-5251 (March 1977).

Review of State of the Art of Processes for Heat Recovery

An important factor affecting the attractiveness of coal conversion processes is the overall thermal efficiency. To maximize the efficiency, effective heat recovery processes and associated equipment culminating in waste heat utilization are important. The processes now being surveyed, appraised, and cataloged are those currently or potentially applicable to the recovery of heat such as that available in coal-gasifier raw off-gas, shift conversion and methanation gases, fluid-bed combustion gases, and hot liquid and solid streams.

Among the processes being considered are fluid-bed contactors, batch (checkerwork) and continuous (rotating matrix) thermal regenerators, direct-contact cooler condensers, soot-blown exchangers, organic Rankine cycle systems suitable for converting a fraction of low-grade waste heat to electrical energy, heat-pipe arrays, and in-plant thermal-energy transport systems utilizing heat transfer salt. Conventional heat transfer equipment will be included only to the extent that the performance is augmented by such approaches as surface-area extension, in-line mixers, spiral tubing, and swirl flow. Augmentation of laminar flows should be particularly worthwhile. Attention is being given to a possible transfer of technology from other industries.

Related information being developed in the heat recovery equipment survey is described in Sect. 9.3.

Hot-Gas Cleanup Processes

The objective of this project is to investigate the present state of the art of hot-gas cleanup processes. The application of such processes is expected to improve the thermal efficiency, and possibly the economics, of coal gasification facilities that require hot gas after cleanup. The application of most interest is the removal of contaminants (i.e., particulates, sulfurous gases, possibly ammonia, alkali metals, etc.) from coal-derived low-Btu fuel gas prior to firing combined-cycle turbines. Possible technology transfer from other industries is being given careful consideration. Architect-engineering and design-construction firms have been contacted for further process information that might be applicable to hot-gas cleanup.

Pertinent literature was reviewed, and inquiries will be made of hot-gas process vendors and/or developers. Major gas turbine developers will be contacted, and available data on hot-gas cleanup will be collected and evaluated. Collected material will be compiled in the form of a file of hot-gas cleanup processes.

9.6 PROGRAM ANALYSIS STUDIES

Several subsystem studies being conducted for OPPA have been described. The gas cleanup and coal beneficiation subsystem studies are discussed below.

Gas Cleanup

This effort includes specific research studies of gas cleanup systems that are part of a broad program of most of the coal conversion and utilization processes. The objective of the program is to provide consistent technical and economic evaluations of competing processes and systems for coal conversion and utilization. The gas cleanup study falls into two major classifications:

1. **Low-temperature acid gas removal.** This includes a study of systems of chemical and physical solvents that remove hydrogen sulfide and/or carbon dioxide and related pollutants. At low temperatures, particulate removal poses no problem.
2. **High-temperature acid gas removal.** This includes a study of solid adsorbents, molten-salt processes, etc., in which the primary goal is removal of hydrogen sulfide. High-temperature particulate removal and prevention of alkali carry-over must also be considered.

These two areas have been studied for application to low-Btu gasification systems. Specific tasks completed thus far are listed below:

1. A survey has been conducted to identify the promising applicable processes, concepts, and systems for cleanup of gas streams resulting from conversion of coal, and a list has been compiled. The survey covered activities both in the United States and in other countries.
2. A list of 34 potential processes, concepts, and systems specific to low-Btu gasification cleanup was prepared from the above survey. The processes were categorized to permit a general analysis leading to selection of applicable systems for treating in situ and low-Btu gas streams.
3. Further screening of the processes, using various criteria such as selectivity for hydrogen sulfide, chemical stability, and lack of toxicity, reduced the number of processes under consideration to 14.

Evaluation of these processes is continuing and will lead to the selection of fewer than ten as candidates for low-Btu gas cleanup. Detailed descriptions of the candidates will be provided, including available cost data.

Coal Beneficiation

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

Oak Ridge National Laboratory is engaged in conducting a survey and in evaluating current and potential coal beneficiation processes for the ERDA–Fossil Energy, OPPA. The objective of the study is to identify and analyze various currently used and potential coal beneficiation processes. The study, which was started in October 1976, is expected to be completed by September 1977. The scope of the study includes

1. identifying and gathering information regarding the various coal beneficiation techniques in use and in the development stage;
2. selecting representative coals from the northern Appalachian, the Interior Basin, and the western regions of the United States as test coals for evaluating the potential beneficiation processes;
3. where sufficient information regarding the process exists, designing and cost estimating conceptual grass-roots type of beneficiation plants based on the candidate beneficiation processes to nominally produce 1500 tons/day (1.36×10^6 kg/day) and 15,000 tons/day (1.36×10^7 kg/day) of moisture- and ash-free (maf) coal;
4. deriving conclusions regarding the beneficiation processes and their potential commercial applicability;
5. if warranted, providing recommendations to hasten the completion of the beneficiation process development effort.

A list of the beneficiation processes to be evaluated is presented in Table 9.1. Various coals that are being considered include representative types from Pennsylvania, West Virginia, western Kentucky, Illinois, Wyoming, and North Dakota.

An interim report[5] has been prepared which presents the results of the work done on this study through March 31, 1977. This report includes a description of several of the beneficiation processes and engineering evaluations of conceptual 1500-ton/day (1.36×10^6 kg/day) and 15,000-ton/day (1.36×10^7 kg/day) plants based on these beneficiation processes. Most of the engineering evaluations were conducted for plants treating bituminous coal from the lower Kittanning coal bed located in Somerset County, Pennsylvania.

Table 9.1. Coal beneficiation processes proposed for evaluation

- Physical and mechanical
  - Dry mechanical separation
    - Crushing and screening
    - Centrifugal separation
    - Low-intensity dry-magnetic separation: the Hazen-Inex process
    - Pennsylvania State University "Dry-Floc" process
    - Ilok process
  - Wet mechanical separation
    - Commercially available beneficiation equipment
      - Jigs
      - Washing tables
      - Cyclones
      - Heavy-medium types
        - Low-flow type
        - High-flow type
    - Froth flotation processes
      - General type
      - USBM two-stage
    - Multistream coal cleaning system developed by General Public Utilities and Heyl and Patterson, Inc.
    - High-intensity–high-gradient magnetic separation techniques
    - CFRI oil agglomeration process
- Chemical
  - TRW-Meyers coal desulfurization
  - Battelle hydrothermal coal
  - PERC sodium hydroxide beneficiation
  - SURC chemical comminution
  - Ledgemont oxygen leaching
  - PERC oxidative desulfurization
  - KVB, Inc., "sulfur oxidation"
- Microbial
- Other
  - ARCO

9.7 IN SITU COAL GASIFICATION STUDIES

The United States has vast supplies of coal, but large amounts of this valuable resource are not economically recoverable with conventional surface- or deep-mining techniques. Gasification in place has been proposed as a means of tapping this valuable source of energy. It has

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

been estimated that the amount of coal potentially exploitable by in situ gasification at depths less than 3000 ft (900 m) is approximately 1155 billion tons (1048 billion metric tons).[6]

In situ coal gasification offers additional advantages, such as minimizing health and safety problems associated with deep-mining operations, and may present more readily controllable environmental effects than either deep- or surface-mining methods.

A report[7] prepared by the Chemical Technology Division presents the results of a preliminary technical evaluation of the processes on which the ERDA-supported in situ projects are based: linked vertical well (LVW), packed bed (PB), longwall generator (LG), and steeply dipping bed (SDB). The objective of this evaluation was to make a preliminary assessment of the applicability of the processes in various regions of the continental United States. This assessment was based only on the technical aspects of the processes. An evaluation of their commercial potential will be addressed in a later report that will cover the economic aspects of the processes.

The four candidate processes were compared on the basis of a qualitative assessment of their technical merits and their suitability for application to various regional resource types and configurations. For purposes of displaying each candidate process to its best advantage, a predominant or representative coal type was selected within each region. The potential applicability of each candidate process to the various regional coal types and resource configurations was then assessed. Russian experience, where it applies to the regional conditions under consideration, was also described. Results of the evaluation are summarized in Table 9.2.

If in situ gasification is to attain its full potential, it will be necessary to develop (1) a process for gasifying thin [<15-ft-thick (5-m)] seams of bituminous coal with little dip (<45°) at depths to 2000 ft (600 m); (2) a process for gasifying thick [>50-ft (15-m)] beds of subbituminous coal at depths to 3000 ft (900 m); (3) reliable, rapid linking techniques for the different coal types, various resource configurations, and diverse geological conditions of the United States; and (4) improvements in drilling technology and equipment.

6. R. C. Rupert et al., "Energy Extraction from Coal In Situ – A Five-Year Plan, Vol. III, Resources," prepared for the Energy Research and Development Administration by TRW Systems and Energy, Sept. 21, 1975, Table 3-2, p. 3–5.

7. W. C. Ulrich, *Evaluation of In Situ Coal Gasification Processes on a Regional Basis,* ORNL-5279 (in preparation).

Table 9.2. Potential in situ coal gasification process applications

Region	Eastern	North central	South central	Western[a]	Western[a]	Western[a]
Process selection	MLG[b]	MLG[b]	LVW	PB	LVW	SDB
Coal province	Eastern	Interior	Gulf	Northern Great Plains	Rocky Mountain	Pacific Coast
Coal type	Bituminous	Bituminous	Lignite	Subbituminous	Subbituminous	Subbituminous and bituminous
Seam thickness	<15 ft (~5 m)	<15 ft (~5 m)	<15 ft (~5 m)	>50 ft (~15 m)	15–50 ft (~5–15 m)	<15 ft (~5 m)
Depth of seam	<1000 ft (~300 m)	<1000 ft (~300 m)	<1000 ft (~300 m)	>1000 ft (~300 m)	<1000 ft (~300 m)	<1000 ft (~300 m)
Dip	<45°	<45°	<45°	<45°	<45°	>45°
Reasons for selection	Directionally drilled holes are used to create linking channels; the natural permeability of the coal and other coal properties (e.g., swelling) are not amenable to LVW; seams are too thin for PB; SDB is not applicable.	Directionally drilled holes are used to create linking channels; the natural permeability of the coal and other coal properties (e.g., swelling) are not amenable to LVW; seams are too thin for PB; SDB is not applicable.	Necessary permeability and drying can be achieved with moderate air pressure; reverse combustion linking is possible; coal properties eliminate need for directionally drilled holes and thus LG or MLG; seams are too thin for PB; SDB is not applicable.	Formations are amenable to permeability enhancement by explosive fracturing to prepare rubbleized bed; coal properties eliminate need for directionally drilled holes and thus LG or MLG; LVW process has not been demonstrated in this resource configuration; SDB is not applicable.	Necessary permeability and drying can be achieved with moderate air pressure; reverse combustion linking is possible; coal properties eliminate need for directionally drilled holes and thus LG or MLG; some seams may be too thin or shallow for PB; SDB is not applicable	PB, LG, and MLG are not applicable, although directionally drilled holes may be used to link the vertical or nearly vertical wells used to exploit this type of resource configuration.
Current status	One directionally drilled hole was placed in a 6-ft-thick seam at Pricetown, W. Va. Plans for use of this hole in future experiments are indefinite.	One directionally drilled hole was placed in a 6-ft-thick seam at Pricetown, W. Va. Plans for use of this hole in future experiments are indefinite.	Several field tests have been carried out in Wyoming subbituminous coal. Eight well-to-well gasification periods have been completed; 6690 tons of coal gasified.	A two-well explosive fracturing test was carried out. A two-well test burn was shut down prematurely because of air bypassing.	Several field tests have been carried out in Wyoming subbituminous coal. Eight well-to-well gasification periods have been completed; 6690 tons of coal gasified.	Not actively funded at present; no field work in progress.
Potential problems	Directional drilling is time-consuming and costly. Neither LG nor MLG process has been field-tested.	Directional drilling is time-consuming and costly. Neither LG nor MLG process has been field-tested.	Because of linking requirements use of LVW process has been limited to lignite and subbituminous coal.	Creation of uniform permeability with explosives is a problem. Gasification of deep seams requires high-injection pressures.	Because of linking requirements, use of LVW process has been limited to lignite and subbituminous coal.	The amount of coal in the United States found in steeply dipping beds is a minor fraction (less than 3%) of the total estimated resources.
Applicable Russian technology	None, with possible exception of Kholmogorsk site. Russians developed directional-drilling techniques.	None, with possible exception of Kholmogorsk site. Russians developed directional-drilling techniques.	Russian technology licensed by Texas Utilities Services, Inc., to gasify Texas lignite. Russians conducted extensive operations at Tula, Shatskaya, and Angren in lignite deposits.	None. There is no evidence that this type of formation exists in Soviet Union. Russians experimented with explosive fracturing in conjunction with underground mining, but quickly abandoned this method.	Much of Russian technology with use of LVW for gasifying lignite is transferable to subbituminous coal beds of similar orientation.	Russians developed successful system for gasifying SDB which was used at Lisichansk, Kamensk, and Yuzno-Abinsk stations on bituminous and anthracite coals.

[a]Because of its size and diversity of coal types and resource configurations, the western region was divided into three subregions corresponding to the Northern Great Plains, Rocky Mountain, and Pacific Coast Coal Provinces.

[b]MLG = modified longwall generator.

10. Separations Chemistry

10.1 NEW SEPARATIONS AGENTS

New separations agents investigated during this report period included molten-salt mixtures (chlorides, sulfates, hydroxides, and carbonates) as scavenging fluxes for removing ash from the unfiltered oil of Solvent Refined Coal and four classes of solvent extraction reagents. Of the five salt mixtures examined, one was found to effectively remove ash from Solvent Refined Coal, and its use has been studied in some detail (see Sect. 10.5). The four solvent extraction reagents evaluated were the carbamoylmethylphosphonates (CMPs), tetraalkyldiphosphonates, crown ethers, and fluorinated β-diketones.

Eight CMPs were tested. Of these, dihexyl[(diethylcarbamoyl)methyl]phosphonate (DHDECMP) and di(2-ethylhexyl) [(diethylcarbamoyl)methyl] phosphonate (DEHDECMP) appear to be the most useful in extracting trivalent actinides and plutonium from strong (2 to 6 *M*) HNO_3.[1] The choice of diluent type is important to the performance of these extractants, both in determining distribution coefficients and in defining the solubility behavior of the extractant and its adducts with nitric acid and with extracted metal nitrates. The tetraalkyldiphosphonates, which are compounds with structures similar to the CMPs, have also been examined but are less useful extractants than the CMPs because of solubility and viscosity limitations.

Earlier investigation of the crown ethers as extractants of mineral acid salts of metal ions showed poor extractability when simple solutions of crown ethers in organic diluents were used.[2] However, these compounds extract organic acid salts much more readily,[3,4] suggesting that the difficulty of solvating the anion in the aqueous phase is the primary hindrance to extraction. We have found that the addition of 2-ethylhexanol or nonylphenol to the organic phase greatly increases the extraction of potassium chloride. In addition, providing an organic-phase-soluble acid such as di(2-ethylhexyl) phosphoric acid (HDEHP) along with the crown ether resulted in more effective extraction of the alkali metals than that shown by either reagent individually and gave an order of extraction of the alkali metals quite different from that observed for HDEHP alone (Fig. 10.1).

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

2. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1976*, ORNL-5172, pp. 28–30.

3. C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.* **11**, 16 (1972).

4. J. M. Lehn, *Structure and Bonding*, vol. 16, pp. 1–70, Springer-Verlag, New York, 1973.

ORNL DWG 77-659R1

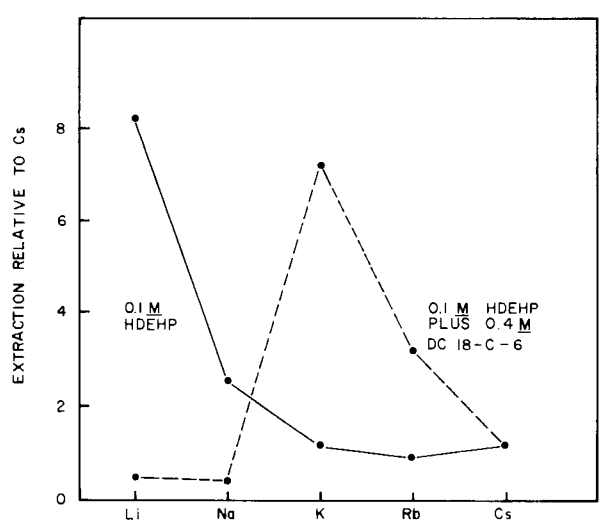

Fig. 10.1. Change in the order of extraction of alkali metals due to the addition of 0.4 *M* dicyclohexyl-18-crown-6 to 0.1 *M* HDEHP.

This result suggests that such combinations could be useful as new extraction systems for a variety of metal ions.[5]

The dialkyl sulfoxides were examined earlier[6] and are now being considered with renewed interest because they show overall similarity to tributyl phosphate (TBP) in both extraction and stripping behavior but do not generate degradation products deleterious to the extraction process as does TBP.[7] We have studied the behavior of di(2-ethylhexyl) sulfoxide (DEHSO) in the extraction of uranium, plutonium, thorium, iron, and trivalent actinides (see Sect. 10.7).

The fluorinated β-diketones are more acidic than their nonfluorinated counterparts and thus extract ions from solutions at lower pH levels.[8] We are examining a variety of these compounds with regard to their solubility and extraction characteristics. The most promising compound identified to date, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, has an extraction coefficient at pH 8 for lithium which is about 1000-fold greater than that obtained by using dibenzoylmethane. With this compound, the separation factor between potassium and rubidium at pH 8 is approximately 3000.

10.2 SEPARATION OF RADIUM AND OTHER RADIONUCLIDES FROM URANIUM ORES AND LEACHED TAILINGS

Samples of representative uranium ores and mill tailings from New Mexico, the Colorado Plateau, and Wyoming were collected and prepared for analysis and leaching tests. The results of leaching tests with nitric acid show that up to 98% of the radium is recovered in two stages with hot 3 *M* HNO_3.[9] The recoveries were generally greater for thorium, but lower for polonium and lead, than for radium. The concentration of radium remaining in the residue after leaching with 3 *M* HNO_3 ranged from 17 to 60 pCi/g for different ore and tailings samples; virtually no difference was found between ore and tailings from either sulfuric acid or carbonate leach mill processes. The lowest value is about an order of magnitude above that in the soils in the western mining districts. It is about the same as the level proposed as a standard for building material in the United Kingdom. The sand fraction (+140 mesh) of the residues after leaching with nitric acid ranged from 33 to 88 wt % and contained 40 to 70% of the radium at approximately one-half of the concentration of that in the slime fraction. A few scouting tests have shown that the residual radium is not dissolved with additional leaching with acid, complexing agents, or roasting. This suggests that the radium is probably in a refractory mineral rather than being present as sulfate or carbonate. The solubility of barium sulfate in nitric acid was measured to aid in the interpretation of the leaching data, and it was concluded that sufficient nitric acid to dissolve all the barium must be present in order to dissolve the maximum amount of radium. The leaching of ore or tailings by distilled water yielded solutions with radium concentrations greater than an order of magnitude above the maximum permissible concentration[10] for drinking water. The penetration of water into tailings was simulated for an arid climate; these tests indicated that the penetration may be limited by the evaporation that occurs between infrequent rains or snows. The radon emanation coefficients of samples of ore, tailings, and nitric acid–leached residues were measured. Although the coefficients varied (8 to 43%), no consistent trend was observed. The rate of radon emanation from nitric acid residues was only 2 to 10% of that for mill tailings. This lower emanation rate was found to be the result of the lower radium content rather than any significant change in radon emanation coefficient.

10.3 SEPARATION OF ALPHA EMITTERS FROM FUEL REPROCESSING WASTE

The tetraalkylcarbamoylmethylphosphonates (see structure, Fig. 10.2) extract tetravalent and hexavalent actinides from 2 to 6 *M* HNO_3 solutions even better than they extract trivalent actinides[11] and provide one

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

6. W. J. McDowell and H. D. Harmon, "Unsymmetrical Dialkyl Sulfoxides as Extractants," *J. Inorg. Nucl. Chem.* **33**, 3107–17 (1971).

7. M. Benedict and T. H. Pigford, *Nuclear Chemical Engineering Processes*, p. 327, McGraw-Hill, New York, 1957.

8. F. G. Seeley and W. H. Baldwin, "Extraction of Lithium from Neutral Salt Solutions with Fluorinated β-Diketones," *J. Inorg. Nucl. Chem.* **38**, 1049–52 (1976).

9. A. D. Ryon, F. J. Hurst, and F. G. Seeley, *Leaching of Radium and Other Significant Radionuclides with Nitric Acid from Uranium Ores and Tailings*, ORNL/TM-5944 (in press).

10. "Interim Drinking Water Standards," *Code of Federal Regulations*, Title 40, Chap. 1, Part 141 (published Dec. 24, 1975; scheduled to become effective June 24, 1977).

11. W. W. Schulz and L. D. McIsaac, *Removal of Actinides from Nuclear Fuel Reprocessing Waste Solutions with Bidentate Organophosphorus Extractants*, ARH-SA-217 (August 1975).

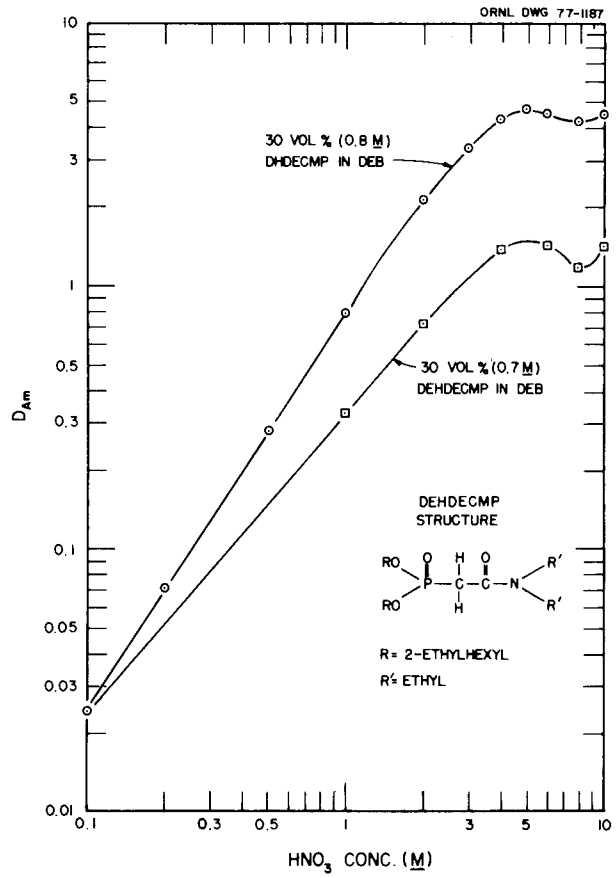

Fig. 10.2. Comparison of americium extraction by diethylbenzene solutions of DHDECMP and DEHDECMP as a function of nitric acid concentration.

possible approach to removing alpha-emitting nuclides from radioactive waste solutions. The two compounds DHDECMP and DEHDECMP appear to be the most useful of the CMPs now available.[1] The lower-molecular-weight and normal-alkyl-substituted members of this group of compounds are more effective actinide extractants, but the higher-molecular-weight compounds have lower aqueous-phase solubilities. A single CH_2-group spacing between the coordinating oxygens is optimum for metal adduct formation with the CMPs.

The solubility of DHDECMP in water is approximately the same as that of TBP in water, and the solubility of DEHDECMP in water is about 3% of that of DHDECMP (0.4 mg/liter when a 0.1 *M* solution of DEHDECMP in cyclohexane is equilibrated with a 1000-fold excess of water). Of the compounds examined, those with branched substituents are more soluble in normal hydrocarbons and more resistant to third-phase formation on contact with nitric acid. (A third phase consists of the nitric acid adduct of the CMP that separates from the bulk of the organic phase after the CMP solution has been contacted with HNO_3.) However, these branched compounds appear to be somewhat poorer extractants, possibly because of steric hindrance in formation of the metal adduct. A mixed aliphatic-aromatic diluent is useful to maximize extraction while maintaining adequate extractant and adduct solubility. Some commercially available mixed diluents are suitable for use with these compounds. Americium extraction by diethylbenzene solutions of DEHDECMP and DHDECMP can be seen in Fig. 10.2. Extractions from solutions of the same nitrate concentration but lower acid content are much higher.

A problem in the process use of the CMPs is the presence, in commercial preparations of these compounds, of acidic impurities that cause serious problems in stripping the actinides from the CMP solution by water or low concentrations of nitric acid. A study of the nature of these impurities and of degradation products produced by heating pure CMP indicates that the principal offending impurity is an alkyl[(dialkylcarbamoyl)-methyl]phosphonic acid.[12] Tests show that the troublesome impurities can be removed by high-vacuum (molecular) distillation or dilution of the crude material in hexane followed by extraction of the hexane solution with aqueous sodium hydroxide solution.

10.4 RESOURCE RECOVERY

Increased use of coal as a fuel will entail the problem of disposing of large amounts of ash [$\sim 6 \times 10^7$ tons per year ($\sim 5.4 \times 10^7$ metric tons)]. Since the ash contains some minerals of value (principally aluminum), is finely divided material, and will require handling for disposal in any case, consideration is being given to recovery of the mineral values and/or conversion of the ash to some useful material. We have studied the leaching of aluminum, iron, uranium, and titanium from fly ash with nitric, hydrochloric, and sulfuric acids over a wide range of acid concentrations and temperatures. In general, maximum recovery for all acids appears to occur at approximately 8 *N* acid under reflux conditions. However, aluminum recovery by acid leach methods has not exceeded 50%. Other possible methods of solubilizing the mineral content of this refractory, glasslike material include roasting or sintering and fusion. Several of these procedures are being evaluated.

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

10.5 WASTE STREAM PROCESSING STUDIES

The purpose of this program is to provide basic technical information that will be required for the satisfactory treatment of the actinide elements in nuclear fuel reprocessing plants. The present studies involve investigations of actinide losses associated with instabilities and solids formation in LWR reprocessing solutions,[13] and with plutonium extraction and stripping behavior in the Purex process.[14]

Precipitates in fuel reprocessing and waste solutions due to zirconium hydrolysis and the formation of zirconium molybdate and plutonium molybdate compounds can provide mechanisms for significant plutonium losses. The principal variables that affect the rate of solids formation have been identified, formation rates have been determined for various conditions of interest, actinide-carrying behavior has been delineated, and solids are being characterized by electron microscopy and x-ray diffraction. Zirconium molybdate promises to be particularly troublesome in reprocessing and waste solutions because this precipitate, which can occur at high acid concentrations, selectively carries high concentrations of plutonium; for example, if zirconium molybdate is allowed to precipitate from typical LWR feed solutions, the solids will carry 2% of the initial plutonium concentration.

In a series of plutonium extraction experiments with radioactive feeds prepared from irradiated UO_2 (∿40,000 MWd per metric ton of uranium), approximately 3 *M* HNO_3 feed solutions were batch contacted with equal volumes of 30% TBP–*n*-dodecane. Phase separations were rapid, and interfacial crud formation was minimal. In every case, greater than 99.99% of the plutonium was extracted. A very small amount of plutonium appears to be inextractable; this behavior is also observed when Pu(IV) is extracted from pure nitric acid.

Five-stage batch stripping tests were made with plutonium-loaded solvents which had been exposed to various amounts of irradiation. Solvent degradation products produced by prolonged exposure of the solvent to high radiation levels did not appear to affect the stripping behavior of Pu(III). Plutonium recoveries in the stripping experiments with 2 *M* HNO_3 were greater than 99.95% and may have been as high as 99.99%; however, it has not yet been possible to determine the precise value because of analytical difficulties in determining low plutonium concentrations in solutions with high salt contents.

Acceptable plutonium recoveries were not obtained in uranium-plutonium co-stripping experiments performed at low acid concentrations; losses ranged from 2 to 10% of the initial plutonium concentration. Studies involving stripping experiments and spectrophotometric analysis of complexed species show that plutonium losses vary with zirconium and uranium contents as well as with the concentration of solvent degradation products. At the high uranium concentrations typical of LWR feed solutions, uranium is preferentially complexed by solvent degradation products, while Pu(IV) complexation is suppressed but not eliminated. At low uranium concentrations, Pu(IV) is strongly complexed by dibutyl phosphate (DBP), monobutyl phosphate (MBP), and butyl lauryl phosphate; however, when zirconium is present, plutonium is preferentially complexed by DBP, and zirconium is preferentially complexed by MBP.

The solubilities of the plutonium-DBP complex and the zirconium-MBP complex are quite limited, and solids which tend to collect at the interface are formed when the solubility is exceeded.

10.6 ASH REMOVAL FROM SOLVENT REFINED COAL

The use of an NaCl-KCl-LiCl eutectic mixture (mp, 346°C) for removing ash from Solvent Refined Coal unfiltered oil has been shown to be effective in wetting and segregating the ash with both vigorous agitation (stirred autoclave) and gentle agitation (rocking autoclave). However, with vigorous agitation the molten-salt-wetted ash is dispersed in the oil, while with gentle agitation it separates as a slag or "clinker" on top of the bulk of the molten salt. Separation of the resulting "clinker" is relatively easy in either case, since the particles are much larger than the original micron-sized ash. Ash contents in the decanted oil as low as 0.07 and 0.001% have been obtained after 30 min of agitation in the rocking autoclave and the stirred autoclave respectively.

An engineering evaluation of a conceptual process based on ash removal using a molten salt suggests that a salt mixture with a high lithium content would not be economical. Tests of other salt mixtures are still in progress. These tests are limited to salts or mixtures which

13. M. H. Lloyd, "Instabilities and Solids Formation in LWR Reprocessing Solutions," *Trans. Am. Nucl. Soc.* **24**, 233–34 (1976).

14. M. H. Lloyd, "Chemical Behavior of Plutonium in LWR Fuel Reprocessing Solutions," presented at the American Nuclear Society Topical Meeting on the Plutonium Fuel Cycle, Miami, Fla., May 2–4, 1977; to be published in the *Proceedings*.

melt below 500°C because of the probability of disproportionation and repolymerization of the hydrogenated coal above this temperature. Future work will concentrate on the choice of a suitable salt mixture, optimization of the method of contacting the oil and the salt, and examination of techniques for separating the segregated ash.

10.7 PHYSICAL SEPARATIONS

Penetration of High-Efficiency Air Filters by Alpha Recoil Aggregates

The migration of alpha-active material through high-efficiency air filters in series in amounts larger than and in patterns different from those expected from the rated filter efficiency[15] has now been observed in three air filtration systems in actual use. One of these was a qualitative observation of ^{252}Cf migration through a three-filter system. Neutron activity on the last of the three filters was observed to be several orders of magnitude higher than expected;[16] no further analysis of these filters was made. Two of the observed instances were from filter plenums in a facility handling ^{239}Pu. Entire 250-ft^2 (23.3-m^2) filter units were removed from each of the four banks in the two plenums, and sample sections were removed from each filter. The plutonium was leached from the filter medium with acid and counted by high-resolution liquid scintillation methods. The results are shown in Table 10.1. The amount of plutonium found on the downstream filters was greatly in excess of that expected from accepted filter efficiency factors; therefore, the actual decontamination factors were quite low. Fitting these data to a mathematical model and calculating the release from the fourth filter (expressed as a fraction of the alpha material on the first filter and assuming linear loading of the first filter during that time) yielded release fractions of 3×10^{-11} and 1×10^{-12} for plenums 1 and 2 respectively. These fractions are five to six orders of magnitude less than those calculated from laboratory data for ^{239}Pu. This difference may be due to the presence of dust and other inert materials mixed with the alpha-active material on the in-plant filters. Another possible explanation arises from the fact that large differences have been observed in the laboratory between various batches of filters in their capability for retaining alpha aggregate recoil particles. Although the release from the filter systems in the plutonium handling facility was not large enough to exceed the 10 CFR 20 limit for any reasonable loading on the first filter, the results thus far suggest that the problem of alpha aggregate migration through air filter systems could be of consequence under some conditions.

15. W. J. McDowell, F. G. Seeley, and M. T. Ryan, "Penetration of HEPA Filters by Alpha Recoil Aerosols," *Proceedings of 14th ERDA Air Cleaning Conference*, CONF-760822 (February 1977), pp. 662–76.

16. L. J. King, ORNL, personal communication, September 1976.

Table 10.1. Plutonium found on filters after in-plant service

Filter No.	Plenum 1: 35 months		Plenum 2: 27 months	
	dis min^{-1} in.$^{-2}$	DF[a]	dis min^{-1} in.$^{-2}$	DF[a]
1	552,000	4.7×10^5	22,950	4×10^4
2	0.89	4.17	0.550	30
3	0.154	2.2	0.0144	4.2
4	0.126		0.0044	

[a]DF = total amount of plutonium assaulting the filter divided by the amount escaping. These numbers are maximum, since the amount escaping is unknown for the last filter. Escape from the system is related to the load on the first filter, not to the aerosol concentration challenging the first filter. Material escaping the system is, therefore, continuous once the first filter is loaded.

Perfusion Impactor

Patent No. 4,012,209, entitled "Liquid Film Target Impingement Scrubber," was issued on March 15, 1977. The abstract is as follows:

An improved liquid film impingement scrubber is provided wherein particulates suspended in a gas are removed by jetting the particle-containing gas onto a relatively small thin liquid layer impingement target surface. The impingement target is in the form of a porous material which allows a suitable contacting liquid from a pressurized chamber to exude therethrough to form a thin liquid film target surface. The gas-supported particles collected by impingement of the gas on the target are continuously removed and flushed from the system by the liquid flow through each of a number of pores in the target.

10.8 DISTRIBUTION EQUILIBRIA

The study of distribution equilibria has been concerned mainly with three classes of solvent extraction reagents: CMPs, crown ethers, and alkyl sulfoxides.

The extraction of americium from nitric acid systems by two different CMPs has been investigated in some detail. The power dependence of the americium extraction coefficient on the concentration of DHDECMP in a mixed aliphatic-aromatic diluent was found to be 3.2. For DEHDECMP in the same diluent, the reagent dependence for americium extraction was 2.5 power. These data suggest that, on the average, three extractant molecules are associated with each americium atom and that the more highly branched DEHDECMP is somewhat sterically hindered in formation of the adduct with americium nitrate. The americium extraction coefficient ($D_{Am} = [Am]_{org}/[Am]_{aq}$) for 0.9 *M* dibutyl[(diethylcarbamoyl)methyl] phosphonate (DBDECMP) in diethylbenzene increases with nitric acid concentration over the range 1 to 10 *M* but the rate of change, $\Delta D_{Am}/\Delta[HNO_3]$, decreases as the nitric acid concentration increases. When the nitrate concentration is increased at constant acid concentration, the increase in D_{Am} is augmented and the slope increases.[17]

A study of the dependence of KCl extraction on the concentration of 2-ethylhexanol or nonylphenol added to a benzene solution of crown ether as an anion solvating agent shows an approximate first-power dependence on the additive concentration. In such a system, potassium extraction is also first-power-dependent on the crown ether concentration (dicyclohexyl-18-crown-6), suggesting a 1:1:1 additive–crown ether–potassium salt compound in the organic phase.[18]

In evaluating the alkyl sulfoxides for use as possible alternatives to TBP in the Purex process, we found that DEHSO extracts uranium and plutonium somewhat more strongly than does TBP and separates these elements from thorium, iron, and the trivalent lanthanides and actinides more effectively than does TBP under the same conditions. Ruthenium is extracted about the same as with TBP, while palladium, platinum, and gold are extracted more strongly. Reagent dependence studies suggest that two sulfoxide molecules are associated with each extracted uranium atom. Figure 10.3 compares the extraction of uranium by DEHSO with results for TBP under similar conditions.

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

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

ORNL DWG 77-662

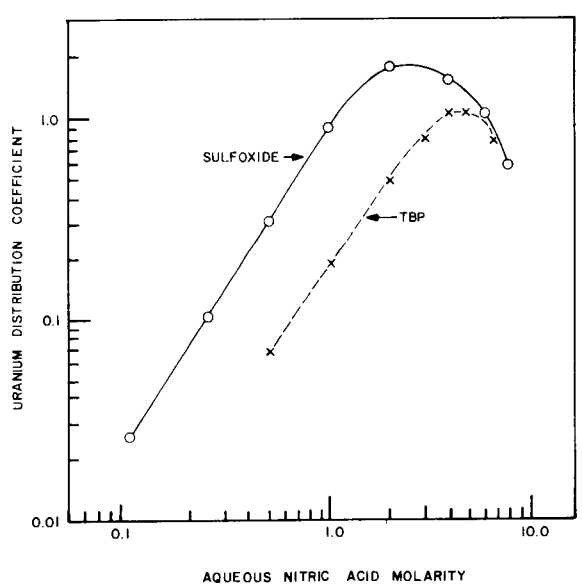

Fig. 10.3. Extraction of uranium by 0.1 *M* di(2-ethylhexyl) sulfoxide in toluene as a function of nitric acid concentration compared with 0.1 *M* TBP.

11. Biomedical Technology

The development of instrumentation for measurements in clinical medicine would, at first glance, seem to be somewhat out of place in a division whose main forte is engineering technology. However, the multidisciplinary nature of this division's staff provides a rather unique environment for the germination of new ideas and concepts in analytical instrumentation. In addition, the resulting instrumentation is, in many cases, providing new and useful information to areas outside of clinical medicine.

11.1 ADVANCED ANALYTICAL TECHNIQUES

High-resolution liquid chromatography provides the degree of specificity needed to accurately evaluate the significance of molecular entities as potential biochemical markers of disease. The availability of new chromatographic supports has enabled this useful tool to be applied to the separation of high-molecular-weight proteins including isoenzymes.

Engineering Development

Engineering efforts were concentrated on two projects having potential for near-term application. These were: (1) the completion of a semiautomated system for the preparation of blood samples, and (2) the development of a system for the separation and direct monitoring of isoenzymes.

System for preparing blood samples. A fourth-generation prototype system for the preparation of plasma, washed erythrocyte, and hemolysate fractions from whole blood was fabricated. An improved mechanical drive system utilizing a clutch-brake assembly was constructed to facilitate the resuspension of packed cells and thus improve their washing. A new swinging-bucket sample ring was designed to improve the loading and unloading of cryovials for collection of hemolysate fractions. A simple wash station was fabricated which uses individual water jets to dislodge packed cellular debris from each of the 24 chambers of the cell-washing rotor. The complete system was transferred to the Human Genetics Department at the University of Michigan for further evaluation.

High-resolution chromatography of macromolecules. Recently, controlled-pore glass (CPG) has become available with a thin layer of glycerol polymer chemically bonded to its surface and ion exchange groups such as diethylaminoethanol (DEAE) attached to this polymer skin. The glycerol coating almost completely eliminates the usual adsorption and subsequent denaturation of proteins on glass surfaces, and the ion exchange groups enable high-resolution separation of macromolecules with similar structures such as the three isoenzymes of creatine phosphokinase (CPK).

Chromatographic separation of isoenzymes is certainly not new; however, we are attempting to couple rapid separation of the three isoenzymes of CPK on CPG-glycophase-DEAE with continuous-flow detection of activity. The detection system utilizes a coupled sequence of enzymatic reactions which ultimately result in the generation of reduced nicotine adenine dinucleotide phosphate proportional to the CPK activity. Sensitive monitoring is provided by an ORNL flow fluorometer. We have demonstrated the separation of these three isoenzymes (CPK-MM, CPK-MB, CPK-BB) in 30 min on reference sera containing them.

Analytical Applications

High-resolution liquid chromatography is being used to measure the protein-bound carbohydrates mannose, galactose, fucose, and sialic acid in sera from patients with breast cancer.[1,2] The purpose of this work is to determine if changes in the concentrations of these

1. J. E. Mrochek, S. R. Dinsmore, and T. P. Waalkes, "Liquid-Chromatographic Analysis for Neutral Carbohydrates in Serum Glycoproteins," *Clin. Chem.* **21**, 1314 (1975).

2. J. E. Mrochek, S. R. Dinsmore, D. C. Tormey, and T. P. Waalkes, "Protein-Bound Carbohydrates in Breast Cancer. Liquid Chromatographic Analysis for Mannose, Galactose, Fucose, and Sialic Acid in Serum," *Clin. Chem.* **22**, 1516 (1976).

potential biochemical markers can predict or be correlated with physical changes in the state of the neoplasm.

Analyses for the protein-bound carbohydrates were used to compare a group of 20 normal women with 22 pretreatment breast-cancer patients. In addition, radioimmunoassays for carcinoembryonic antigen (CEA), another biochemical marker of cancer, were available[3] for the 22 cancer patients. (CEA measurements were not performed on this group of normal women.)

For this group of pretreatment cancer patients, 95% (21 out of 22) were found to have concentrations of fucose and sialic acid above the upper limit ($+2\sigma$, 95% confidence) for normal women. On the other hand, CEA was elevated above normal limits (>2.5 ng/ml for nonsmokers) in only 64% (14 out of 22) of these same patients. Figure 11.1 illustrates the rather large differences between the group of normal women and the 22 patients based on their fucose and sialic acid analyses. It also shows clearly the abnormality of those patients having CEA assays within the normal range (<2.5 ng/ml).

3. Data provided by Dr. T. P. Waalkes, Johns Hopkins University Hospital, Baltimore, Md.

11.2 DEVELOPMENT OF THE CENTRIFUGAL FAST ANALYZER

Development of the new portable Centrifugal Fast Analyzer (CFA) has continued with the fabrication of the first fully operational instrument. The capability of this analyzer to monitor fast reactions (0.1 to 2 sec) was successfully demonstrated. A continuation of developmental efforts on analytical applications of CFA technology has resulted in the adaptation of kinetic assays for leucine aminopeptidase, 5′-nucleotidase, and two isoenzymes of creatine phosphokinase. A new turbidimetric method for sensitive measurement of sulfate has been tested and is showing promise as a useful field assay for this environmental pollutant.

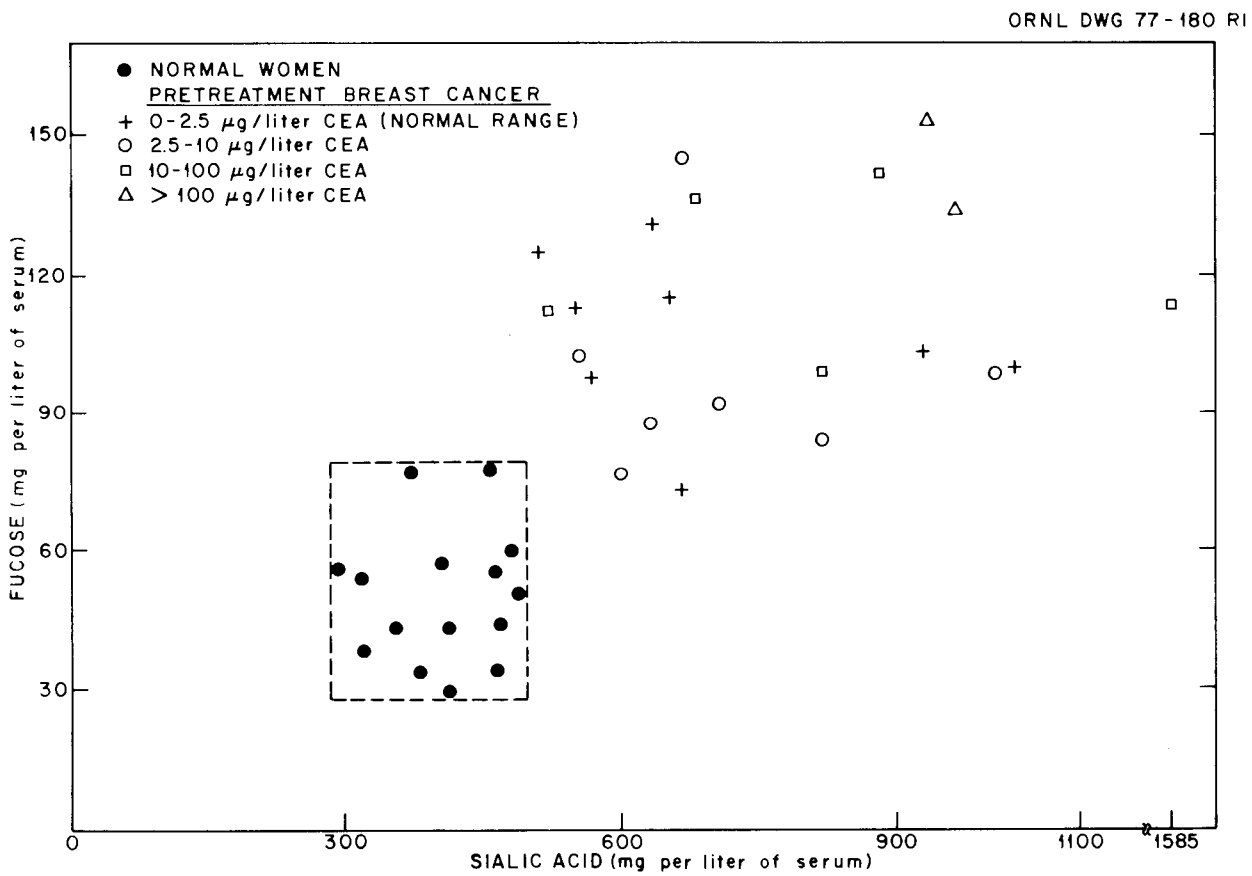

Fig. 11.1. Protein-bound fucose and sialic acid in pretreatment breast-cancer patients as a function of their serum CEA concentrations.

Engineering Development

A production prototype of the portable CFA was fabricated for use by the Environmental Sciences Division. This instrument, a new development in CFA technology, was introduced in the previous annual report[4] with a brief description of the first prototype system. This analyzer differs in a number of important details from the miniature CFA,[5] a previous ORNL development which has just recently entered the commercial market as a new product.[6] These differences include: (1) the use of a clutch-brake assembly to enable rapid acceleration and braking of the plastic rotor, (2) the use of a microcomputer to allow the complete instrument to be made easily portable, (3) the incorporation of a driven filter-bar assembly for both the transmission and the fluorescence light sources to enable multiple wavelengths to be monitored during a single analysis, and (4) the use of a new temperature control system which has a PID (proportional, integral, and derivative modes) controller and a thermoelectric heat pump to regulate rotor temperature at one of three setpoints (25, 30, or 37°C).[7]

Several of the functional capabilities of the new portable CFA were evaluated under laboratory-use conditions to measure overall accuracy and precision. The optical system was evaluated for linearity by measuring the absorbances of eight concentrations of reduced nicotine adenine dinucleotide at 340 nm. Measured under varying conditions of rotor speed (1000, 2000, and 3500 rpm) and signal averaging (1, 4, and 16 revolutions averaged), the data were linear with a correlation coefficient of 0.9999 and a relative standard deviation of 0.59% in slope. The temperature control system was studied using a special rotor containing a thermistor in one of the cuvets. Equilibration times of 4 and 6 min provided adequate preheating to achieve setpoints of 30 and 37°C respectively. After liquid transfer, temperatures within the single cuvet were within ±0.07 and ±0.14°C of the two nominal setpoints over a 6-min period.

One of the more exciting capabilities of the new portable CFA is its ability to monitor rapid kinetic reactions. This capability was demonstrated by monitoring the rate of formation of 12-molybdophosphoric acid from phosphate and Mo(VI). This reaction, substantially completed within 3 sec at low acid concentrations (<0.5 *M*), yields rates that are proportional to phosphate concentration. Figure 11.2(*a*) illustrates the actual optical measurements obtained for four concentrations of phosphate over the time span of 78 to 2000 msec after initial solution contact. The excellent linearity of the resulting reaction rates, determined by linear regression on the integral microcomputer, is illustrated in Fig. 11.2(*b*).

4. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1976*, ORNL-5172, p. 46.

5. C. A. Burtis, W. F. Johnson, J. C. Mailen, J. B. Overton, T. O. Tiffany, and M. B. Watsky, "Development of an Analytical System Based around a Miniature Fast Analyzer," *Clin. Chem.* **19**, 895 (1973).

6. The IL Multistat III Micro Centrifugal Analyzer, a product of Instrumentation Laboratory, Inc. Lexington, Mass.

7. J. E. Mrochek, C. A. Burtis, W. F. Johnson, M. L. Bauer, D. G. Lakomy, R. K. Genung, and C. D. Scott, "A New Portable Centrifugal Analyzer with Expanded Versatility," *Clin. Chem.* **23**, 1416 (1977).

ORNL DWG. 77-1159 R1

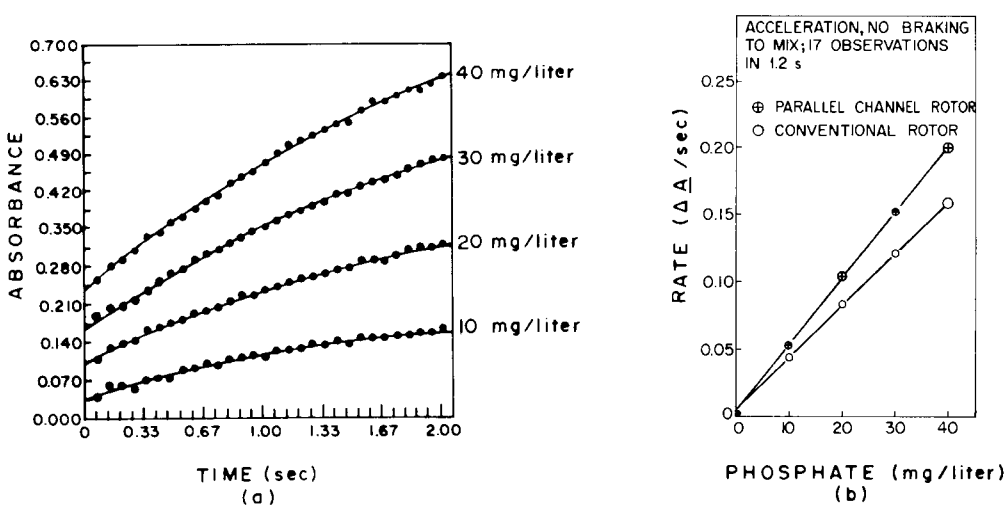

Fig. 11.2. (*a*) Data acquired on the portable CFA for the kinetically fast reaction of phosphate with molybdate; (*b*) rates obtained by linear regression on the portable CFA for the data shown in (*a*).

Analytical Applications

Adaptation of additional kinetic assays of enzyme activity continues to provide clinical information in the diagnosis and study of disease. Procedures were adapted for the assay of leucine aminopeptidase and 5′-nucleotidase on the CFA. These assays, in conjunction with assays of alkaline phosphatase and γ-glutamyl transferase, were evaluated as potential biochemical markers of liver metastasis in cancer patients. Results suggested that this battery of enzyme assays would be extremely useful in confirming the spread of malignancy to this vital organ.[8]

A literature procedure[9] for the measurement of the isoenzymes of CPK was adapted to the CFA and evaluated for its efficacy in measuring the isoenzyme of CPK (CPK-MB) that is most prevalent in heart muscle. Elevated activity of this isoenzyme in serum is indicative of a myocardial infarction (MI). Rapid analysis and high precision are important to the utilization of this measurement as a diagnostic aid in confirming MI, and the CFA was able to provide both of these. However, some questions arise concerning the ability of this activation procedure to provide a unique measurement of CPK-MB.[10]

In addition to its well-known utility for clinical measurements, the CFA also has many potential applications to the field of environmental analysis. A turbidimetric method for the rapid assay of sulfate, using 2-aminoperimidine,[11] was adapted for use on the CFA. The method was found to be useful for sulfate concentrations ranging from about 4 to 20 mg/liter and had a precision of better than 3% on the CFA. An enzyme amplification procedure was developed for the extremely sensitive kinetic measurement of ATP + ADP (adenosine phosphates) at concentrations as low as 80 ng/ml (as ATP). For reaction concentrations in the range of 0.5 to 2.5 mg/liter, the average precision of this method was approximately 0.7%. The adenosine phosphate compounds are useful for the measurement of microbial biomass and microbiological activity.

8. J. E. Mrochek and W. D. Bostick, *Chemical Profile of Body Fluids, Progress Report for January 1, 1976, to December 31, 1976* (unpublished annual report submitted to the National Cancer Institute).

9. P. S. Rao, J. J. Lukes, S. M. Ayres, and H. Mueller, "New Manual and Automated Method for Determining Activity of Creatine Kinase Isoenzyme MB, by Use of Dithiothreitol: Clinical Applications," *Clin. Chem.* **21**, 1612 (1975).

10. W. D. Bostick and J. E. Mrochek, "Evaluation on the Centrifugal Fast Analyzer of a Chemical Activation Procedure for Creatine Kinase MB Isoenzyme," *Clin. Chem.* **23**, (in press).

11. P. A. Jones and W. I. Stephen, "The Indirect Spectrophotometric Determination of Sulphate Ion with 2-Aminoperimidine," *Anal. Chim. Acta* **64**, 85 (1973).

12. Environmental Studies

During this report period, our efforts relative to the development of environmental monitors, the isolation of soluble organic constituents and pollutants, and the determination of chlorination effects on cooling waters were continued. In addition, a program funded by the Environmental Protection Agency to investigate the chemical effects of disinfection treatment of wastewaters was initiated.

12.1 ENVIRONMENTAL MONITORING

The development of continuous monitoring systems for sensitive on-site monitoring of dissolved aquatic pollutants constitutes a very practical, necessary approach to one facet of our growing concern for the perturbation in our environment caused by various anthropogenic energy sources. The objective of this program is the development of such monitoring systems through the design, fabrication, and evaluation of prototype instruments. Two instruments have been developed: (1) a continuous chemical oxygen demand (CCOD) monitor that is particularly sensitive to phenolic compounds, and (2) an inexpensive flow fluorometer for monitoring dissolved polynuclear aromatic hydrocarbons (PAH). Both instruments have been incorporated into a single system for monitoring waste streams from coal processing plants.

The CCOD monitor is based on cerate oxidimetry, that is, the measurement of the fluorescent Ce(III) resulting from the reduction of Ce(IV) by any oxidizable compound in the stream being monitored. Instrumental parametric studies were continued. During this report period, it was determined that, although the sensitivity of the CCOD monitor increases with decreasing cerium concentration (0.5 to 5 m*M*) in the fluorescent, the linear range and instrument response to higher sample concentrations decrease with a decrease in the ratio of reagent concentration to sample concentration. This dichotomy is overcome by diluting the sample-reagent mixture just before it enters the fluorometer.

Since many of the organic contaminants (particularly PAH) found in wastewaters and the aquatic environment are strongly fluorescent, an inexpensive, continuous-flow fluorometer for monitoring aquatic pollutants is being developed. Two different instrumental concepts are being investigated: (1) a bifurcated quartz fiber optic (BFO) fluorometer; and (2) a small, conventional, right-angle fluorometer with a quartz tube flow cell. During this report period, we have concentrated on using the fluorometers as monitors for dissolved PAH, since they are both highly fluorescent and potentially very hazardous even at very low concentrations.

Initially, a qualitative study of the relative solubilities and fluorescences of 24 PAH was made by dissolving each compound in methanol, diluting with distilled water until no precipitation occurred, and measuring the fluorescence of the resulting solutions with a fluorometer, using 254-nm excitation and a 0.53 Corning filter as the secondary filter. The four most highly fluorescing compounds were detectable at 0.1 μg/liter, 11 were detectable at 1 μg/liter, three had measurable fluorescence at 10 μg/liter, and the remainder either were insoluble or had no measurable fluorescence at their maximum solubility.

Both the CCOD monitor and the flow fluorometer have been incorporated into a prototype aquatic environmental monitor (Fig. 12.1) initially for use in monitoring the COD and PAH levels in treated aqueous effluent from a coal conversion process. It has also been used to determine the level of pollution of secondary sewage effluent from the Oak Ridge East Wastewater Treatment Plant before and after chlorination. The effluent was found to contain 9 μg per ml of COD both before and after chlorination, but the fluorescence was reduced $\sim$20% by chlorination.

12.2 POLLUTANT IDENTIFICATION

The major objectives of this program are: (1) to develop methodology for the analysis of organic constituents present at microgram-per-liter concentrations in complex mixtures in aqueous solutions, and (2) to obtain qualitative and quantitative information about

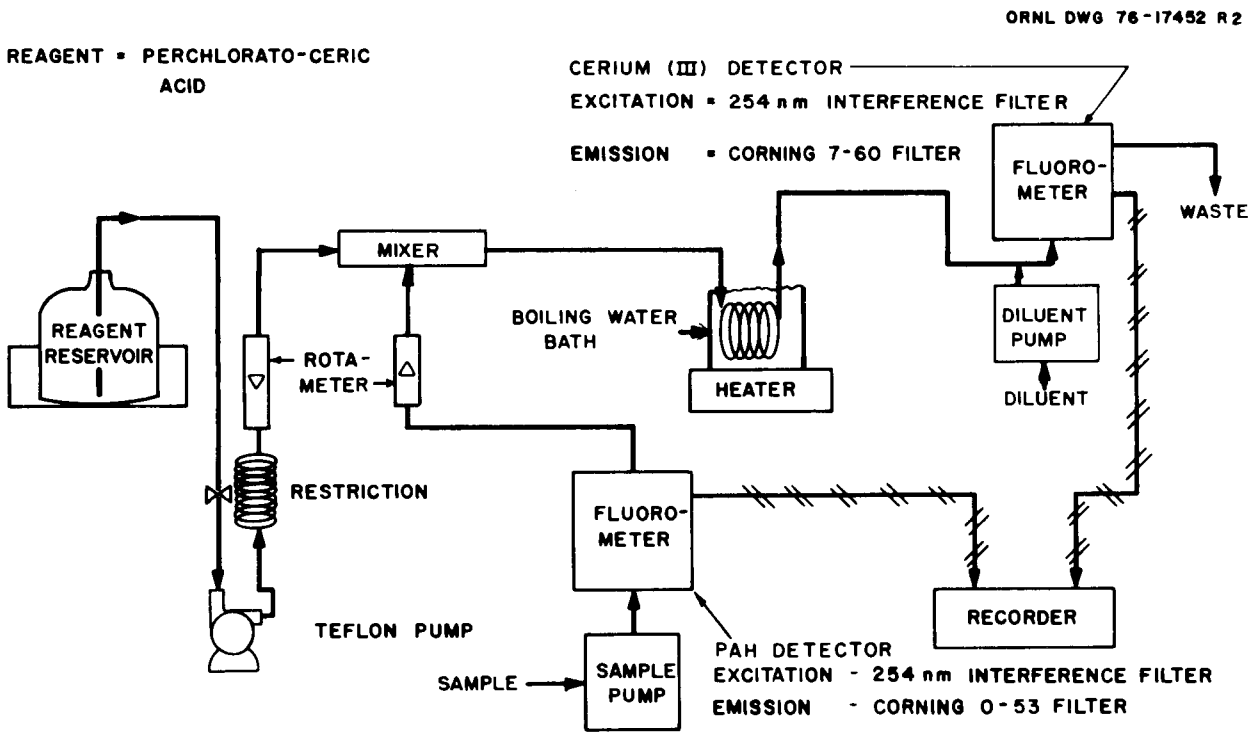

Fig. 12.1. Prototype aquatic environmental monitor.

the identity and concentration of organic pollutants in waters of environmental concern. High-pressure liquid chromatography (HPLC) is the principal separations method used in this research. Separated constituents are processed through a multicomponent analytical scheme for the determination of chemical structure and quantitation.[1,2] Data generated from this program will facilitate determination of possible health and environmental effects associated with consumption or use of polluted waters and aid in development of water treatments for removal of hazardous pollutants.

Coal hydrocarbonization process. A bench-scale study of the coal hydrocarbonization process is being conducted in the Chemical Technology Division.[3] As part of this study, the organic constituents in the aqueous stream from the product scrubber are being characterized. Samples were collected for analysis during a hydrocarbonization experiment in which the following run conditions were used: average bed temperature, 1030°F; total pressure, 150 psig; hydrogen partial pressure, 122 psig; coal feed rate, 16.3 lb/hr or 13.6 lb/hr on a moisture-and-ash-free basis (maf); hydrogen feed rate, 0.18 scf/lb of maf coal. A 10-ml aliquot of the aqueous sample was chromatographed on the preparative-scale UV-Analyzer.[1] Over 100 uv-absorbing constituents were detected and separated on the HPLC chromatogram. Initial use of gas chromatography (GC) and mass spectrometry (MS) on separated constituents resulted in the identification of 18 constituents (Table 12.1) and the characterization of 25 additional constituents. The identified constituents were principally phenolic and were present in concentrations in the original sample ranging from less than 1 mg/liter to approximately 2000 mg/liter. The total dissolved organic carbon in the original sample was 9250 mg/liter. Several of the substituted pyridines and carbazole were identified only by interpretation of GC/MS data. Refer-

1. R. L. Jolley, S. Katz, J. E. Mrochek, W. W. Pitt, Jr., and W. T. Rainey, "Analyzing Organics in Dilute Aqueous Solutions," *Chem. Technol.* **1975**, 312–18 (1975).

2. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1976*, ORNL-5172, pp. 52–53.

3. *Ibid.*, pp. 65–77.

Table 12.1. Soluble organic constituents in an aqueous sample from the product scrubber of a bench-scale hydrocarbonization unit

Constituent	Identification method[a]	Concentration (mg/liter)	
		FID[b]	Prep. AC[c]
Dimethyl- or ethyl-substituted hydroxypyridine	MS	20	
Methyl carbazole	MS	4	
Hydroxypyridine	GC,MS	10	
Methylhydroxypyridine	MS	10	
Palmitic acid	GC,MS	0.3	
Oleic acid	GC,MS	0.2	
Linoleic acid	GC,MS	0.2	
Stearic acid	GC,MS	0.8	
Substituted pyrimidine (mol. wt = 112)	GC,MS	0.7	
Catechol	AC,GC,MS		∿1700
Hydroquinone	AC,GC,MS	4	7
Resorcinol	AC,GC,MS	29	30
Methylresorcinol	AC,GC,MS		∿2000
Orcinol	AC,GC,MS		∿2000
Methylcatechol	AC,GC,MS	11	30
C_2-Substituted dihydroxybenzene	MS	<1	
C_3-Substituted dihydroxybenzene	MS	<1	
C_4-Substituted dihydroxybenzene	MS	<1	

[a]AC – anion exchange chromatographic elution time; GC – gas chromatographic retention time; MS – mass spectrum.

[b]Based on flame ionization detector response during gas chromatography.

[c]Based on uv absorbance of the preparative-scale HPLC peak.

ence standards for these compounds are being obtained for comparative purposes.[4,5]

Cursory examination of the literature revealed little information concerning the toxic effects of hydroxy- and substituted hydroxypyridines that are identified in this research. However, phenolic compounds are known toxicants.[6,7] Continuing identification efforts and analytical studies are planned on aqueous process streams from coal liquefaction processes.

Organics in drinking water. Relatively few data exist concerning the identities and concentrations of nonvolatile organics in drinking water, although the major portion of dissolved organics in potable waters consists of nonvolatile organics.[8] Because of the determination that toxic halogenated organic compounds are formed during the chlorination of drinking water, some investigators have expressed concern that nonvolatile organics, either chlorinated or unchlorinated, may have similar toxic properties.[9] Thus several preliminary studies have been made of drinking water using ion exchange car-

4. R. L. Jolley, W. W. Pitt, Jr., and J. E. Thompson, "Organics in Aqueous Process Streams of a Coal-Conversion Bench-Scale Unit Using the Hydrocarbonization Process: HPLC and GC/MS Analysis," pp. 25–28 in *Proceedings of the 23d Annual Technical Meeting of the Institute of Environmental Sciences,* Los Angeles, Calif., Apr. 25–27, 1977.

5. W. W. Pitt, Jr., R. L. Jolley, and G. Jones, "Characterization of Organics in Aqueous Streams of Coal Conversion Processes," to be presented at the Second Pacific Chemical Engineering Congress (Pachec '77), Denver, Colo., Aug. 28–31, 1977 (to be published in *Proceedings*).

6. P. G. Stecher, ed., *The Merck Index,* 8th ed., Merck & Co., Inc., Rahway, N.J., 1968.

7. R. I. Freudenthal, G. A. Lutz, and R. I. Mitchell, *Carcinogenic Potential of Coal and Coal Conversion Products,* A Battelle Energy Program Report, Battelle-Columbus Laboratories, Columbus, Ohio, 1975.

8. A. A. Rosen, "The Foundations of Organic Pollutant Analysis," pp. 3–14 in *Identification and Analysis of Organic Pollutants in Water,* ed. L. H. Keith, Ann Arbor Science, Ann Arbor, Mich., 1976.

9. A. A. Stevens, C. J. Slocum, D. R. Seeger, and G. G. Robeck, "Chlorination of Organics in Drinking Water," pp. 85–114 in *Proceedings of the Conference on The Environmental Impact of Water Chlorination,* CONF-751096, ed. R. L. Jolley, 1976.

tridges for concentration of the organics and HPLC for separation and detection.[2,10]

In a preparative-scale high-resolution chromatographic separation of the organics adsorbed and concentrated from a 40-liter aliquot of chlorinated drinking water from an East Tennessee municipal drinking water plant using anion and cation exchange cartridges, only one uv-absorbing constituent was detected, although several cerate oxidizable peaks were detected and separated. Using the multicomponent identification method,[1,2] phosphate, glycerine, *O*-methylinositol, benzoic acid, palmitic acid, oleic acid, linoleic acid, and stearic acid were identified among the separated constituents. In addition, ten unknown constituents were characterized with respect to GC/MS properties.[10]

Waterborne goitrogens are being investigated as causative factors of endemic goiter in western Colombia. In collaboration with Dr. Eduardo Gaitan of Colombia, several methanol and ether extracts of well water from Candelaria, Colombia, were examined by HPLC and GC/MS. Nine organics were characterized. However, although compared with several library files of mass spectral data, none were identified.[10]

12.3 ENVIRONMENTAL EFFECTS OF ANTIFOULANTS

Chlorine is the principal biocide for antifoulant treatment of cooling systems for electric power generating plants. Chloro-organics are formed during the chlorination of cooling waters and process effluents.[11] Cumming and co-workers have shown that 5-chlorouracil, a chloro-organic reaction product, is incorporated into the DNA of bacteria and mice.[12,13] Thus bioaccumulation and incorporation of the chloro-organic reaction products in the biota are a matter of environmental concern. Therefore, two test species, *Chironomus* sp. and *Corbicula* sp., have been selected for preliminary examination. Sixty grams of *Chironomus reparius*, the bloodworm below the chlorinated sewage outfall of the Oak Ridge West Wastewater Treatment Plant, was collected. The DNA was separated from the 60-g sample and hydrolyzed. Cation exchange chromatography of the DNA hydrolysate indicated that the nucleoside 5-chlorodeoxyuridine was not present. This experiment will be repeated because of gross RNA nucleoside contamination that made it difficult to draw definitive conclusions concerning incorporation of 5-chlorouracil from the chlorinated wastewater into the DNA of the test species. This work was a collaborative effort with personnel of the Environmental Sciences Division and the Biology Division.[10] Methods of examination for incorporation of other classes of chemical compounds (e.g., nonpolar fat-soluble chloro-organics) are being developed.

In the analytical phase of this program, the concentration method using adsorption on anion and cation exchange resin cartridges has been evaluated in several tests with 40-liter aliquots of chlorinated cooling water. Although the method has potential, it is being discontinued in favor of vacuum concentration. Satisfactory development of this alternative concentration method requires a greater demand of time and funding than can presently be allocated. Organics separated from a concentrate of a 40-liter aliquot of the chlorinated cooling water from the Kingston Steam Plant are being processed through the multicomponent identification procedure. A Hall electrolytic conductivity detector is being used to monitor the gas chromatographic separations for halogenated compounds.

12.4 CHEMICAL EFFECTS OF DISINFECTANTS

The severity of waterborne diseases and disease epidemics has been greatly reduced because of the use of disinfection treatment of wastewater and potable waters. Principal disinfectants in the last half century have been chlorine and ozone. It has only been recently established that chloro-organics are formed during the disinfection of wastewater effluents and potable waters with chlorine.[11] Because of these findings and the possible harmful effects of exposure to chlorinated organics, considerable interest has arisen in the use of alternatives to chlorine such as ozone or irradiation with ultraviolet light. The objective of this program, funded by the U.S. Environmental Protection Agency, is to characterize the nonvolatile organics in wastewater effluents which have been disinfected with either chlorine, ozone, or ultraviolet light. The organics would be characterized chemically, that is, identified and

10. R. E. Leuze et al., *Experimental Engineering Sect. Semiannu. Prog. Rep. Sept. 1, 1976–Feb. 28, 1977,* ORNL/TM-6022 (in preparation).

11. R. L. Jolley, ed., *Proceedings of the Conference on the Environmental Impact of Water Chlorination,* CONF-751096, 1976.

12. R. B. Cumming, D. L. George, M. F. Walton, and B. J. Elmhorst, "Mutations Produced by 5-Chlorouracil and 5-Bromouracil in *Escherichia coli,*" pp. 135–36 in *Biol. Div. Annu. Prog. Rep. June 30, 1975,* ORNL-5072.

13. R. B. Cumming, B. C. Pall, M. F. Walton, and W. L. Russell, "Studies on Potential Effects of 5-Chlorouracil in Mammals," pp. 134–35 in *Biol. Div. Annu. Prog. Rep. June 30, 1975,* ORNL-5072.

quantified where possible, and screened for mutagenic activity.

Initial efforts have been directed toward establishing parameters for ozonation of secondary effluent from wastewater treatment plants. In the typical secondary effluent from the Oak Ridge East Wastewater Treatment Plant, an ozone dose of approximately 14 mg of ozone per liter of effluent is required for ≥99.99% bacterial kill (Fig. 12.2).

Large differences were detected between high-resolution anion exchange chromatograms of concentrates of unozonated wastewater effluent and those that had been ozonated for 5-, 15-, and 30-min periods with an ozone gas concentration of 6 mg per liter of oxygen gas. This treatment resulted in total doses of 0.7, 3.5, and 6.9 mg of ozone per liter of wastewater effluent. The chromatograms of the uv-absorbing and the cerate-oxidizable constituents in the control sample and the ozonated samples are shown in Figs. 12.3 and 12.4.[14]

14. S. Katz and W. W. Pitt, Jr., "A New Versatile and Sensitive Monitoring System for Liquid Chromatography: Cerate Oxidation and Fluorescence Measurement," *Anal. Lett.* 5(3), 177–85 (1972).

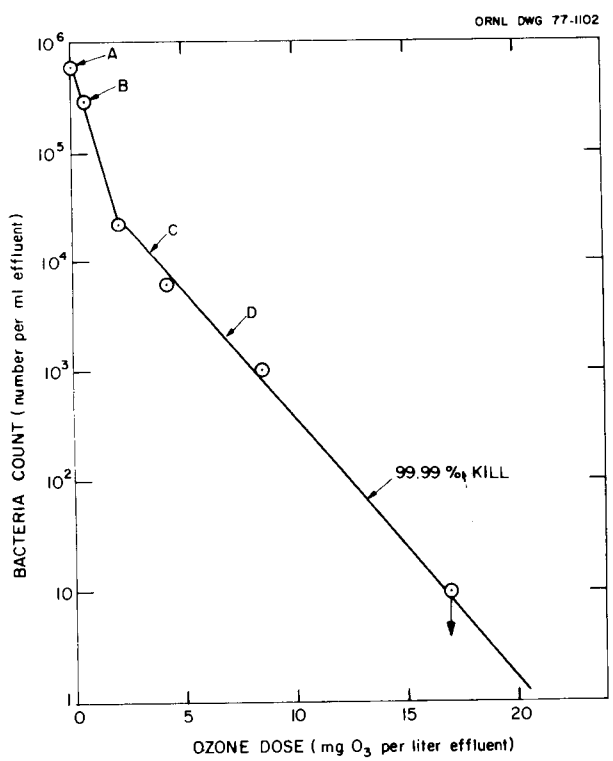

Fig. 12.2. Disinfection of secondary effluent with ozone.

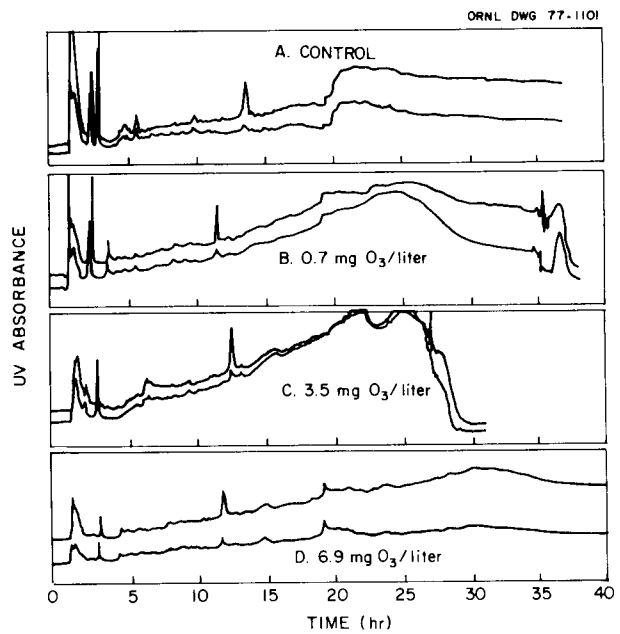

Fig. 12.3. Comparison of uv-absorbing constituents in secondary effluent sample with samples disinfected with ozone. Sample *A* is the unozonated control. Samples *B*, *C*, and *D* were ozonated at ozone doses of 0.7, 3.5, and 6.9 mg/liter respectively. Chromatograms were determined for 1.0-ml aliquots of 2500-fold concentrates using standard UV-Analyzer chromatographic procedure (ref. 2).

The ozone dosages of these samples are labeled *A*, *B*, *C*, and *D* on Fig. 12.2 for comparative purposes.

It is apparent that ozone initially reacts with organic constituents that are probably of a higher molecular weight and are not separated in this chromatographic procedure, although some may be associated with the first chromatographic peak. The higher-molecular-weight constituents are broken down into smaller-molecular-weight fragments that are separated chromatographically and detected as uv-absorbing and oxidizable peaks. As ozonation proceeds, these, in turn, are oxidized and decomposed. These chemical reactions may compete with the disinfection process, as indicated by correspondence of the inflection in the disinfection curve shown in Fig. 12.2, with apparent maximum concentrations of chromatographic constituents indicated in Figs. 12.3 and 12.4.

Future studies will further define nonvolatile reaction products of ozonation, chlorination, and uv irradiation during the disinfection of secondary effluents from several wastewater treatment plants. Tests for mutagenic activity will be initiated on these reaction products.

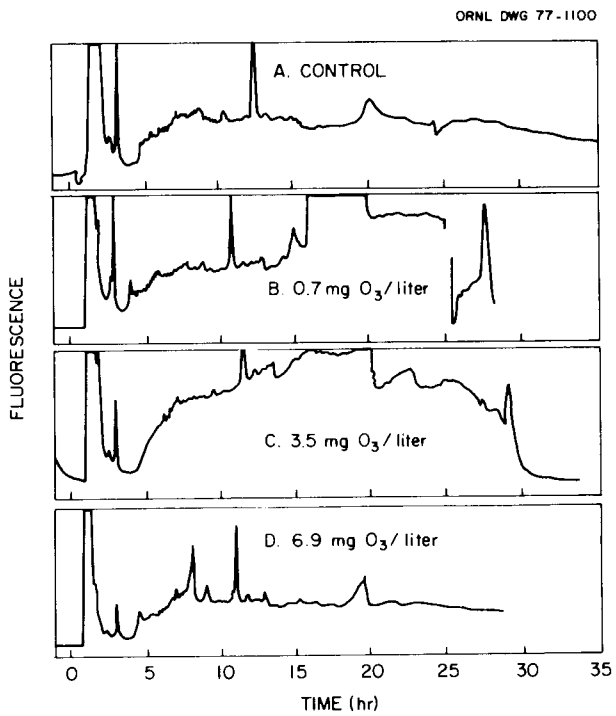

Fig. 12.4. Comparison of oxidizable constituents in a secondary effluent sample with samples disinfected with ozone. Sample *A* is the unozonated control. Samples *B*, *C*, and *D* were ozonated with ozone doses of 0.7, 3.5, and 6.9 mg/liter respectively. Chromatograms were determined for 1.0-ml aliquots of 2500-fold concentrates using standard cerate oxidimetry chromatographic procedure (ref. 14).

12.5 ASSESSMENT OF ENVIRONMENTAL CONTROL TECHNOLOGY FOR COAL CONVERSION PROCESSES

In order to commercialize the production of clean (i.e., low-sulfur) boiler fuel for coal, ERDA has contracted to develop various coal conversion processes to the demonstration scale. This assessment program represents an attempt to define the wastewater problem for a commercial hydrocarbonization plant. The disposal of wastewater from coal conversion plants will not be a trivial problem. Approximately 80 large (12,000 to 20,000 tons/day) coal conversion plants will be required to meet a goal of replacing 20% of the present U.S. oil consumption with clean fuels from coal.[15] A coal conversion industry of this size would produce a very large amount of wastewater (400×10^6 to 800×10^6 tons/year).

15. C. E. Jahnig and R. R. Bertread, "Environmental Aspects of Coal Gasification," *Chem. Eng. Prog.* **72**(8), 51 (1976).

Hydrocarbonization is a likely process for commercialization for three main reasons: (1) only premium, low-sulfur gaseous and liquid products are produced; (2) hydrocarbonization is a noncatalytic process; and (3) no difficult solid-liquid separation is utilized. For these reasons, an environmental evaluation of hydrocarbonization is a timely project.

Aqueous wastes from coal conversion are often compared with their counterpart in the coke production industry. For this reason, the phenolic and light oil components of the waste are characterized and have, in general, been well-considered. Hydrocarbonization will produce greater quantities of these pollutants and will have more serious ammonia, hydrogen sulfide, and trace-element problems.

Some 71 process streams involved in a typical hydrocarbonization process have been identified, and their potential for wastewater management has been evaluated. Of these, 15 wastewater streams were singled out, and coal conversion literature was surveyed for the purpose of predicting the characteristics of these streams. Theoretically, many of the wastewater streams will be completely recycled internally, and this may not be of concern. Others are fairly well-defined, and adequate chemical technology exists to bring these streams into compliance with any reasonable regulations.

However, a number of streams are not well-characterized, either in quantity of flow or in pollutant content. This is particularly true of the organic content (PAH, phenols, etc.) of the cooling tower streams and the trace-element content of the ash slurry to the ash pit. These streams will also be the ones that will most likely present some problems in the application of adequate cleanup technology. Therefore, the following recommendations have been given:

1. Additional research should be conducted on the characterization of critical wastewater streams including: (*a*) coal storage and plant runoff; (*b*) water streams from the hydrocarbonization reactor, ammonia stripping, and condensate from the hydrocarbon separation unit; and (*c*) ash and slag quenching and sluicing water and leachate from stored ash and slag.
2. Additional reliability studies should be made to quantify leak rates through the many heat exchangers that will be needed in a coal conversion plant.
3. Future research studies should be performed to determine site effluent limits of PAH and a variety of trace elements. This should be done from the

standpoint of the best available technology, as well as based on the relative hazards of the potential pollutants.

In addition, existing federal effluent guidelines have been surveyed in order to anticipate effluent guidelines for future conversion plants. Table 12.2 summarizes both the anticipated federal effluent guidelines and the related process data.[16]

16. J. A. Klein and R. E. Barker, "Assessment of Environmental Control Technology for Hydrocarbonization," paper to be presented at the Second Pacific Chemical Engineering Congress (Pachec '77), Denver, Colo., Aug. 28–31, 1977.

A variety of environmental control technologies have been briefly examined for their ability to remove and/or recover quantities of phenolics and other organics, trace elements, and PAH. These technologies include biological oxidation, adsorption (mainly activated carbon), ozonization, coagulation and flocculation, membrane processes (such as reverse osmosis), and solvent extraction. Those systems that appear most promising or that have large gaps in available information will be investigated by a series of screening tests to judge their adaptability to coal conversion wastewater cleanup.

Table 12.2. Summary of hydrocarbonization wastewater data

Effluent parameter	Total waste[a] (kg/day)	Main sources	Maximum concentration (ppm)	Existing treatment technology available	Anticipated regulations (ppm)
pH				Neutralization	6–9
TSS		Coal storage, ash handling, and water treatment	200,000	Clarification sedimentation	3–14
Phenolics	1600–11,000 (may be recovered)	Hydrocarbonization	6,000	Liquid-liquid extraction and biological oxidation (expensive and unproven for coal conversion wastes)	0.03–0.3
Other soluble hydrocarbons (benzene, fatty acids, etc.)	500–1100	Hydrocarbonization	1,000	Liquid-liquid extraction and biological oxidation (expensive and unproven for coal conversion wastes)	BOD 4–30 COD 20–350
Oil and grease	11,000	Leaks, plant washdown, and hydrocarbonization	10,000	Separators	1–6
Dissolved gases (NH_3, H_2S, etc.)	Recovered for sales	Hydrocarbonization and acid gas treatment	NH_3 30,000 H_2S 1,000	Stripping columns	NH_3 0.8 –5 S^{2-} 0.02–0.1
Trace elements		Ash handling and coal storage		None	
Chromium	220		14		0.1–1
Manganese	730		0.2		1
Lead	390		0.04		0.1
Zinc	6120		0.4		1
Other soluble contaminants					
CN^-	9–220	Hydrocarbonization and acid gas treatment	200		0.02–0.1
SCN^-	90–2200		2,000		
PAH	1–23	Hydrocarbonization, leaks, and spills		None	Unknown

[a]Based on 15,000 tons per day of coal.

13. Bioengineering Technology

This program is concerned with the development of biochemical engineering technology whereby individual process steps, at least one of which utilizes a biological entity, can be integrated to result in a highly useful overall process. Areas of concern to ERDA which will benefit directly from this technology include energy production and conservation, resource recovery, and pollution abatement. Investigations specific to problems in nuclear waste management include the removal of radionuclides and chemical contaminants from aqueous process and effluent streams and are discussed in Sects. 5.2 and 5.3. Additional investigations involving bioengineering research and bioprocess development and demonstration are summarized in Sects. 13.1 and 13.2.

13.1 BIOENGINEERING RESEARCH

Bioengineering research activities were focused on two areas during this report period: (1) enzyme catalysis and (2) treatment of aqueous effluents from coal conversion processes.

Investigations associated with the enzyme-catalyzed reduction of water to produce hydrogen included studies of enzyme separation, purification, stabilization, and immobilization. A material designated RPC-5 was used as an adsorbent for various enzymes and proteins (including the ferredoxin-hydrogenase enzyme system) and was found to be quite versatile and effective. Studies were made to elucidate the kinetics of ferredoxin reduction by dithionite, an important step in the ferredoxin-hydrogenase-catalyzed reduction of water by sodium dithionite. The portable Fast Analyzer, discussed in Sect. 11.2, was used to measure the rapid absorbance change as ferredoxin was converted from the oxidized to the reduced state. These experiments demonstrated that the reaction was complete in a few seconds and indicated that it is not the rate-limiting step in the hydrogen evolution reaction.

Studies continued on the biological treatment of aqueous effluents from coal conversion processes. Whereas previous experiments had utilized synthetic feed streams, tests of bacterial phenol and thiocyanate degradation in aqueous waste from the coal hydrocarbonization unit were made in a tapered fluidized-bed bioreactor (TFBBR). The bioreactor contained 1.0 to 1.5 liters of –30 +60 mesh anthracite coal, which served as a surface for bacterial cell adhesion. The reactor vessel had a 1- to 3-in.-diam tapered reaction zone and was 42 in. long. The bed of fluidized coal particles was seeded with 10 g of Phenobac. Initial phenol degradation rates were about 1.5 g day^{-1} $liter^{-1}$ at a space time of 9 min. In some instances the high solids content of the hydrocarbonization scrubber waste necessitated pretreatment by acidification, settling, and filtration.

Additional bioreactor studies were made using a synthetic feed. A new oxygen sparger design was tested in the TFBBR, but there was no detectable improvement in oxygen transfer to the liquid phase. Sea sand was tested as a support material for bacterial cell adhesion, but phenol degradation rates were much lower than those attained using anthracite coal. Also, the thickness of the microbial film coating the particles was much more difficult to control. Reactor comparison tests were made and included packed bed (PBR) and continuous stirred tank (CSTR) designs. Phenol degradation rates were much lower than those achieved using the TFBBR. Also, column plugging was a severe problem with the PBR.

13.2 BIOPROCESS DEVELOPMENT AND DEMONSTRATION

Much progress has been made in the large-scale TFBBR tests and in the Anflow pilot plant at the Oak Ridge East Wastewater Treatment Plant during this report period.

A large-scale TFBBR, consisting of four sections, was fabricated from steel and painted with epoxy. Starting from the bottom, the first tapered section was 8 in. in diameter to 12 in. in diameter by 48 in. long. The second section, which was straight, was 12 in. in diameter by 48 in. long. The third tapered section was 12 in. in diameter to 16 in. in diameter by 48 in. long. The

fourth section consisted of 55-gal drums to catch solid particles if they overflowed. The operating volume of the tapered fluidizing section was 266 liters. Each section was equipped with viewing windows and sample ports (Fig. 13.1).

The initial hydraulic tests using water and coal particles (–30 +60 mesh) indicate excellent fluidization characteristics. The pumping power needed to fluidize the coal particles, indicated by hydraulic pressure drop, is smaller for the larger bioreactor compared with the 1- to 3-in.-diam by 48-in.-long bench-scale TFBBR, because the ratio of the wall friction area compared with the bioreactor volume is smaller in the larger unit. At an average denitrification rate of 40 g of N (NO_3^-) per day per liter, this unit could degrade about 37,000 lb of nitrate per year.

The Anflow demonstration pilot plant was started up on November 12, 1976, at the Oak Ridge East Wastewater Treatment Plant. The pilot plant reactor is a packed column, 1.5 m (5 ft) in diameter and 3.0 m (10 ft) in packed height (Fig. 13.2). It is packed with 25-mm-diam (1-in.) Raschig rings. Both column and packing were manufactured by the Norton Company (Akron, Ohio) as its part of a cooperative effort by ORNL, Norton, and the City of Oak Ridge.

Fig. 13.2. Anflow pilot plant bioreactor.

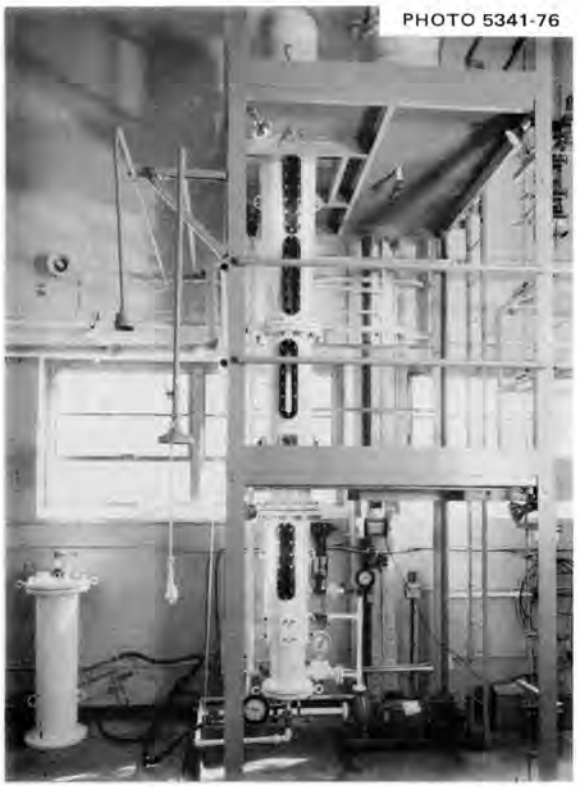

Fig. 13.1. Large-scale tapered fluidized-bed bioreactor.

The column was packed dry and was inoculated by filling it with liquid cattle rumen and a synthetic feed mixture that provided food for the microorganisms during the transition. After the rumen cooled, raw sewage was fed to the column at a rate of 4.0 m^3/day (1100 gal/day).

Since start-up, the performance of the pilot plant has improved greatly. Off-gas has increased to 23 liters/day, and the methane concentration is 20 vol %. Typically, the total carbon concentration in the raw sewage is 125 mg/liter, and 35% is removed by the Anflow column. Total organic carbon is 110 mg/liter with 50% removal, and biochemical oxygen demand "5 days" (BOD_5) is 150 mg/liter with 55% removal. Total suspended solids average 200 mg/liter with 75% removal, and volatile suspended solids are 190 mg/liter with 78% removal.

14. Preparation of UO_2

14.1 RECOVERY OF ^{233}U FROM WASTE UO_2 AND SCRAP UO_2-ThO_2 PELLETS

During this report period the binary scrap dissolver was operated to recover 103 kg of ^{233}U and 3.5 metric tons of thorium from scrap UO_2-ThO_2 pellets generated at the Bettis Atomic Power Laboratory. Ninety-one dissolution cycles were performed using a dissolvent of the composition 12 *M* HNO_3–0.04 *M* F^-–0.10 *M* $Al(NO_3)_3$. The UO_2 dissolver was operated to recover 6.5 kg of ^{233}U in seven dissolutions.

In addition, seven dissolution cycles were made to recover 6.1 kg of uranium and 266 kg of thorium from scrap generated at Nuclear Fuel Services, Inc., Erwin, Tennessee, and stored at ORNL for the past four years.

14.2 ^{233}U PURIFICATION SYSTEMS

Ten runs were conducted in the single-cycle solvent extraction system to purify 232 kg of ^{233}U. The uranium loss to the extraction column raffinate averaged 0.7%, and the thorium contamination in the uranium product ranged from 500 to 2000 ppm. Approximately 200 kg of uranium was purified in eight runs in the high-pressure ion exchange system. Analyses confirmed that no nonrecoverable losses of material occurred during this operation.

14.3 CONVERSION OF ^{233}U FROM NITRATE SOLUTION TO CERAMIC-GRADE DIOXIDE POWDER

A total of 248 kg of ceramic-grade UO_2 powder was prepared. The uranium was processed through the conversion facility in nominal 1.0-kg (uranium) batches. Half of one batch was rejected because of incomplete drying and impurity content.

15. Actinide Oxides, Nitrides, and Carbides

15.1 THERMODYNAMICS OF THE U-C-O SYSTEM

Measurements of CO pressures over UO_2 + $UC_{1.91-x}O_x$ + C were made in the temperature range 1201 to 1774 K. These measurements allowed us to derive the 298 K heat of formation, −86.53 ± 0.2 kJ/mole, and the 298 K entropy, 68.2 ± 2.8 J/K-mole, for $UC_{1.91-x}O_x$. The content of $UC_{1.91-x}O_x$ was found to be sufficiently large that $x \cong 0.1$ at 1782 K.

A computer program has been written to perform thermodynamic calculations in multicomponent systems. This program, which is based on one developed by Eriksson,[1] is discussed in detail and listed in ORNL/TM-5775.[2] The abstract of the report follows:

"SOLGASMIX-PV, a Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems," by T. M. Besmann. *Abstract*: The use of the computer program SOLGASMIX-PV for calculating equilibrium compositions is described. The program can calculate equilibria in systems containing a gaseous phase, condensed phase solutions, and condensed phases of invariant or variable stoichiometry. Either a constant total gas volume or a constant total pressure can be assumed. Unit activities for condensed phases and ideality for solutions are assumed, although nonideal systems can be handled provided activity coefficient relationships are available.

15.2 TRANSITION METAL–U-C PHASE EQUILIBRIA

Studies are under way to determine the thermodynamic conditions for the interaction of iron, chromium, and nickel with compounds in the U-C system. An extended abstract[3] describing some of the results of this work follows:

"Basic Compatibility Studies of Advanced Fuels with 3-*d* Transition Metals," by E. C. Beahm and C. A. Culpepper,[4] Compatibility of uranium nitride or uranium carbide fuels with 3-*d* transition metals used in stainless steel may be restricted at some temperatures, compositions, and nitrogen pressures by the formation of one or more of the following types of compounds:

1. Intermetallic compounds of uranium with the transition metals. These compounds will be Laves phases such as UFe_2 or UNi_5.
2. Ternary compounds involving uranium, transition metals, and either carbon or nitrogen. In nitrides, U_2CrN_3 may form; in carbides, $UCrC_2$, $UFeC_2$, $UNiC_2$, or U_2NiC_3 may form.
3. Nitrides or carbides of the transition metals, such as Cr_2N or $Cr_{23}C_6$.

Combinations of more than one type of compound may occur in one overall fuel–transition metal reaction. This will be illustrated below. In addition, compounds of any of the three types listed above may contain more than one transition metal. Thus, there is a need for studies of the compatibility of carbide or nitride fuels with combinations of different transition metals rather than with an individual metal. We have been investigating the formation of compounds listed in categories 1 and 2.[5]

We have studied the formation of Laves phases of the type UM_2, where M = Cr, Mn, Fe, Co, Ni. Pauling's description of metal bonds was used to calculate bond numbers and *d* orbital participation in bonding. Limits to compound formation were found to be related to limits in *d* orbital participation in bonding. Simple equations were derived to calculate interatomic distances and composition limits of these compounds.[5]

1. G. Eriksson, "Thermodynamic Studies of High-Temperature Equilibria," *Chem. Scr.* **8**, 100 (1975).
2. T. M. Besmann, *SOLGASMIX-PV, a Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems*, ORNL/TM-5775 (April 1977).
3. E. C. Beahm and C. A. Culpepper, "Basic Compatibility Studies of Advanced Fuels with 3-*d* Transition Metals," *Trans. Am. Nucl. Soc.* **24**, 152 (1976).
4. Solid State Division.
5. E. C. Beahm, C. A. Culpepper, and O. B. Cavin, "Laves Phases of Uranium and 3*d* Transition Metals," *J. Less-Common Met.* **50**, 57 (1976).

Chromium does not form binary compounds with uranium, but the present work demonstrates that chromium, with one or more of the elements Mn, Fe, Co, and Ni, may combine with uranium to form Laves-phase compounds. Lattice constants for Laves phases in the U-Cr-Fe, U-Cr-Co, U-Cr-Ni, and U-Cr-Fe-Ni systems were determined.

These Laves phases will form when uncombined uranium is present in either nitride or carbide fuels or as a result of a reaction which produces a Laves phase in combination with either a ternary carbide or a transition metal carbide. For example, Anselin et al.[6] observed the following reaction at 900 to 1300°C:

$$2UC + 6Ni \rightarrow UNi_5 + UNiC_2 \ . \qquad (1)$$

This reaction produces both a metallic compound and a ternary carbide. A similar reaction may be written involving an iron-nickel solid solution:

$$2UC + 6(Ni_{5/6}Fe_{1/6}) \rightarrow UNi_5 + UFeC_2 \ . \qquad (2)$$

At 900°C we calculate a free energy change of $\Delta G \approx -12$ kcal/mole for Eq. (2). Since $UFeC_2$, $UCoC_2$, and $UNiC_2$ are isomorphous with almost identical lattice constants,[7] it is likely that iron can substitute for nickel over the whole range, $x = 0$, in $UNi_xFe_{1-x}C_2$. Iron and nickel form a nearly ideal solution; thus a reaction with UC may be expected over a wide iron-nickel solid solution composition range.

The complex nitride U_2CrN_3 has been observed in the U-Cr-N system.[8,9] Iron does not form an analogous nitride with uranium; however, our experimental results show that iron may substitute for up to one-sixth of the chromium at 1300°C.

Our calculations and experimental results show that compatibility problems are more likely to occur with combinations of 3-*d* transition metals than in individual transition metal–fuel interactions. Thus, the compatibility of stainless steels with advanced fuels is more limited than would be expected if the compatibility of each component of the steel is considered separately.

The results summarized above form the basis of a paper to be published in *Nuclear Technology*. The abstract of this paper follows:

"Basic Compatibility Studies of Advanced Fuels with 3*d* Transition Metals," by E. C. Beahm and C. A. Culpepper.[4] *Abstract*: - Equilibrium compatibility studies have shown that frequently more than one type of compound is formed in a single fuel–transition metal reaction. In addition, the compounds thus formed may contain elements in varying proportions. These observations have been formulated into a simple rule and examined by experimental studies and thermodynamic calculations. The results deal mainly with the equilibrium compatibility of uranium carbides with (Cr-Fe-Ni) alloys.

6. F. Anselin, D. Calais, G. Dean, and A. Van Craeynest, "Reactions between Nickel and the Carbides and Nitrides of Uranium and Their Solid Solutions," *C. R. Acad. Sci.* **275**, 3916 (1963).

7. R. Pascard, "Discussion on Phases in U-Cr-C, U-Ni-C, and U-Fe-Cr-C," *Symposium on Carbides in Nuclear Energy, Harwell*, vol. 1, p. 245, Macmillan, London, 1964.

8. R. Benz and W. H. Zachariasen, "Crystal Structures of Th_2CrN_3, Th_2MnN_3, U_2CrN_3, and U_2MnN_3," *J. Nucl. Mater.* **37**, 109 (1970).

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

16. Chemical Engineering Research

The Chemical Engineering Research Program contains a variety of fundamental studies funded by the ERDA Division of Physical Research. The studies are usually in areas of particular interest to the more applied ERDA programs or in areas where ORNL has special capabilities. However, all of the studies attempt to generate information fundamental to chemical engineering as well as useful to ERDA.

The current program includes studies useful to coal conversion, separation processes, and nuclear fuel processing.

16.1 THREE-PHASE FLUIDIZED-BED REACTING SYSTEM

Three-phase fluidized beds are of particular importance to some coal conversion processes and bioreactors. They contain solid particles fluidized by the upward cocurrent flow of gas and liquid. Details of our studies of such systems, using various packings in 7.62- and 15.2-cm-ID columns, are reported elsewhere.[1,2]

The minimum gas and liquid velocities necessary to fluidize a bed were determined as a function of the particle size and density; no effect of the initial bed height or column diameter was found. As either the gas velocity is increased or the particle diameter or density is decreased, the minimum liquid fluidization velocity decreases. In a comparison of alumina beads with glass beads for low gas velocities, the influence of particle diameter was found to override that of particle density. At higher gas velocities (>7 cm/sec) the two systems behaved identically.

Accurate design of three-phase fluidized-bed reactors for hydrocarbon or coal processing is complicated by such factors as axial variation in reactor properties, particularly the distribution of the solid catalyst. No data or equations exist for predicting reactor performance under high fluid flow rates where these axial variations are important. During this report period an experimental technique was developed for measuring local concentrations of solid, liquid, and gas in a fluidized-bed reactor. The electroconductivity of the reactor's contents was measured at various axial positions and related to the fraction (holdup) of the reactor volume occupied by the liquid phase at each position. Combination of these results with measurement of the pressure gradient in the reactor allows the fraction occupied by each of the three phases in the reactor to be determined.

A typical plot of the axial variation of the holdup of each phase is shown in Fig. 16.1. The liquid holdup remains uniform near the bottom of the bed and then increases with distance from the bottom to a constant value in the gas-liquid regions above the bed. The calculated bed height (48 cm) is that measurement obtained from the intersection of the pressure gradients in and above the bed. The solid holdup decreases with increasing axial position in the bed, and the actual observed upper limit of solids is 64 cm, which corresponds closely to the point where the solid holdup curve drops to zero. Neither the column diameter nor the liquid velocity affects the width of this "transition region" from three phases to two phases; however, increasing the gas velocity significantly increases the width of the transition region. This observation agrees with previous reports of indistinct bed heights in columns operating with high fluid flow rate.[3,4]

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

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

3. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1976,* ORNL-5172.

4. J. M. Begovich and J. S. Watson, "An Electroconductivity Technique for the Measurement of Axial Variation of Holdups in Three-Phase Fluidized Beds," submitted for publication in the *AIChE Journal.*

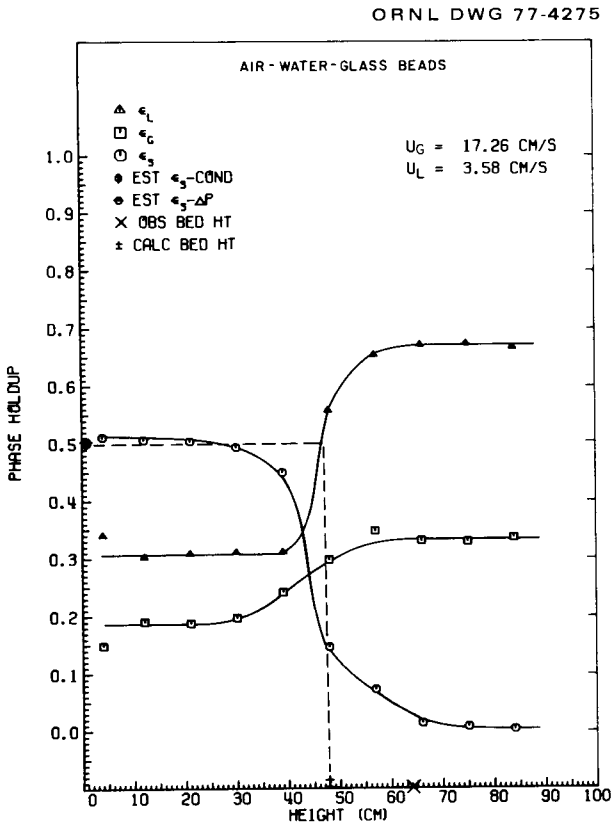

Fig. 16.1. Axial variation of phase holdups in a three-phase fluidized bed.

The results of this study are being used to develop predictive equations for rational design of reactors where local conditions throughout the bed must be considered. The same electroconductivity system is also being used in some recently initiated residence-time-distribution experiments to measure the degree of axial dispersion present in the liquid phase of three-phase fluidized beds. When dispersion has been characterized, gas-liquid mass transfer experiments will be conducted.

16.2 CONTINUOUS CHROMATOGRAPHY

The continuous chromatograph is being developed primarily as a tool for large-scale preparative separations. The separation of nickel-cobalt components found in a commercial leach liquor has been studied.[2,5]

A number of improvements have been made in the Plexiglas chromatograph. The feed system has been redesigned to permit higher feed rates, and a layer of glass beads has been added above the resin to allow the feed to undergo hydrodynamic spreading before interaction with the resin begins. This permits accurate measurement of initial bandwidths. The bottom of the chromatograph has been improved to prevent circumferential mixing. A total of 180 discrete exit points are found on the chromatograph. The band scanning device[3] has been improved by tuning the light to the optimum wavelength for the nickel and cobalt species. A new drive system utilizing a feedback-controlled digitally set drive motor with digital readout of the motor rotation rate has been installed to permit accurate selection of rotation rates.

Visual examination of the chromatographic nickel and cobalt bands revealed a change in slope which occurred at the point of the nickel-cobalt split. This phenomenon is responsible for an inconsistency in some of the previous data. Since the data were usually taken from a point below the position where nickel separates from cobalt, it was not meaningful to extrapolate back through the discontinuity to the feed point. Several runs now have been made with a single species in the feed. These experiments gave straight bands on the chromatograph. Results of some of these experiments are given in Table 16.1. The distribution coefficients were calculated by regression analysis, and the height equivalent to a theoretical plate was calculated from bandwidth and elution position data.

The continuous chromatograph can now be operated in the gradient elution mode. This operating mode involved the use of a manifold header system and indirect control of the eluent velocity. The header system was described previously.[2] The control system consists of an optical meniscus detector and associated electronics to regulate the gas pressure in the chromatograph head space. A side glass was built into the outer wall of the chromatograph with the bottom of the wall adjacent to the layer of glass beads. An optical detector observes the meniscus in the side glass and initiates action to maintain the liquid (eluent) level to within $\pm 1/16$ in. of the set point. The eluents are pumped through the header system at constant rates, and very small variations in air pressure ($\sim\pm 1\%$) are adequate to maintain constant liquid level. This method of control has an advantage over liquid-rate control systems because increasing the number of eluents does not cause control problems. This system has operated successfully for periods of several hours with no operator attention. The optical detector does suffer somewhat from extraneous light variations. A second-generation continuous chromatograph is likely to utilize a mechanical liquid-level detector.

5. C. D. Scott, R. D. Spence, and W. G. Sisson, "Pressurized Annular Chromatograph for Continuous Separations," *J. Chromatogr.* **126**, 381–400 (1976).

Table 16.1. Results from regression analysis of nickel and Co-1 on the continuous chromatograph; 95% confidence limits are given

Run	pH	Feed rate (cc/min)	Eluent velocity (cm/min)	Distribution coefficient		Height equivalent to theoretical plate (cm)
				Nickel	Co-1	
A1	8.07	2.00	1.33	3.43		0.168 ± 0.031
A2	8.07	2.00	2.67	3.17		0.224 ± 0.022
A3	7.94	2.00	0.65	2.81		0.208 ± 0.022
A4	7.97	2.00	2.00	3.29		0.300 ± 0.087
B1	8.02	2.00	0.71		6.38	0.037 ± 0.007
B2	7.86	2.00	1.34		5.45	0.098 ± 0.028
B3	8.05	2.00	1.95		5.25	0.151 ± 0.077
B4	7.94	2.00	2.49		4.66	0.164 ± 0.075

Studies in gradient elution continuous chromatography are continuing. Efforts are now centered on the design of the second-generation chromatograph for higher-pressure operation and on a search for separations for which the continuous chromatograph is particularly well-suited. Areas under preliminary study include lanthanide separations, americium separation for waste partitioning, and separations related to the resource recovery program, particularly fly-ash utilization. Flowsheets involving ion exchange separations of metals in the acid leach process for fly-ash separation are being examined.

16.3 HYDRAULIC CYCLONE STUDIES

Hydraulic cyclones (hydroclones) are potentially useful devices for removing solids from coal liquids, but their ability to separate particles from relatively viscous liquids has not been adequately evaluated. Therefore, experiments using a 10-mm-diam hydroclone were continued to study particle separation as a function of feed rate, density of particles, and density and viscosity of the liquid medium.

Experiments have been conducted[6] using slurries of 5 wt % solids in water-glycerin solutions with viscosities from 1 to 85 cP. Slurry from a stirred tank is recirculated by a pump through a 10-mm-diam Dorr-Oliver hydroclone.[7] The inlet, overflow, and underflow streams are sampled for each pressure drop, and particle size distributions are determined using a ZB Coulter counter with a model H4 Channelyzer. Samples of the overflow and underflow are dried and weighed to determine solids concentrations. The particles used in these experiments included aluminum oxide, a commercially available test dust ("Air Cleaner Test Dust"), and fly ash with respective densities of 3.72, 2.64, and 2.28 g/cm^3. The powders have been screened to less than 400 mesh (37 μ in diameter).

Performance criteria are usually defined by cyclone efficiency, inlet-to-overflow pressure drop, and the ratio of the underflow rate to the overflow rate. Experiments were conducted to determine the effect of flow rate and viscosity on both pressure drop and hydroclone efficiency.[6] The pressure-drop-vs-feed-capacity data at 1 cP agree well with both the data supplied by Dorr-Oliver and the correlations in the literature,[8] which predict that the pressure drop is proportional to the square of the feed rate. Density of the solid does not seem to affect the relationship. However, the viscosity of the fluid does have a pronounced effect on the correlation between pressure drop and flow rate. At low viscosities, the centrifugal acceleration, which is proportional to the square of the velocity, has a more predominant effect than viscous drag on pressure drop. However, as viscosity increases, the viscous force becomes more important, and the pressure drop is proportional to the velocity (as one observes for laminar Newtonian flow in a pipe).

Hydroclone efficiency is also affected by an increase in viscosity. Figure 16.2 shows that the rate at which

6. T. Trinh, J. J. Monge, and W. A. Chrusciel, *Efficiency of Particle Removal from Viscous Liquid with a Hydroclone*, ORNL/MIT-237 (October 1976).

7. *The DorrClone*, Dorr-Oliver, Inc., Stamford, Conn. (1976).

8. D. Bradley, *The Hydroclone*, pp. 63–88, Pergamon, New York, 1965.

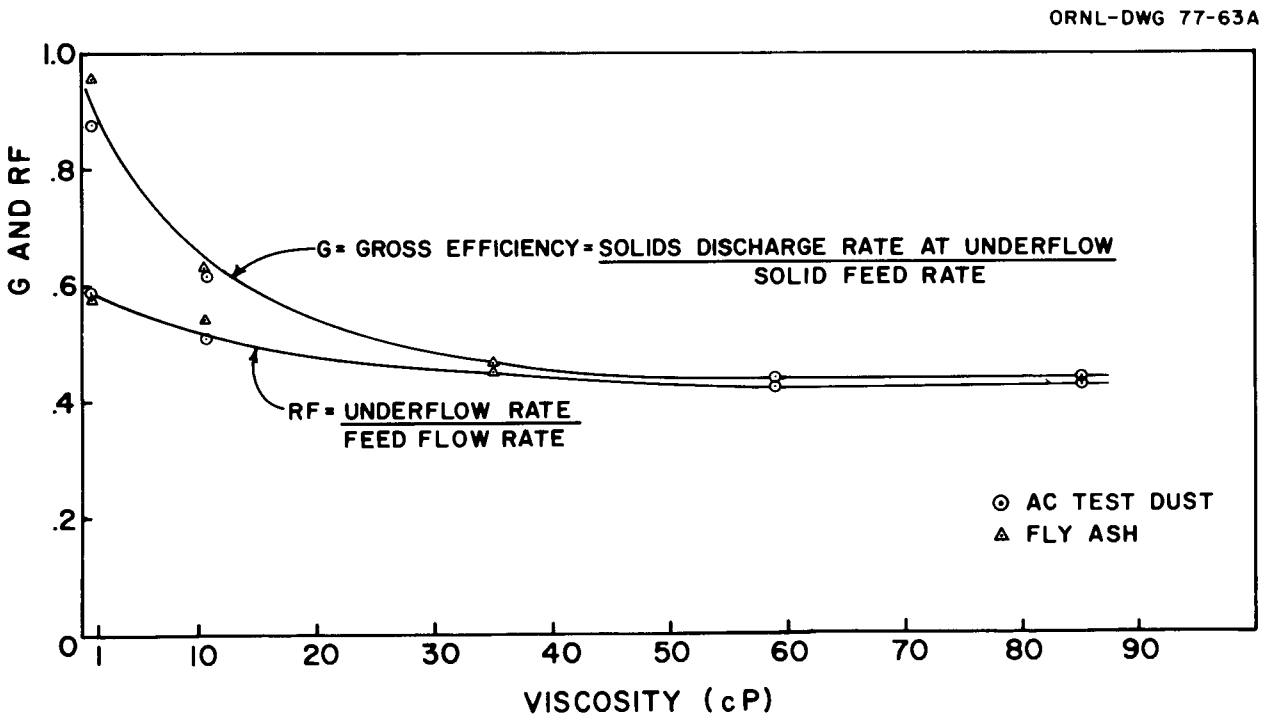

Fig. 16.2. Effect of viscosity on gross efficiency and underflow-to-feed rate ratio.

solids and liquids are discharged to the underflow decreases at higher viscosities. At viscosities greater than 30 cP, the fraction of solids and the fraction of liquid that go to the underflow are essentially equal. Overall centrifugal efficiencies are calculated for various flow rates. Centrifugal efficiency, E, is defined as follows:

$$E = \left(\frac{G - R_f}{1 - R_f} \right),$$

where

G = gross efficiency = ratio of solids discharge rate at underflow-to-solid feed rate,

R_f = ratio of underflow rate to feed flow rate.

As expected, efficiency increases with increasing flow rate, but again viscosity has a pronounced effect above about 30 cP. At high viscosities the centrifugal efficiency is essentially zero. Particle size distributions are being determined to evaluate the hydroclone efficiency at various particle sizes. Suitable correlations will be developed to predict hydroclone performance over the wide range of physical properties studied.

16.4 MASS TRANSFER STUDIES USING STIRRED, NONDISPERSING WATER-MERCURY CONTACTORS

Mechanically agitated, nondispersing two-phase contactors are useful devices for applications where entrainment must be minimized. An electrochemical technique was used to study aqueous film mass transfer coefficients in a water-mercury system. This year an extensive set of experiments has been performed to determine the effects of the aqueous-phase physical properties on mass transfer rates in contactors with square cross sections. The results from one size contactor and one set of phase volumes are given in Fig. 16.3. At low agitator speeds, the mass transfer coefficient is proportional to the agitator speed to a power near 0.8, and at high agitator speeds, the power changes to approximately 1.8. This change is abrupt and does not appear to be a strong function of viscosity. Similar behavior has been observed in aqueous organic systems.

16.5 ADIABATIC COMBUSTION OF GRAPHITE

Graphite oxidation studies were conducted to investigate recycling of burner gases for controlling temperatures and burn rates in an insulated reactor. Solid

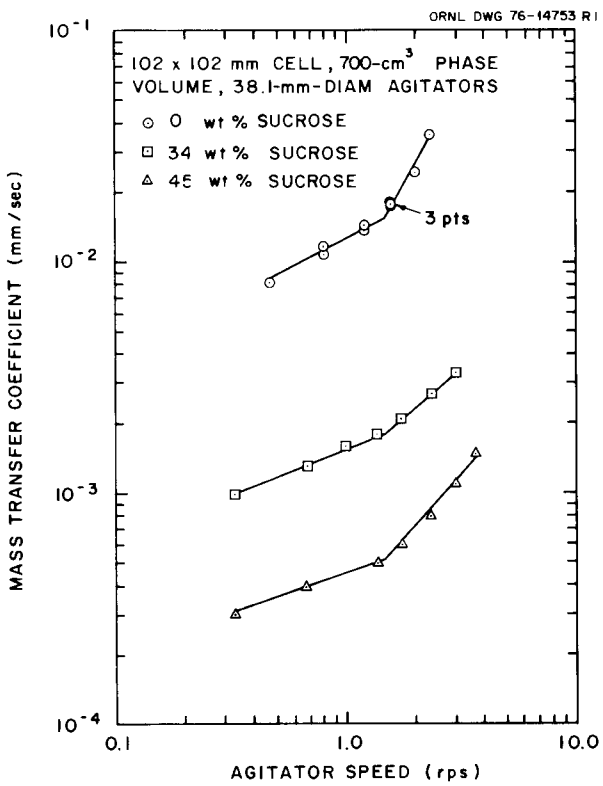

Fig. 16.3. Effect of agitator speed and aqueous-phase viscosity on mass transfer coefficient in the 102 × 102 mm cell with 700-cm³-phase volume and 38-mm-diam agitators.

graphite rods were burned in a vertical reactor; the reactions involved and the equipment used have been described previously.[9] Design and procedure have been discussed elsewhere.[10] The reactor operated with oxygen feed and flue-gas recycle. Graphite temperatures ranged from 1000 to 1200°C. Gas stream temperatures and compositions (CO, CO_2, O_2) are continuously monitored and recorded.

Oxygen concentration and gas flow rate are the major variables affecting burn rate and temperature. By operating at the highest gas flow possible for this equipment and with 30% O_2 in the feed, a carbon burn rate of 0.030 g cm^{-2} min^{-1} was obtained. However, oxygen utilization at such high burn rates is relatively poor (74%) and necessitates 35% excess oxygen. At lower carbon burn rates (0.02 g cm^{-2} min^{-1}), oxygen utilization as high as 90% (requiring only 11% excess oxygen) can be achieved. Inlet gas temperatures ranged from 30 to 225°C, and exit temperatures were 600 to 1100°C. Temperature rises as high as 1000°C across the reactor were achieved.

For instantaneous gas-solid reactions, the relation

$$BR/X_{O_2} = k_g^* \tilde{\rho} \tag{1}$$

can be used to adjust the burning rate per unit area (BR) for varying oxygen concentrations; X_{O_2} is the mole fraction of oxygen. The average mass transfer coefficient, k_g^* (cm/sec), can then be calculated from the gas molar density, $\tilde{\rho}$ (g-moles/cm^3), and the burn rate. Mass transfer data are plotted in Fig. 16.4 as a function of the product of the logarithmic mean Reynolds and Schmidt numbers. The Reynolds number for the annular cross section is

$$N_{Re} = \frac{4G}{\pi\mu(D_o + D_i)}, \tag{2}$$

where G is the mass flow rate of gas (g cm^{-2} sec^{-1}), μ is the gas viscosity (g cm^{-1} sec^{-1}), D_o is the diameter of the furnace interior (cm), and D_i is the graphite rod diameter (cm). The Schmidt number is

$$N_{Sc} = \mu/\rho D , \tag{3}$$

where ρ is the gas density (g/cm^3), and D is the O_2 mass diffusivity (cm^2/sec). The Reynolds-Schmidt product is

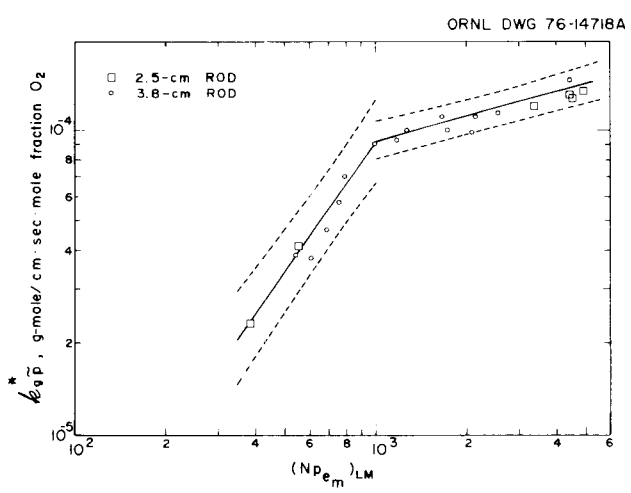

Fig. 16.4. Effect of mass transfer Peclet number on oxygen transfer.

9. C. D. Scott et al., *Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Sept. 1, 1974, to Feb. 28, 1975,* ORNL/TM-4961 (January 1976).

10. C. D. Scott et al., *Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Sept. 1, 1975, to Feb. 29, 1976,* ORNL/TM-5533 (to be published).

a function of only mass flow rate, gas density, diffusivity, and the diameters of the rod and reactor. With the dimensions fixed, this product is a function of only mass flow rate, temperature, and pressure. Often called the Peclet number for mass transfer (N_{Pe_m}), this product can be used to correlate the data on burning. Laminar data for graphite burning are shown on the left side of Fig. 16.4 and are best represented by the equation

$$k_g^* \hat{\rho} = (8.20 \pm 5.80) \times 10^{-9} (N_{Pe_m})_{LM}^{1.40 \pm 0.35} \ . \quad (4)$$

The dashed lines indicate the 95% confidence level. The turbulent and transition data are shown on the right side of Fig. 16.4 and are best represented by

$$k_g^* \hat{\rho} = (1.54 \pm 0.10) \times 10^{-5} (N_{Pe_m})_{LM}^{0.26 \pm 0.07} \ . \quad (5)$$

The constants in Eqs. (4) and (5) are g-moles cm^{-2} sec^{-1}. The correlation coefficients for the laminar and turbulent data are 0.97 and 0.93 respectively.

16.6 PACKED COLUMNS FOR CRYOGENIC SORPTION SYSTEMS

Several high-efficiency packing materials are under consideration for use in cryogenic gas–liquid sorption systems for treatment of off-gas streams in nuclear fuel processing plants and have potential applications in cryogenic distillation processes. To evaluate these packings, an experimental study of flooding rates and mass transfer characteristics in air–carbon dioxide–water systems was undertaken. Flooding rates for four metallic packings have been reported elsewhere.[11] Liquid-phase volumetric mass transfer coefficients, K_La, determined with Goodloe packing[12] in the 6.35- and 15.2-cm-ID columns are shown in Fig. 16.5. As the superficial liquid flow rate, L_m, is increased, K_La increases. Varying the gas flow rate from 1.6 to 2.5 liters/sec does not significantly affect K_La.

The goal of this study is to experimentally determine the effects of column diameter, packing type, liquid flow rate, and gas flow rate on column flooding rates and mass transfer characteristics. These results are being

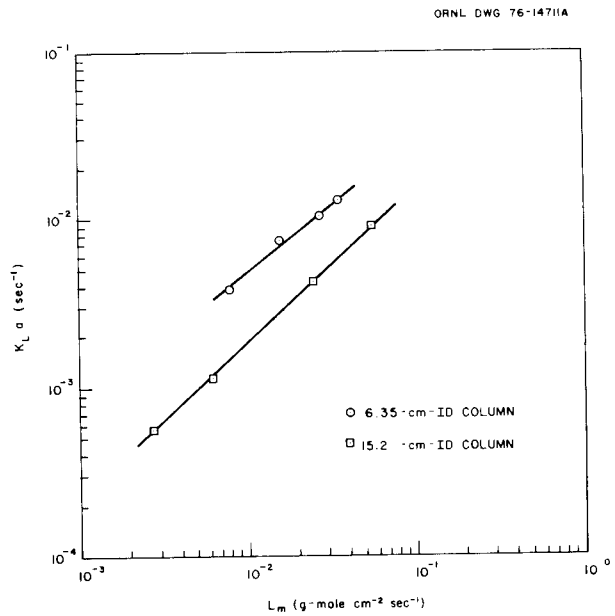

Fig. 16.5. Effect of liquid flow rate on K_La in Goodloe-packed columns.

extended in the Goodloe-packed columns to include liquid-to-gas mass flow ratios up to two orders of magnitude larger than those studied previously.[13,14]

16.7 AGGLOMERATION STUDIES

The tendency for particles to agglomerate and precipitate, or to disperse and stabilize, is characterized by a number of physical parameters,[15–17] the most obvious of which are size and density relative to the suspending matrix. Generally, colloidal dispersions are defined as those dispersions containing particles with diameters less than 1 μ, an artificial limit corresponding roughly to the maximum size particle that will stay in suspension for a reasonable time. In heavy organic systems, such

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

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

13. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1976,* ORNL-5172.

14. J. M. Begovich and J. S. Watson, *Flooding Characteristics of Goodloe Packing,* ORNL/TM-5212 (August 1976).

15. E. J. W. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids,* Elsevier, New York, 1948.

16. Ayao Kitahara, "Zeta Potential in Nonaqueous Media and Its Effect on Dispersion Stability," *Prog. Org. Coat.* **2,** 81–98 (1973/74).

17. Ayao Kitahara, Fujii Todishi, and Seiji Katano, "Dependence of Zeta Potential upon Particle Size and Capillary Radius and Streaming Potential Study in Nonaqueous Media," *Bull. Chem. Soc. Jpn.* **44,** 3242–45 (1971).

as coal liquefaction products, unconverted coal and mineral matter may be present both as a suspension (particles >1 μ) and as a colloidal dispersion (particles <1 μ). The former particles are not difficult to remove by conventional techniques. However, the remaining particles often constitute up to 50 vol % of the total particle mass[18] and must be removed to meet stringent EPA specifications. The current agglomeration studies will examine the efficacy of agglomerating the particles in two ways: coagulation and flocculation.

In coagulation, agglomeration of colloidal dispersions is accomplished by changing the nature of the interfacial forces by the addition of electrolytes or surface-active agents. The agglomerating tendency is often related to the "zeta potential." Determination of zeta potential has traditionally required dilute solutions (<2% solids). However, there are many heavy organic-solids systems of much higher concentrations; the Solvent Refined Coal (SRC) liquefaction reactor product contains approximately 10 wt % solid material. For these solutions, special techniques (electrophoretic mass transport) have been employed.

A Micromeritics Corporation electrophoretic mass transport analyzer[19] was obtained and operated initially on kaolin-water mixtures. Five runs with 20 wt % kaolin gave $\bar{\zeta} = -0.095$ V, with a standard deviation (σ) of ± 0.032 V. This may be compared with values reported by Micromeritics for this system, $\zeta = -0.059$ V. Eight runs using 5% carbon black in benzene gave $\bar{\zeta} = -0.274$ V, $\sigma = \pm 0.167$ V. In a benzene–carbon black system where both components were meticulously purified, Kitahara et al.[17] found that $\zeta = 0$. Since our components were used as received, this demonstrates the importance of small concentrations of impurities in these sensitive measurements. Additional experiments with nonaqueous-solid systems are planned.

Flocculation was found to occur when certain solvents were added to the SRC reactor effluent.[20–22] It was proposed[23,24] that some long-chain organic component in the mixture of coal liquids was precipitated by these solvents and that the precipitated polymer served as a flocculating agent for the colloid particles. In order to identify the component responsible for flocculation, the coal liquid was separated into the following components:[25] solids, carbenes and carboids, asphaltenes, and oils and resins. Decane, a proven flocculation solvent for coal liquids, was added to each fraction and to combinations of fractions.

When 8% filtered solids were suspended in oils and resins and 30% *n*-decane was added, the solids remained dispersed. However, when asphaltenes were present with *n*-decane, the solid phase agglomerated (see Fig. 16.6), proving that asphaltenes are a necessary component for agglomeration in these systems. The asphaltenes themselves appear to bind the solids together, with *n*-decane functioning to precipitate these asphaltene components from the oil and resin solution. Efforts are under way to separate the asphaltenes into distinct classes, which will hopefully allow a more precise determination of their agglomerating effect.

16.8 HYDROGEN PERMEATION-OXIDATION STUDIES

The large permeation rates of tritium through containment barriers at even moderate temperatures (300 to 500°C) will complicate the handling of tritium in fusion reactors. Oxidation of tritium to a nonpermeating and recoverable form should make secondary containment simpler and more practical; in addition, the technique could be used for recovering tritium produced in some blanket designs. Low concentrations of oxygen will inevitably be present in either a helium coolant or system containment atmosphere, and higher concentrations of oxygen could be added. Atomic tritium, permeating a metal barrier, should react with oxygen sorbed on the metal surface to form the oxide. An experimental study has been completed to determine the oxidation efficiency of deuterium permeating a metal wall at conditions expected within fusion power reactor

18. B. R. Rodgers and S. Katz, *Supporting Research and Development on Separations Technology, Phase II Report: Scouting Experiments,* ORNL/TM-4968 (October 1975).

19. R. J. Akers, "Zeta Potential and the Use of the Electrophoretic Mass Transport Analyzer," *Am. Lab.,* pp. 41–53 (June 1972).

20. B. R. Rodgers and S. Katz, *Supporting Research and Development on Separations Technology: Final Report,* ORNL/TM-5843 (to be published).

21. B. R. Rodgers, "Use Solvent to Separate Micron-Sized Particles from Liquid Streams," *Hydrocarbon Process.,* p. 191 (May 1976).

22. B. R. Rodgers and P. R. Westmoreland, "Agglomeration and Separation of Micron-Sized Particles from Liquid Streams," Paper No. 19C, presented at the 81st National A.I.Ch.E. Meeting, Kansas City, Mo., April 1976.

23. B. R. Rodgers and P. R. Westmoreland, "Removing Micron-Size Particles from Coal Liquids," pp. 28–36 in *Coal Processing Technology: Vol. 3,* a CEP Technical Manual (1977).

24. S. Katz and B. R. Rodgers, "Reformation of Inorganic Particles Suspended in Coal-Derived Liquids and Improved Separation," *Liquid Fuels from Coal,* pp. 173–81, Academic Press, New York, 1977.

25. M. J. Mima, H. Schultz, and W. E. McKinstry, *Method for the Determination of Benzene Insolubles, Asphaltenes, and Oils in Coal-Derived Liquids,* PERC/R1-76/6 (September 1976).

ORNL DWG 77-1161

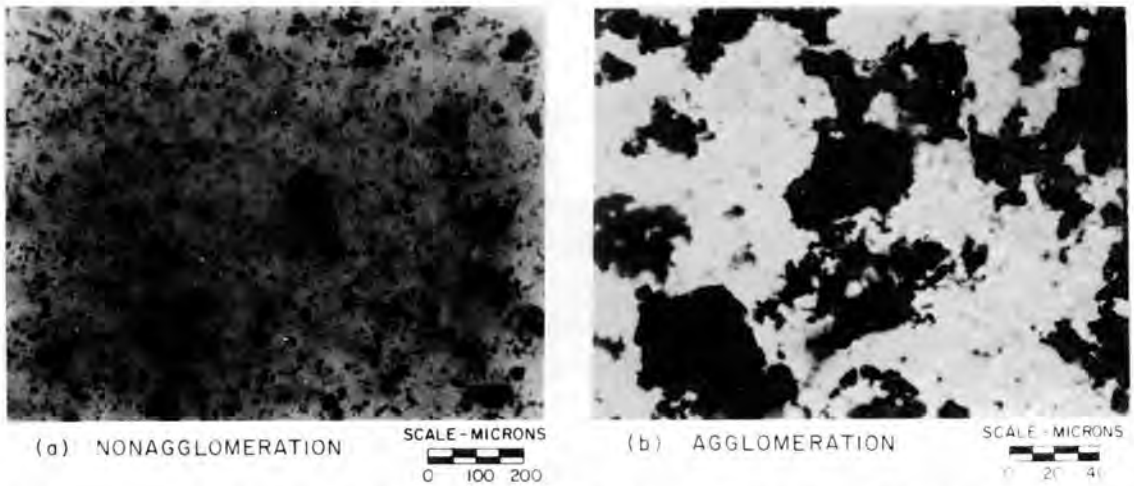

Fig. 16.6. (*a*) SRC oils and resins with 8% filtered solids and 30% *n*-decane; (*b*) SRC oils, resins, and asphaltenes with 2% filtered solids and 30% *n*-decane.

systems. Data were obtained with deuterium permeating through palladium, nickel, and type 304-L stainless steel tubes.

The deuterium oxidation efficiency at the metal surfaces increased with increasing temperature but was unaffected by oxygen partial pressure variations in the range of 0.005 to 0.2 torr. With a palladium tube at 25°C, the conversion of permeating deuterium to heavy water was approximately 90%, and increasing the palladium temperature to 60°C increased the deuterium oxidation efficiency to 97%.[10] With a nickel surface, the deuterium oxidation efficiency increased from 88% at 200°C to 94% at 500°C.[11] With a type 304-L stainless steel surface, the conversion efficiency increased from 57% at 300°C to 91% at 600°C.[26]

Hydrogen permeation-oxidation studies at conditions expected for fusion power reactor systems have been completed. With temperatures up to 600°C and oxygen partial pressures up to 0.2 torr, it can be concluded that the catalytic effectiveness of a stainless steel surface is insufficient to achieve deuterium oxidation efficiencies significantly greater than 90%. No further permeation-oxidation measurements have been planned.

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

17. Fusion Energy Studies

The Fusion Energy Program in the Chemical Technology Division is concerned with the fuel cycle and with tritium containment. Current experimental efforts are aimed toward developing cryosorption vacuum pumps for removing unburned fuel and impurities from the plasma, studying deep-bed sorption pumps for roughing and transfer operations, investigating methods for recovery of tritium bred in blankets of lithium or lithium alloys, and studying containment of tritium that permeates metal walls. In addition, the ORNL Fusion Energy Division is being given assistance in the design of a Tokamak reactor proposed for construction during the early 1980s.

Many of the experimental studies are relatively fundamental in nature and are funded by the ERDA Division of Physical Research – Molecular Science. The vacuum pump development and the design studies are more closely related to specific fusion energy problems and are funded by the ERDA Division of Magnetic Fusion Energy.

17.1 CYOSORPTION VACUUM PUMPING FOR FUSION REACTORS

Fusion reactors will require vacuum pump systems to remove leaking or diverted plasma during the reactor pulses (burns) and to remove unburned fuel and ash from the reactor between burns. At the beginning of the burn, pumps will recover a 1:1 mixture of deuterium and tritium; at the end of the burn and between burns, the pumps will recover a mixture containing as much as 10% helium.

Cryosorption pumps operating at 4.2 K could, in principle, meet all fusion reactor requirements in a single pump. However, experimental results[1] have shown that vacuum pumps based on the molecular sieve (type 5A) may not be able to pump hydrogen isotopes and helium on a single panel, because condensed deuterium and tritium block the adsorbent surface. This problem can be alleviated either by developing new cryosorption pumps based on different adsorbents or by developing compound pumps employing separate panels for pumping helium. If the latter approach is pursued, 4.2 K cryosorption pumps are probably the only logical choice for helium pumping. An experimental program at ORNL uses the Excalibur CVR 1106 cryosorption pump, which contains a sorption panel of molecular sieve. A description of the experimental apparatus and experimental results for hydrogen and deuterium pumping have been presented in a previous report.[1] Results obtained for helium and a mixture of 95% deuterium–5% helium are presented here.

Helium pumping speeds fall into two regimes. At feed rates below 6.2×10^{-6} torr-liter sec^{-1} cm^{-2}, speeds decrease with loading from 2.2 liters sec^{-1} cm^{-2} to 0.3 liter sec^{-1} cm^{-2} as shown in Fig. 17.1. At feed rates

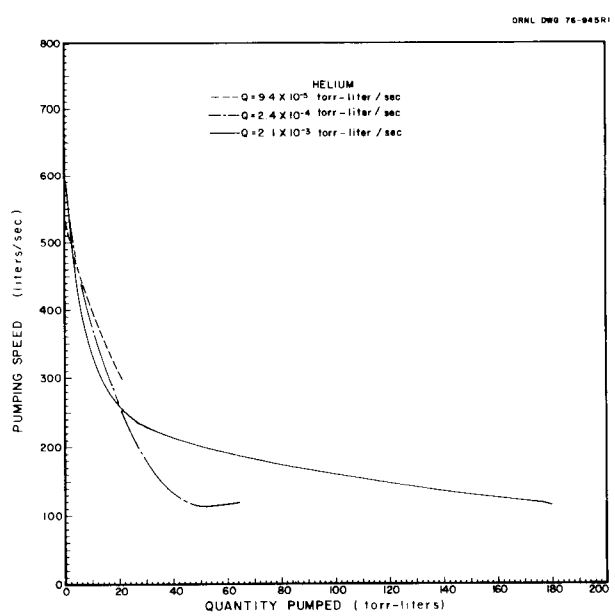

Fig. 17.1. Helium pumping speeds at low loading rates.

1. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1976,* ORNL-5172 (September 1976).

higher than 6.2×10^{-6} torr-liter sec^{-1} cm^{-2}, the pumping speed varies periodically with loading (Fig. 17.2). A typical cycle begins with speeds near 1.7 liters sec^{-1} cm^{-2}; speeds fall to near 0.6 liter sec^{-1} cm^{-2} at which time the pump goes through a rapid transition and reverts to its original high pumping speed. During the transition, the system reaches pressures greater than 10^{-2} torr. The amount of helium accumulated on the pump during each cycle is a function of the loading rate.

Three distinct types of behavior were observed for pumping 95% deuterium–5% helium.[2–6] At low feed rates (below a helium rate of 6.2×10^{-6} torr-liter sec^{-1} cm^{-2}), speeds decrease monotonically with loading and generally range from 2 to 3 liters sec^{-1} cm^{-2}. Figure 17.3 shows that, at high feed rates, the pump response was dependent on the temperature of the inner chevron. If the inner chevron is cooled by liquid helium boil-off vapor, the speed first decreases causing rapid boiling; the pumping speed then increases and remains steady near 2 liters sec^{-1} cm^{-2}. Condensation of deuterium on the cold inner chevron leaves the panel free to pump helium. If the inner chevron is maintained at 77 K, the pump does not recover from its initial loss of speed, and operation must be terminated due to cryogenic runaway.

The behavior of the CVR 1106 pump during helium pumping and for helium and helium-deuterium mixtures is complex. Helium speeds are a function of total mass accumulated, helium accumulation during individual runs, feed rate, and the treatment of the pump between runs. Many aspects of pure helium pumping also appear when mixtures containing helium are pumped. Better understanding of these phenomena is desirable so that the next generation of pumps can be designed to more nearly fit the needs of fusion reactors.

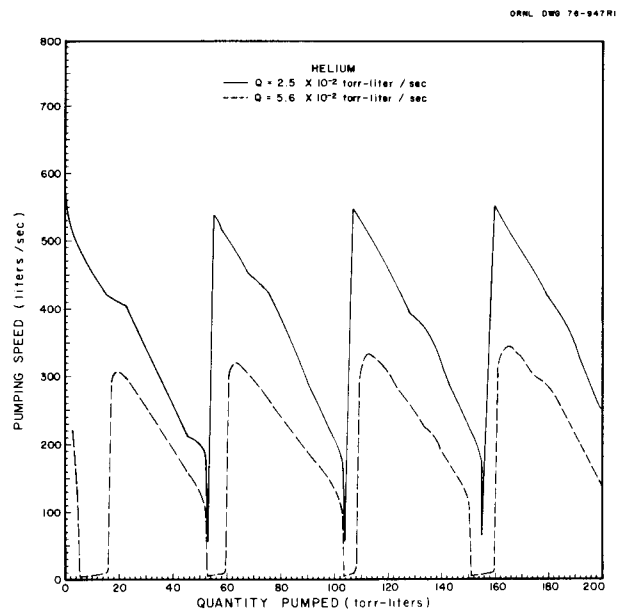

Fig. 17.2. Cyclic behavior at high loading rates.

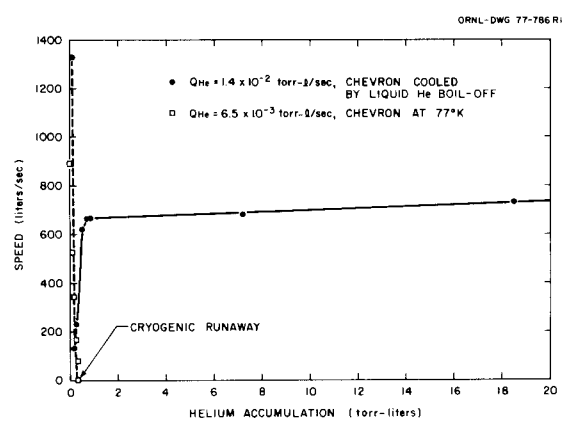

Fig. 17.3. Pumping of a 95% deuterium–5% helium mixture with an Excalibur CVR 1106 cryosorption pump.

17.2 TRITIUM SORPTION STUDIES

Molten lithium appears to be the most promising blanket material for breeding tritium in fusion reactors. Three recovery techniques are being considered for

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

3. J. S. Watson and P. W. Fisher, "Vacuum Pumping for Controlled Thermonuclear Reactors," *Proceedings of the Ninth Symposium on Fusion Technology,* Garmisch-Partenkirchen, Federal Republic of Germany, June 14–18, 1976.

4. J. S. Watson et al., "Current CTR-Related Tritium Handling Studies at ORNL," *Proceedings of the Second Topical Meeting on the Technology of Controlled Nuclear Fusion,* Richland, Wash., Sept. 21–23, 1976, CONF-760935-P3, p. 895.

5. P. W. Fisher and J. S. Watson, "Cryosorption Vacuum Pumping of Deuterium, Helium, and Hydrogen at 4.2°K for CTR Applications," presented at the 1976 International Conference of the American Nuclear Society, Washington, D.C., November 1976 (published in the *Proceedings* of the Remote Systems Section).

6. P. W. Fisher and J. S. Watson, "Cryosorption Pumping of Helium at 4.2°K by Type 5A Molecular Sieve," to be presented at the National Meeting of the American Nuclear Society, New York, June 12–17, 1977.

removal of tritium from liquid lithium: (1) extraction with a molten salt, (2) permeation through a niobium window, and (3) sorption on a hydrogen-gettering metal. Tritium sorption from molten lithium (833 ± 54 ppb tritium) has been studied in a batch contactor at 300 and 400°C using metal sorbent samples of yttrium and zirconium. At 300°C, a sample of yttrium weighing 3.45 g, with a geometric surface of 13.1 cm^2, reduced the concentration of tritium in lithium (8 g) by a factor of 2 in 24 min. The controlling mass transfer resistance appeared to be in the liquid lithium phase; consequently, the mass transfer rate could be increased with forced convection, perhaps by an order of magnitude.

Twenty-one sorption runs were made at 300°C with the same yttrium metal sample. The results of these runs, in which the tritium concentration remaining in the lithium divided by the initial concentration is plotted as a function of the contact time, are shown in Fig. 17.4. Except for runs 1, 15, 18, and 19, the tritium concentration in the lithium decreased with contact time as two distinct first-order reactions. The reaction half-time increased from 24 min (for the first 30 min of contact time) to 20 hr (for contact times greater than 2 hr). The low mass transfer rates in run 1 can be explained by an activation of the yttrium surface.[3,7–9] The apparent rate decrease in runs 15, 18, and 19 can be explained by the accumulation of tritium in the yttrium and, thus, a reduction in the driving force. Comparing runs 2 and 15, the bulk tritium concentration in the yttrium sorber increased from 2 to 20 ppm.

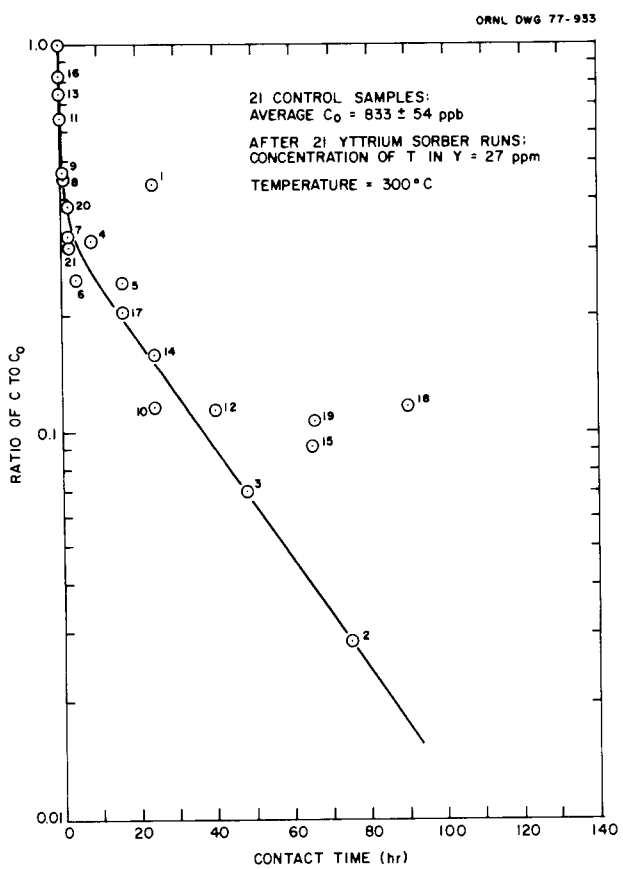

Fig. 17.4. Normalized tritium concentration in lithium as a function of contact time to yttrium sorber experiments.

Runs 9, 11, 13, and 16 (respective contact times of 30, 15, 10, and 5 min) were used to obtain an average mass transfer coefficient of $(6.1 \pm 1.1) \times 10^{-4}$ cm/sec. The driving force was assumed to be the tritium concentration in the lithium, and the ratio of yttrium surface area to lithium volume for the four runs was 0.82 ± 0.02 cm^{-1}. For a natural convection system, the magnitude of the mass transfer coefficient would indicate that the controlling mass transfer resistance is in the liquid lithium phase.

At the end of run 21, the yttrium sample was analyzed for tritium by dissolving the metal in dilute hydrochloric acid. During the sorption experiments, the estimated accumulation of tritium in the yttrium was 0.78 Ci, and the tritium found during dissolution was 0.90 Ci (115% recovery).

Four sorption runs were made at 300 and 400°C with tritiated lithium and a sample of zirconium. Even after 140 hr of contact time, the amount of tritium removed from the lithium in the batch contactor was less than 5%.

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

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

8. S. D. Clinton, P. W. Fisher, J. B. Talbot, and J. S. Watson, "Recent Experimental Engineering Studies Related to Controlled Thermonuclear Reactors," *Radiation Effects and Tritium Technology for Fusion Reactors*, CONF-750989, vol. III, pp. 519–38 (March 1976).

9. F. W. Wiffen and J. S. Watson, "Radiation Effects and Tritium Technology for Fusion Reactors," *Nucl. Fusion* **16**, 175–82 (1976).

17.3 TRITIUM RECOVERY FROM IRRADIATED LITHIUM-ALUMINUM AND SINTERED ALUMINUM PRODUCT ALLOYS

Tritium release rates from irradiated aluminum and sintered aluminum product (SAP) containing small concentrations of lithium have been studied. Solid Li-Al alloy has been suggested as a potential tritium breeding material for fusion reactors, and SAP has been suggested as a blanket or structural material.[10,11] This study differs from current studies[12] of solid aluminum alloy blanket material at other laboratories because of the low (ppm) lithium concentration, the incorporation of oxygen within some of the samples (SAP), and the use of large [1-in.-long (2.5-cm) wafers] samples rather than powders.

To study tritium recovery rates from irradiated Li-Al and SAP samples, a sample is heated to a desired temperature, and the released tritium is swept to a tritium monitor. The tritium-bearing argon is then routed to a trapping system composed of a CuO bed (600°C), two water bubblers, a moiecular-sieve trap, and another tritium monitor to detect the tritium released to the ORNL "hot" off-gas stack.

A series of six runs has been made to measure tritium release from irradiated SAP samples. The objective of the first run was to determine the temperature at which a significant tritium release was observed; this took place at ~250°C. The temperature of sample 1 was steadily increased to 450°C over a 30-hr period. The next two runs (samples 1 and 3) were made at a sample temperature of 400°C. It was difficult to control the temperature of sample 1; the temperature decreased to 340°C after 10 hr, then increased to 420°C after 15 hr. The temperature controller was adjusted, and the 400°C experiment was repeated with sample 3. Samples 2 and 6 were heated to 450 and 500°C, respectively, and sample 5 was heated to 450°C for a 100-hr run.

From analysis of the data, the release rates follow the pattern expected for bulk diffusion in the solid. Solid diffusion is indicated by the slope of one-half in the curves. The release rates observed by Wiswall and Wirsing[12] for Li-Al (powder form) did not follow a one-half slope, and attempts to interpret their results were not successful. Also, the exact sizes of the Li-Al, $LiAlO_2$, and Li_2SiO_3 particles were not known (materials were crushed and screened). From our experiments on diffusion in solid slabs, the diffusion coefficients at 400, 450, and 500°C were 2.12×10^{-10}, 8.36×10^{-10}, and 2.35×10^{-9} cm^2/sec respectively. From an Arrhenius relationship, shown in Fig. 17.5, the dependence of the diffusion coefficient on temperature was

$$D = 2.64 \times 10^{-2} \exp(-24{,}890/RT) ,$$

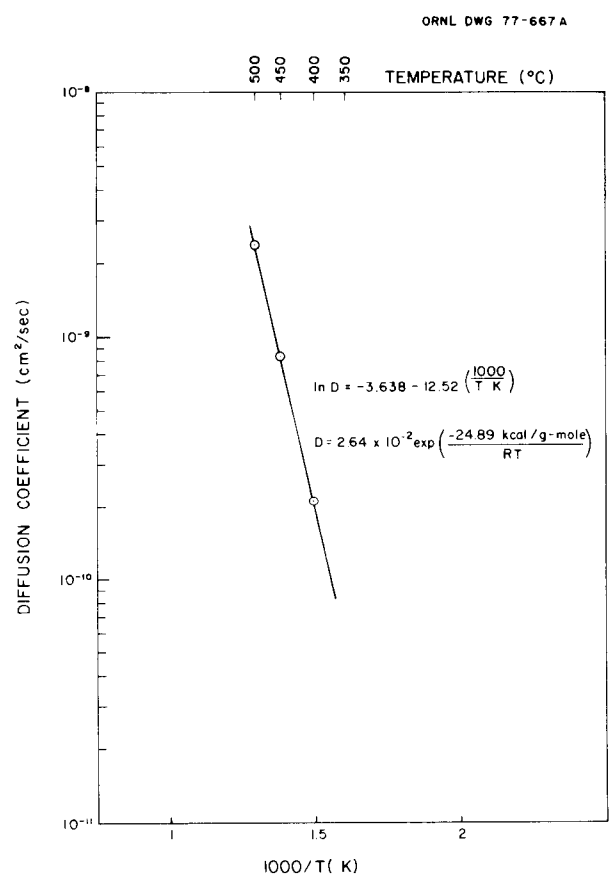

Fig. 17.5. Diffusion coefficients for solid Li-SAP alloy.

10. J. R. Powell et al., *Studies of Fusion Reactor Blankets with Minimum Inventory and with Tritium Breeding in Solid Lithium Compounds: A Preliminary Report,* BNL-18236 (June 1973).

11. J. B. Talbot, F. J. Smith, J. F. Land, and P. Barton, "Tritium Sorption in Lithium-Bismuth and Lithium-Aluminum Alloys," *J. Less-Common Met.* **50,** 23–29 (1976).

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

where

D = diffusion coefficient, cm^2/sec,

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

T = sample temperature, K.

The experiments with SAP samples indicate that reasonably rapid removal rates are possible. Three additional runs will be made at other temperatures of interest.

17.4 SORPTION PUMPING OF GASES BY DEEP BEDS OF SORBENTS

Sorption pumping by deep beds of sorbents has been used extensively as roughing pumps for small vacuum systems. These systems have used small pumps in only one or two sizes, and there is little need for careful or optimum design of the pump. However, fusion reactors and some hydrogen storage techniques need large beds of sorbents that can function as roughing pumps or as transfer pumps. In these larger systems, rational designs are essential, but no suitable design procedures have been reported for such systems. To meet this need, a program was initiated to develop a computer procedure for designing and predicting the performance of deep-bed sorption pumps.

An experimental effort was also begun to provide data for comparison with the calculations. The experimental apparatus measured the rate at which beds of molecular sieve (type 5A) pumped carbon dioxide from a test chamber. This system was chosen because the molecular sieve is a typical sorbent used in roughing applications, the carbon dioxide sorbate gas involved no hazard, and the gas could be sorbed conveniently at ambient temperature. The experimental equipment has been described previously.[13]

The mathematical model assumes that the sorbent consists of spherical particles and that the diffusion coefficient of the sorbate gas in the particle is independent of pressure or sorbent loading. In our calculations the equilibrium relation between sorbent loading and gas pressure was assumed to be linear (Henry's law), but, in principle, any type of sorption isotherm could be used. The bed is assumed to be isothermal, and flow down the bed is assumed to be by viscous flow. However, a modification is suggested which would permit treatment of molecular flow through the bed.

Once measurements of the carbon dioxide diffusivity in the sieve, equilibrium relations, and bed permeability were completed, the mathematical model was used to predict the rate at which beds of various depths would "pump down" a test chamber. Agreement between the measured and calculated pumping rates was acceptable. The most important conclusion was that the calculations accurately predicted the differences in behavior observed at different bed depths. The only disagreement between the calculated and observed pump-down curves occurred during the first few seconds of a run. These differences probably result from simplifications in the mathematical model. It was not possible to determine which particular assumptions were most responsible for the differences, but failure to account for diffusion resistance in the macrostructure of the molecular sieve particles is believed to be a major contributor to the problem. A procedure for selecting a proper bed depth was included in the mathematical analyses.

17.5 TNS SUPPORT STUDIES

At the beginning of FY 1977, ORNL initiated design studies for a Tokamak reactor experiment to be built after the Tokamak Fusion Test Reactor (TFTR) under construction at Princeton is completed. The device has been temporarily named The Next Step (TNS), since a major goal of the design study is to evaluate what can be done to most effectively advance fusion power after the TFTR. ORNL is the prime contractor for the study, but much of the work is subcontracted to Westinghouse Electric Corporation. Although all of the detailed engineering design is to be done by Westinghouse, ORNL is responsible for supervising and guiding the Westinghouse work. A similar and competitive design study is being made under the guidance of General Atomic Company (GA) with Argonne National Laboratory as the subcontractor.

TNS is an outgrowth of the Experimental Power Reactor (EPR) design studies conducted at ORNL,[14] GA, and ANL during FY 1976. One of the important conclusions of the EPR study was that the criteria for the EPR resulted in a device that was too large a technological step beyond TFTR. TNS will be smaller than

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

14. C. A. Flanagan et al., *Nuclear Engineering,* ORNL/TM-5575 (December 1976).

EPR, but recent developments in plasma physics are likely to hold the power to comparable levels. Comparisons are being made of several magnetic-field options, but TNS is likely to be an ignition device with superconducting magnets, at least for the TFTR coils.

The Chemical Technology Division is concerned with the design of the fuel cycle and tritium containment systems for TNS. Our role is to follow and direct the Westinghouse design, but not to do detailed design work. We have reviewed their work, requested changes in the vacuum pumping and fuel processing systems, and assisted in developing a list of research and development needs for TNS. However, recent activities in fuel handling design were limited while Westinghouse completed "trade studies" which compared costs for different TFTR coil designs.

Efforts are also being made to obtain better estimates of particle and energy confinement times for reactors with and without magnetic diverters. The need for a diverter and the performance of a plasma-diverter system have been identified as the most crucial uncertainties affecting fuel handling needs. A diverter can decrease the particle confinement (residence) time in the plasma by one to several orders of magnitude, and this directly affects the throughput of the fuel processing system. Diverter designs have been proposed for TNS which could not physically be pumped by vacuum pumps mounted outside the TFTR coils. The only feasible pumping system would involve deuterium-tritium trapping material (e.g., liquid lithium) as the diverter target. Although such a system was proposed, it introduced many serious problems of lithium contamination throughout the reactor, complicated tritium recovery from the lithium, caused lithium damage to the externally placed helium vacuum pumps, and impeded flow of lithium across the magnetic field lines in the diverter target. These problems appeared to be so difficult that recent efforts were directed toward determining if TNS could meet reasonable goals without the use of a diverter; this now appears likely.

At present, various options in TNS design are being compared, and no reference design has been developed. Such a design will be prepared during the second half of FY 1977.

18. Iodine Studies

During the processing of spent nuclear fuel elements, a high level of iodine retention is required, particularly for short-cooled fuels in which ^{131}I is present in large quantities. Although iodine removal from gas streams is the most widely studied procedure, the removal of iodine from aqueous solution offers an alternative method.

A process has been studied[1] for the removal of iodine from fuel dissolver solutions by using hydroxylamine nitrate (HAN) to reduce the iodine to iodide, which forms highly insoluble PdI_2 with the fission product palladium already in the solution. The limit of iodine removal by this method should depend ultimately on the saturation solubility of the PdI_2 in the dissolver solution. An ^{131}I-traced PdI_2 technique was used to determine these solubilities in nitric acid solutions; a special, specific ion electrode technique was used to determine these solubilities in water, calcium nitrate, and sodium perchlorate solutions. The tracer technique measures all the soluble iodine species, whereas the specific ion electrode technique measures only simple iodide ions (I^-).

Plots of log S/S_0 vs $(\mu)^{1/2}$ for nitrate and perchlorate solutions are shown in Fig. 18.1,[2] where S is the solubility of PdI_2 in a given aqueous solvent, S_0 is the solubility in water, and μ is the ionic strength of the solution. When compared on the basis of ionic strength, the solubilities determined in the nitrate solutions by the two methods were in reasonable agreement. This is evidence that the only important soluble iodine species is iodide. The solubilities in perchlorate solutions were much higher than those in nitrate solutions of the same ionic strength, which indicates differences in the soluble ionic species in the two systems. One possible explanation is that Pd^{4+} ions exist in the perchlorate media, but this was not resolved in this work.

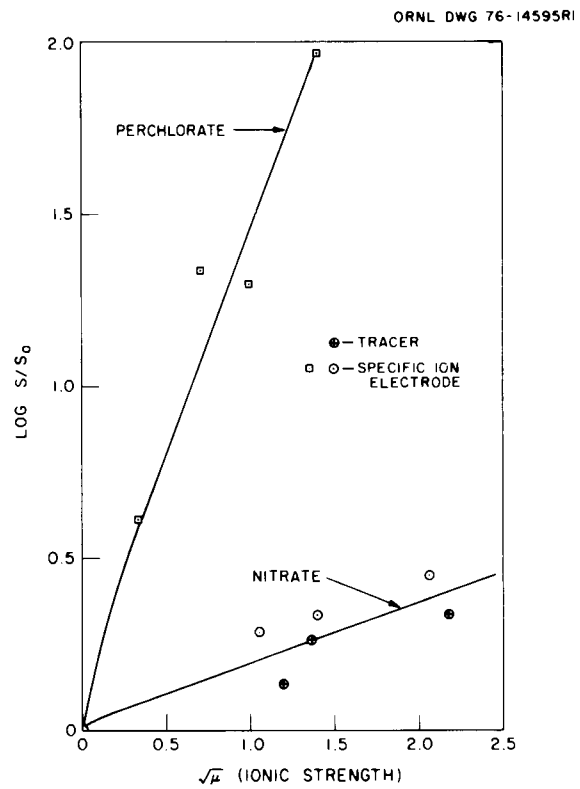

Fig. 18.1. Solubilities of PdI_2 in nitrate and perchlorate solution at 25°C.

At 25°C the activity product constant, $K_{ap(PdI_2)} = (2.5 \pm 0.4) \times 10^{-23}$, was calculated from the PdI_2 solubility obtained in water. With this value and the standard electrode potentials from the literature, the free energy of formation for PdI_2 was calculated to be −13.6 kcal/mole. This agrees well with the literature value of −14 kcal/mole given for the free energy of PdI_2 calculated from thermochemical data[3] and thus confirms the solubility value in water.

1. J. C. Mailen and D. E. Horner, "Removal of Iodine from Reactor Fuel Solutions as Insoluble PdI_2," *Nucl. Technol.* **33**(3), 260 (May 1977).

2. D. E. Horner, J. C. Mailen, and H. R. Bigelow, "Solubility of PdI_2 in Nitrate and Perchlorate Solutions," *J. Inorg. Nucl. Chem.* (in press).

3. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Selected Values of Chemical Thermodynamic Properties – Series I*, NBS Technical Notes 270-4 (1969).

19. Reactor Safety Research

19.1 FISSION PRODUCT RELEASE FROM LWR FUEL

The primary objectives of the experimental program are to determine the quantities of radiologically significant fission products released from defected fuel rods in steam and air at temperatures characteristic of spent fuel transportation accident (SFTA; 700°C maximum cladding temperature) and controlled loss-of-coolant accident (LOCA; 1200°C maximum cladding temperature) conditions and to identify their chemical and physical forms. The experiments carried out in the program are not intended to simulate any particular postulated accidents; rather, the observed physicochemical behavior will be translated into specific accident behavior by means of computer models being assembled by Battelle Columbus Laboratories.

During this report period, five tests were conducted with irradiated fuel capsules.[1–3] Also, the Implant Test Series was concluded.[4–7] Detailed information about the experimental apparatus used in these tests has been provided in previous reports.[4,6,8]

The two tests in the Low-Burnup Series were conducted with fuel that had been irradiated in the General Electric Test Reactor to burnups of about 1000 MWd/metric ton and had experienced peak linear heat ratings of about 20 kW/ft. The fuel utilized in the High-Burnup Test Series had been irradiated in the Carolina Power and Light Company's H. B. Robinson Reactor to a burnup of 30,000 MWd/metric ton and had attained a maximum peak linear heat rating of 10 kW/ft. Because of the high temperatures experienced by the low-burnup fuel, centerline voids (caused by grain growth, crystal restructuring, and UO_2 vapor transport) occurred. The irradiation temperature of the H. B. Robinson fuel was not high enough to cause fuel restructuring. Fission product gap inventories of irradiated fuel are directly related to the linear heat rating as demonstrated by the fission gas release values shown in Table 19.1. Since only volatile fission products from the fuel-clad gap, fuel cracks and voids, and plenum are released under SFTA and LOCA conditions, the importance of the linear heat rating is noted.

Each of the five irradiated capsules was predrilled (0.159-cm-diam hole) prior to testing to simulate a defect. Determinations of radial gap size[3] via a gas flow technique indicated a pellet-to-clad gap space in the H. B. Robinson fuel rod segments of about 20 μm. The specimens were heated with a resistance heater, and a

1. R. A. Lorenz, J. L. Collins, and O. L. Kirkland, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period July–September 1976,* ORNL/NUREG/TM-73 (December 1976).

2. R. A. Lorenz, J. L. Collins, and O. L. Kirkland, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period October–December 1976,* ORNL/NUREG/TM-88 (March 1977).

3. R. A. Lorenz, J. L. Collins, O. L. Kirkland, and R. L. Towns, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period January–March 1977,* ORNL/NUREG/TM-122 (June 1977).

4. R. A. Lorenz, J. L. Collins, and S. R. Manning, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period October–December 1975,* ORNL/TM-5290 (March 1976).

5. R. A. Lorenz, J. L. Collins, and S. R. Manning, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period January–March 1976,* ORNL/NUREG/TM-30 (July 1976).

6. R. A. Lorenz, J. L. Collins, S. R. Manning, and O. L. Kirkland, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period April–June 1976,* ORNL/NUREG/TM-44 (August 1976).

7. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, and S. R. Manning, "Fission Product Release from Simulated LWR Fuel," presented at the Proceedings of the Specialists' Meeting on the Behavior of Water Reactor Fuel Elements Under Accident Conditions, Spåtind, Nord-Torpa, Norway, Sept. 13–16, 1976; to be published in the *Proceedings.*

8. R. A. Lorenz, M. F. Osborne, J. L. Collins, and S. R. Manning, *Behavior of Iodine, Methyl Iodide, Cesium Oxide, and Cesium Iodide in Steam and Argon,* ORNL/NUREG/TM-25 (July 1976).

Table 19.1. Fission product release from irradiated fuel rods

	Low-Burnup Test Series		High-Burnup Test Series		
	LBU-1: 700°C, 5 hr	LBU-2: 900°C, 2 hr	HBU-4: 500°C, 20 hr	HBU-1: 700°C, 5 hr	HBU-2: 900°C, 2 hr
Burnup, MWd/metric ton	995	1000	30,745	30,745	30,745
Peak linear heat rating, kW/ft	18–20	19–21	9.95	9.95	9.95
Average gap inventory of Kr and He, %	11.4	19.6	0.26	0.26	0.26
Total ^{137}Cs inventory, mg[a]	5.27[b]	5.30[b]	208.6[c]	208.6[c]	208.6[c]
^{137}Cs released, μg	0.016	6.49	0.0075	0.062	1.191
^{137}Cs released, μg/hr	0.003	3.246	0.00038	0.012	0.596
Release of total ^{137}Cs inventory, %	2.95×10^{-4}	0.122	3.60×10^{-6}	2.95×10^{-5}	5.71×10^{-4}
Release of total ^{137}Cs inventory, %/hr	5.9×10^{-5}	6.1×10^{-2}	1.80×10^{-7}	5.91×10^{-6}	2.85×10^{-4}

[a]To obtain the total cesium mass, multiply the ^{137}Cs mass by 2.99 for low-burnup fuel and by 2.25 for high-burnup fuel.

[b]Calculated by making use of ORIGEN data for 169.8 g of 12% enriched uranium irradiated 19 days to 1000 MWd/metric ton (decayed 9.0 years).

[c]Calculated for burnup of 30,745 MWd/metric ton, 183.3 g of uranium originally in 12-in. segment, and a 911-day decay period (see Table 3 of ref. 3).

flowing 85% steam–15% argon atmosphere was provided. As shown in Table 19.1, the ^{137}Cs mass releases in the tests with low-burnup fuel were similar to those obtained in the tests with high-burnup fuel under identical conditions despite the large difference in total inventories (208.6 mg of ^{137}Cs in the high-burnup fuel vs 5.2 mg of ^{137}Cs in the low-burnup fuel). This further demonstrates the importance of the gap inventory in determining the extent of fission product release.

Only 0.2% of the *released* cesium in any of the three tests with high-burnup fuel was transported downstream beyond the quartz furnace tube. Gamma scanning showed that most of the released cesium was deposited on the quartz furnace tube liner near the simulated defect opening. Any elemental cesium or cesium oxide exiting the capsule would react with the steam to form CsOH, which in turn would react with the quartz to form a less-volatile silicate.

Quantitative measurements of the ^{129}I released in each of the irradiated-fuel tests are in progress. Two other radionuclides, ^{125}Sb and ^{106}Ru, were released in very small quantities in the tests with high-burnup fuel.

19.2 FISSION PRODUCT TRANSPORT TESTS

The initial objective of this task is to establish the need and the cost of a facility for experimentally validating computer models which predict fission product holdup in the LWR primary loop following a LOCA. The evaluation of need will review (1) the advantages of such a facility with respect to reactor licensing procedures, (2) the most critical test conditions for computer model verification purposes, and (3) the availability (or nonavailability) of existing facilities which may be employed for this objective.

The objective of the test facility, that is, the validation of codes for predicting fission product holdup in LWR primary systems following a LOCA, will be met by measuring the deposition levels of simulated fission products in scaled models of primary system components. At present, the following PWR components are being modeled: the hot- and cold-leg pipes, the steam generator, and the primary loop circulator. A preliminary flowsheet for the system is shown in Fig. 19.1.

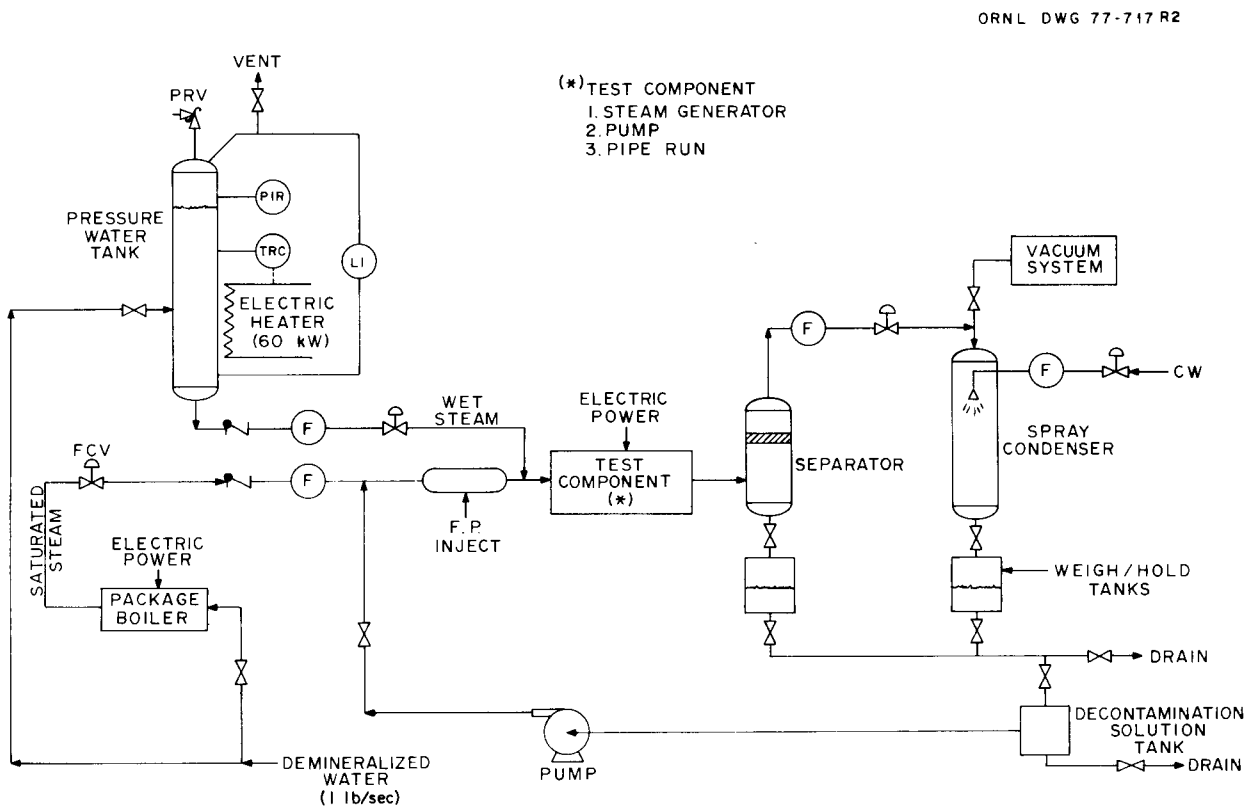

Fig. 19.1. Preliminary flowsheet of apparatus used in fission product transport tests.

The total cross-sectional area (flow area) of each model component has been selected to be $1/200$ of the prototype area. Model mass flows per unit area and steam conditions must simulate the range of conditions anticipated in the primary systems from controlled LOCAs to meltdown events.

The basic elements of the facility, in addition to the test components, are the steam supply system, provision for injection of appropriately tracer-labeled fission product simulants, a means of collecting and monitoring contaminated condensate before disposal, and a system for decontaminating the interior surfaces of all parts which will contain fission products. Component inserts must be removed so that internal surfaces may be scanned directly for activity. This mode of operation is necessitated by health physics regulations which limit the allowable quantities of tracer material. As an example, the effect of on-site regulations is to restrict the addition of tracer to less than 1 μCi per run and to limit the total accumulation to 10 μCi. These low levels preclude the use of external gamma scans as a diagnostic tool. Instead, clean deposition surfaces will have to be provided as inserts prior to each run, and deposition levels will be determined by leaching these surfaces and gamma-counting the leachate.

In addition, contamination control procedures must be incorporated into the loop design, as indicated in Fig. 19.1. Provisions must be made to cleanse the loop following each injection and for proper disposal of the fission product simulants.

Injection of three types of fission product simulants is being considered; the deposition characteristics of cesium (as CsOH), elemental iodine, and water-insoluble particulates will be modeled. The current design is to inject the cesium as a solution of CsOH through an atomizing spray nozzle into dry steam. Iodine will be injected as a gas through a designed constriction which is opened at the appropriate time.

19.3 TRANSIENT RELEASE FROM LMFBR FUEL

Development of the Capacitor Discharge Vaporization Technique

The capacitor discharge vaporization (CDV) technique has been developed to provide the capability of duplica-

ting, in gram quantities of UO_2, the high fuel internal energy conditions postulated during fast breeder reactor accidents. This method is used as a nonnuclear tool for studying fuel disassembly and the properties of the resulting aerosols, in support of the Nuclear Regulatory Commission's overall program of studies of radionuclide release and transport.[9,10]

The CDV technique involves preheating the UO_2 sample by direct electrical means to a fully molten state ($\sim$1600 J/g) and then supplying additional energy at about 1 MW/g until containment failure and disassembly occur. The energy for the high-rate phase is stored in capacitors.

During this report period, the ORNL CDV system, the containment research vessel (CRI-III), and the associated data collection and sampling equipment were completed. To date, 14 experiments have been performed, and preliminary results have been reported.[11–14] An average energy in excess of 3000 J/g (from 298 K) has been achieved before sample disassembly. Three grams of aerosol has been produced from a 20-g UO_2 pellet stack.

During capacitor bank firing, electrical data are recorded by digital and conventional storage oscilloscopes with a tape recorder backup. An example of the energy resolution achieved in our studies is shown in Fig. 19.2. Visual data are taken by TV as well as a high-speed (10,000 frames/sec) motion-picture camera. After disassembly, the aerosols are serially sampled to determine plate-out rates and concentrations vs time. Andersen impactor samples and nuclei counts are used to follow the change in aerosol properties. Electron photomicrograph grid samples are obtained by both diffusion and electrostatic precipitation, so that primary particle sizes may be determined. These results are then correlated with the energy density corresponding to a comparable hypothetical core disruptive accident (HCDA) reactivity ramp rate.

High-Density Uranium Oxide Aerosols

The generation and characterization of highly concentrated aerosols of uranium oxide (UO_2 or U_3O_8) and fission products as simulants for LMFBR-HCDA mixed aerosols are being conducted in our largest facility (CRI-II) as part of the Aerosol Release and Transport Program.

The present method of generation employs an adaptation of the metallurgical dc electric arc cold-hearth furnace and generates either UO_2 or U_3O_8 vapor, which condenses immediately to form a finely dispersed aerosol in a semicontinuous process. Operating times of 1 to 10 min have been used, and aerosol concentrations ranging from 1 to 12 g/m^3 have been attained. Since the furnace housing must be water-cooled, the intense thermophoretic gradients tend to cause large fractions of the aerosol to deposit locally instead of being carried into the test vessel. The physical arrangement of the aerosol generator and the 4.5-m^3 CRI-II vessel are shown in Fig. 19.3. Optimization of the hearth design and the argon flushing process is expected to yield concentrations up to about 20 g/m^3. A tungsten hearth will be used for concentrations above this level; eventually a new generator, based on the ignition of powdered uranium in oxygen in a dc plasma metal-spray torch, may be substituted.

Our future test program includes an investigation of the effect of high levels of radioactive krypton on the agglomeration rate of mixed aerosols and a study of the coagglomeration and/or partition of the most significant fission products[15] with the fuel aerosol.

9. M. J. Kelly et al., "Development and Application of Capacitor Discharge Vaporization Technique for Fuel Aerosol Studies," presented at the International Meeting on Fast Reactor Safety and Related Physics, Chicago, Oct. 6–8, 1976.

10. M. H. Fontana and T. S. Kress, *LMFBR Aerosol Release and Transport Program Quarterly Progress Report for April–June 1976,* ORNL/NUREG/TM-59 (December 1976).

11. M. H. Fontana and T. S. Kress, *LMFBR Aerosol Release and Transport Program Quarterly Progress Report for July–September 1976,* ORNL/NUREG/TM-75 (February 1977).

12. M. H. Fontana and T. S. Kress, *LMFBR Aerosol Release and Transport Program Quarterly Progress Report for October–December 1976,* ORNL/NUREG/TM-90 (March 1977).

13. M. H. Fontana and T. S. Kress, *LMFBR Aerosol Release and Transport Program Quarterly Progress Report for January–March 1977,* ORNL/NUREG/TM-113 (in press).

14. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1976,* ORNL-5172.

15. G. W. Parker, "Fast Reactor HCDA Fuel Aerosols, Physical and Chemical Behavior," presented at the Annual Meeting of the American Ceramic Society, Chicago, Apr. 23–25, 1977.

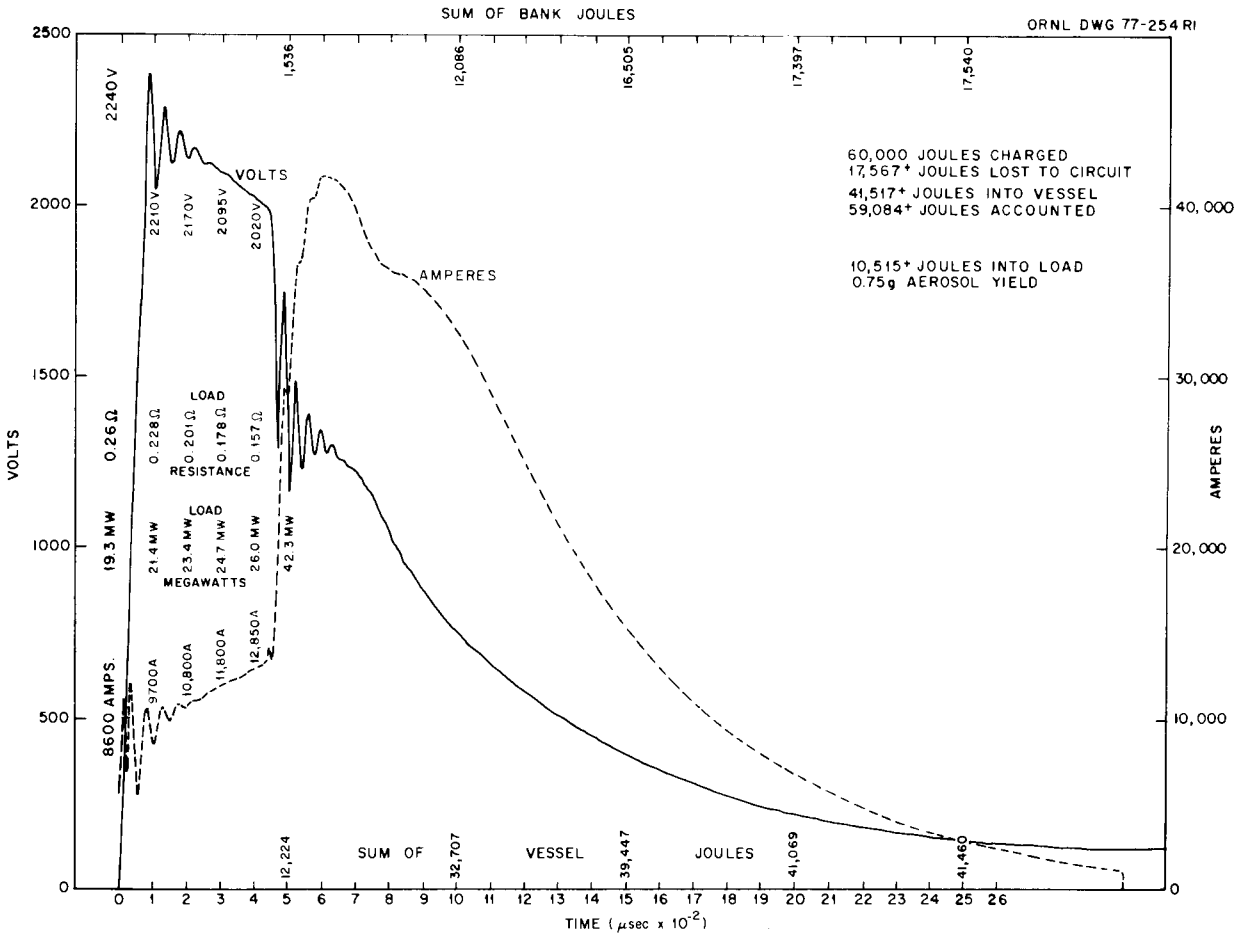

Fig. 19.2. Typical energy resolution curve obtained with CDV system.

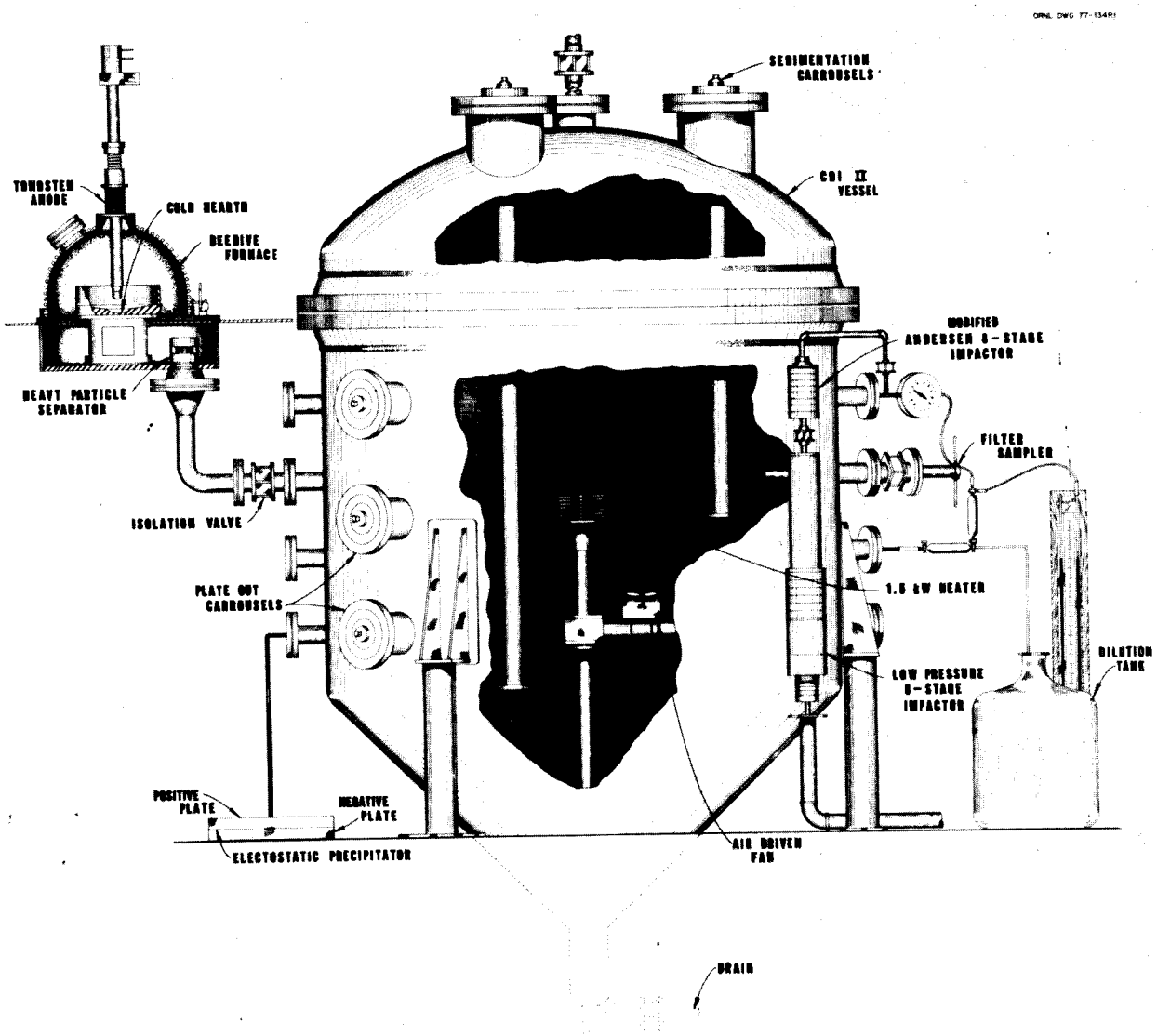

Fig. 19.3. CRI-II vessel, aerosol sampling equipment, and electric arc cold-hearth furnace.

20. Nuclear Regulatory Commission Programs

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

Engineering survey studies were conducted to provide the Office of Standards Development of the U.S. Nuclear Regulatory Commission (NRC) with the technical information required to formulate appropriate ALARA guidelines for the release of radioactive materials from all segments of the nuclear fuel cycle. A draft report on the conversion of yellow cake to UF_6 by the "dry" process was prepared and submitted to NRC for review.[1] The report is being revised to reflect the suggestions made in the review and to include recently available data on the actual releases of radioactive materials from an operating plant. A report on the conversion of recycle uranium to UF_6 was also prepared during this period.[2] The engineering reports present incremental capital and operating costs for changes and additions to systems and develop corresponding source terms for radioactive emissions and noxious effluents. These systems cover the range from present practice to the foreseeable limits of available technology on the basis of expected operation over the life of the facilities. Estimates of errors inherent in the development of these data are stipulated. The environmental part of each study describes the behavior of radionuclides and other noxious materials in the environment and quantitatively estimates the radioactive exposure to the public.

1. M. B. Sears, R. E. Blanco, B. C. Finney, G. S. Hill, R. E. Moore, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle – Conversion of Yellow Cake to Uranium Hexafluoride. Part I. The Fluorination-Fractionation Process,* ORNL/NUREG/TM-7 (in preparation).

2. J. W. Roddy, R. E. Blanco, B. C. Finney, G. S. Hill, R. E. Moore, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle – Conversion of Recycle Uranium to UF_6*, ORNL/NUREG/TM-37 (in preparation).

20.2 SAFETY REVIEW OF NUCLEAR FACILITIES

Federal regulations require that privately owned fuel reprocessing plants and fuel storage facilities be licensed by the NRC prior to start of operation. In connection with the licensing process, the Chemical Technology Division, with assistance from the General Engineering and Instrumentation and Controls Divisions, is providing technical support to the NRC in reviewing the safety of these facilities and in the preparation of safety evaluation reports and related generic reports. During this report period, we participated in the safety review of Allied General Nuclear Services' Barnwell Nuclear Fuel Plant Separations Facility, the Exxon Fuel Recovery and Recycling Center Separations Facility, the General Electric Morris Operation modified Fuel Storage Facility, and the Stone and Webster Independent Spent Fuel Storage Facility. Peripheral activities included the preparation of expert witness testimony for the California hearing and participation in a visit to the Nuclear Fuel Services reprocessing plant located at West Valley, New York, to determine the current status of the plant facilities.

20.3 SAFEGUARDS STUDIES

The Chemical Technology Divisions's safeguards work for the NRC involves the study and development of requirements, criteria, and operating characteristics of storage vaults that offer an extremely high degree of protection for material kept in the vault. Results of the study will assist the Materials Protection Standards Branch of NRC in the preparation of standards, guides, and criteria for vault storage systems within the licensee fuel cycle sector.

Early in November a draft report on the Desirability and Feasibility of Vault Automation was submitted to the NRC. Following a brief review period, we met with NRC officials, and it became apparent that significant changes were required. Additional information was needed, and the thrust of the document had to be

changed to more effectively meet the needs of the NRC. This work was initiated immediately and by mid-February had progressed to a point where a visit by our NRC staff contact, F. A. Costanzi, was requested.

At the heart of the changes was the development of a method to evaluate the safeguards functions of the vault. The basic framework of this method, in which detection, delay, and diversion could be quantified, was discussed extensively with Costanzi, who felt it was a substantial contribution to the report.

Other significant activities include obtaining rather extensive user data on the operability and maintainability of a specific type of mechanical equipment which might be installed in an automated vault.

Since high system reliability and availability of automated handling equipment in a vault are of paramount importance and have a favorable effect on safeguards, we have contracted with J. B. Fussell, University of Tennessee, to develop a method of calculating system availability utilizing available user data. In a parallel effort, we have initiated work on a value/impact statement for the type of an automated system that might be installed in a vault.

20.4 ENVIRONMENTAL STATEMENT ON PLUTONIUM UTILIZATION (GESMO)

Staff members of the Chemical Technology Division, providing technical support to the NRC, assisted in the preparation of the Final Generic Environmental Statement on the Use of Recycle Plutonium in Mixed Oxide Fuel in Light-Water-Cooled Reactors (GESMO). Reactor concepts[3] associated with plutonium utilization were developed, and computer-derived bases for estimating the radioactivities in spent fuel were provided for the various modes of fuel-cycle operations addressed in GESMO. Technical assistance was provided for both the preparation of Chapter IV, "Environmental Impact Due to the Implementation of Plutonium Recycle," and the development of tables summarizing the environmental impact of fuel-cycle operation. Staff members prepared Section H, Chapter IV, "Radioactive Waste Management," delineating the sources of radioactive waste from the LWR industry and the ultimate disposal of the wastes. Special emphasis was given to geologic disposal. The GESMO document was published in August 1976 as NUREG-0002. Staff members appeared as expert witnesses at the GESMO public hearings in the areas of waste management, fuel reprocessing, transportation, and the estimation of the amounts of radioactive materials contained in LWR plutonium (mixed oxide) recycle reactors.

20.5 WASTE MANAGEMENT PARAMETRIC STUDIES

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

Intensive literature surveys were made to identify all feasible options for managing the radioactive wastes associated with reprocessing LWR fuels. This information was assembled into option diagrams for the individual types of wastes. Each diagram considers a particular type of waste and lists all options available for the operating plant, on-site storage, shipping, and disposal. Option diagrams for the management of tritium, fuel cladding hulls, ^{14}C, ^{85}Kr, iodine, and intermediate-level liquid wastes have been completed. A report on the management of ^{14}C and ^{85}Kr wastes from LWR fuel reprocessing is being prepared. Three alternative technologies, caustic scrubbing, molecular sieve adsorption, and fluorocarbon absorption, have been considered for the removal of ^{14}C as CO_2 from the dissolver and vessel off-gas streams. Cryogenic absorption and fluorocarbon absorption have been selected as the treatment methods for ^{85}Kr. Two locations in the process effluent stream have been analyzed for the caustic scrubber and the molecular sieve system. In the first analysis, the CO_2 removal units are located in a relatively uncontaminated stream and follow the other treatment systems. The units processing the combined dissolver and vessel off-gas stream (6000 scfm) do not require shielding. In the second analysis the units are located only in the dissolver off-gas stream (100 scfm), follow a preliminary iodine and a high-efficiency NO_x removal system, and require shielding. The capital and annual cost estimations for the conceptual design of a caustic scrubber system using either a slaked-lime gas slurry contactor or

3. J. W. Wachter, *Model Plutonium Recycle Reactor for Environmental Analysis of the Mixed Oxide Fuel Cycle* (in preparation). (Draft is available in NRC Public Document Room.)

a double alkali scrubber unit for conversion and retention of CO_2 to $CaCO_3$ have been completed. Transportation and disposal cost options for the ^{14}C-containing $CaCO_3$ product have been included. The conceptual design and the cost estimates for the system incorporating molecular sieves for the removal of CO_2 from the two gaseous effluent streams have been completed.

20.6 WASTE MANAGEMENT GENERIC STUDIES

On January 12 to 14, 1977, ORNL sponsored a Radwaste Management Workshop in New Orleans, Louisiana, to obtain operating data on the uses of evaporation, ion exchange, filtration, and solid radioactive waste (radwaste) practices at nuclear power plants. The collected data are being used (1) to update three earlier generic reports done at ORNL on the status of evaporation,[4] ion exchange,[5] and solid radwaste practices[6] at nuclear power plants; and (2) to prepare a new report on filtration. This survey was conducted at the request of the Effluent Treatment Systems Branch of the NRC. All segments of the nuclear power industry were invited to participate, and a total of 188 representatives came from utilities, nuclear steam supply system vendors, archtitect-engineering (A-E) firms, radwaste equipment vending companies, national laboratories, private research organizations, the Energy Research and Development Administration, and the NRC. Utility attendees accounted for 36% of the total attendance.

Prior to the workshop, questionnaires on evaporation, ion exchange, filtration, reverse osmosis, and solid radwaste practices were sent to all attendees. Many of the questions had been suggested by the attendees at the request of the workshop steering committee. The response to this approach was exceptionally large, indicating that the workshop was filling a special need. There were four major workshop groupings: Volume Reduction; Solidification; Physical and Chemical Separations; and Corrosion, Decontamination, and Retrofitting. The majority of the chairmen, cochairmen, speakers, and reporters (i.e., summarizers) for each of the sessions came from utilities, A-E firms, and national laboratories.

The power plant representatives at the workshop discussed the merits and shortcomings of their radwaste systems. These discussions indicated that a general shift toward emphasis on radwaste personnel training has occurred, and in the majority of plants a larger staff has been assigned to radwaste service. Most utility people at the workshop felt that the burden of radwaste treatment must be eased by greater availability of better, more reliable systems that would lessen manpower demands. Almost all believed the responsibility for system improvement is the responsibility of the A-Es and vendors. Generally, the power plant operators expressed a preference for robust physical methods for handling radwaste rather than depending upon intricate chemical adjustment of the radwaste system. The utility representatives expressed concern that frequent regulatory changes may force them to make expensive radwaste retrofits that may not be any more tenable than the conditions they replaced.

Rough drafts of the four generic reports based on the data obtained from the workshop and from the responses to the questionnaires should be available in the early part of 1978.

---

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

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

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

21. Miscellaneous Programs

21.1 STUDIES INVOLVING TESTS OF OBSOLETE CASKS

In recent years, there has been a great deal of interest in the safety aspects of nuclear-related programs. The transportation of radioactive materials has generated considerable discussion, since some of these highly radioactive materials are moved through the public sector. Such movements must be accomplished with a high degree of safety and confidence.

At present, the proof that containers used to transport radioactive material will be safe, even in severe accidents, is based on engineering calculations and, in a few cases, model testing. Large, full-size casks are being destructively tested to develop the necessary data base in an effort to demonstrate that package behavior can be predicted with confidence.

Over the past year, the 23-ton (21-metric ton) Heavy Water Components Test Reactor cask was subjected to two end-on drop tests. In the first test, the cask was dropped from a height of 30 ft (9 m) onto the armor-plate surface of a temporary, reinforced concrete impact pad at the ORNL Tower Shielding Facility (TSF). This facility has the capability of lifting 110 tons (100 metric tons) to a height of 30 ft, or 22 tons (20 metric tons) to a height of 200 ft (61 m). In the first full-scale drop test with an impact limiter, a prototype balsa device was placed over the closure end of the cask. The impact limiter provided sufficient cushioning upon impact so that the shock loading to the cask was negligible and damage to the closure was not discernible. The second drop test was carried out without the impact limiter to demonstrate the shock loading and deformation that had been previously predicted by a computer program. In a third test the cask was dropped 40 in. (1 m) onto a 6-in.-diam (15-cm) steel piston to demonstrate the bending effects from such a test.

A permanent impact pad has been installed at the TSF to serve as the "essentially unyielding surface" described in regulations. The structure consists of 600 tons (545 metric tons) of reinforced concrete with a 70-ton (64-metric ton) armor-plate structure embedded in the top surface. This structure is designed for impacts of casks weighing up to 60 tons (55 metric tons).

Two 22-ton (20-metric ton) obsolete casks, both Knapp Mills 13 X 129 spent fuel casks, have been purchased for use in the next phase of the cask testing program. One of the casks is being decontaminated at the Nevada Test Site. The results of these tests will be used to compare the damage caused by impacting on an essentially unyielding surface to that experienced in real-life accidents.

21.2 CEMENT AND CONCRETE TECHNOLOGY

The Cement and Concrete Technology Program is supported by the Office of Waste Isolation (OWI) Borehole Plugging Program. The objective of this program is to develop the expertise required to assist OWI in devising and testing cementitious mixtures suitable for plugging drill holes that may represent a hazard to a waste isolation repository. These holes range in size from small exploratory holes to mine shafts. The primary characteristics that the solids resulting from these mixtures must demonstrate are high density, low permeability, and long-term durability. Sufficient data must be collected in parametric studies to allow tailored mixtures to be formulated in the event it is required to match the characteristics of the wall rock. The dominant theme throughout the program will be the reliability of the physical and chemical measurements and the quality control that is available or can be exercised on the ingredients used to make the plug material. Thus a major emphasis of the investigation is on the development of suitable methods, techniques, and knowledge for measuring the physical and chemical properties of cementitious solids and aggregates. Most of the work will involve pozzolanic (fly ash), expansive, and hydrothermal cements, but some studies will be devoted solely to the research and development required for thermophysical property measurements of natural rocks. Later, the techniques will be used in referee measurements made periodically to determine the precision of values obtained by other subcontractors.

During the past year, laboratory space was modified to accommodate the needs of the program, and most of the major equipment for mixing and testing samples was installed. A number of procedures were established for the physical testing of cement and concrete based on information obtained from the literature and discussions with leading cement technologists. A computer program, DASAVOR (Data Storage and Variable Output Recovery System),[1] was developed to handle the large quantities of data that will be generated in this project. The program allows rapid collation of the data in three usable forms: (1) a listing of all data on each experiment, (2) a listing of selected columns of data, and/or (3) a plot of any set of data points.

Parametric studies are in progress to determine the effect of fly-ash composition and concentration on the physical properties of cement–fly ash mortars and pastes. This investigation involves up to 14 different cements, 7 different fly ashes, 1 to 5 fly-ash concentrations, 3 curing times, and 2 curing temperatures. In the initial control tests, the seven-day compressive strength values showed the following linear relationship:

$$Y = 28.43 - 1.46X ,$$

where Y is the compressive strength in MPa, and X is the wt % fly ash present in the mortar. The coefficient of variation (r^2) was 0.98. These results were obtained from tests made on specimens containing 23 wt % Kingston fly ash plus Marquette type I cement, 63.2 wt % Ottawa standard sand, and 13.8 wt % water. The specimens were cured at 30°C and >90% relative humidity.

21.3 CONVERSION OF CONSOLIDATED EDISON URANIUM FROM A NITRATE SOLUTION TO UO_3

We are designing conversion and storage systems that will permit us to convert 1047 kg of uranium (76.5% ^{235}U, 9.67% ^{233}U, 1.40% ^{234}U, 5.63% ^{236}U, 6.84% ^{238}U) to UO_3 powder. This uranium, from the Consolidated Edison Indian Point Reactor, is stored as a nitrate solution. Laboratory studies using synthetic solutions indicate the feasibility of converting the material, by direct denitration, to UO_3 powder in nominal 3-kg batches. We plan to install and test equipment in FY 1978 and perform the conversion operation in FY 1979.

21.4 NUCLEAR SAFETY ASSISTANCE

Nuclear Safety is a bimonthly technical journal prepared for the U.S. Nuclear Regulatory Commission (NRC) by the Nuclear Safety Information Center (NSIC). The scope of the journal is limited to topics relevant to the analysis and control of hazards associated with nuclear reactors, operations involving fissionable materials, and the products of nuclear fission and their effects on the environment. The fields covered are divided into sections, each the responsibility of a section editor. The sections are General Safety Considerations, Accident Analysis, Control and Instrumentation, Plant Safety Features, Consequences of Effluent Release, Operating Experiences, and Current Events.

The Plant Safety Features section has been edited by some member of the Chemical Technology Division for a number of years. The subject area of this section covers a broad spectrum, including waste management, contamination control, containment, structural design, component design and testing, fire safety, and, in fact, most features of any plant involved in the nuclear fuel cycle. The section editor solicits articles from qualified authors all over the world, edits the articles for technical content, submits them for peer review by two or more persons (preferably outside ORNL) knowledgeable in the subject area, and generally coordinates the preparation and publication of two articles for each bimonthly issue of the journal.

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

"The Safety of Reactor Pressure Vessels,"

"Improving Reactor Pressure-Vessel Availability by Design,"

"Equipment Cell Liners for LMFBRs,"

"Neutron Irradiation Embrittlement of Reactor Pressure-Vessel Steels,"

*"Relation of Intermediate-Sized Pressure-Vessel Tests to LWR Safety,"

"Reliability of Piping in LWRs,"

"The Ice-Condenser System for Containment Pressure Suppression,"

1. R. T. Jubin and J. G. Moore, *A User's Guide for the Computer Program DASAVOR – Data Storage and Variable Output Recovery System*, ORNL/TM-5807 (May 1977).

"Emergency-Shutdown Cooling Towers,"

"Phenomenological Investigations of Postulated Meltdown Accidents in LWRs,"

"The Fourteenth ERDA Air-Cleaning Conference,"

"Trends in the Design of PWR Containment Structures and Systems."

The number of paid subscriptions to *Nuclear Safety* averaged about 2200 per issue in 1976; in addition, over 2000 copies per issue were distributed free by ERDA and the NRC to depository libraries. The number of paid subscriptions compares favorably with those of other journals in the nuclear field. *Nuclear Safety* has won first place for the past two years in the communication competition by the Society for Technical Communication, and in the same periods, the Plant Safety Features section won awards of distinction for the best article in each year. The article identified above* is the 1977 winner.

21.5 ASSISTANCE TO THE OFFICE OF WASTE ISOLATION

The transportation/logistics study being undertaken for OWI involves the identification of problems and concerns that must be addressed within the period 1977–1985 to ensure the existence of a viable transportation system that will enable shippers to transport their waste to the final geological repository after 1985. Following the identification phase, a program plan will be developed aimed at solving the problems through research and development or special studies activities. As a corollary to the study, a logistics model will be developed that will enable OWI or other personnel to determine modes of shipments and shipping schedules, to optimize routes, and to minimize costs, personnel exposures, etc.

Potential subcontractors who have experience in the radioactive materials transportation field and can provide information on expected problem areas are being interviewed. Problem identification and a program plan must be completed by the end of FY 1977.

Publications, Speeches, and Seminars

BIOCHEMICAL TECHNOLOGY

Bostick, W. D., "Applications of Centrifugal Fast Analyzers in Biochemical Research," presented at the University of South Florida, Tampa, Aug. 13, 1976.

Bostick, W. D., "Enzymatic Determination of Ammonia and Nitrate Nitrogen in Water by Use of the Centrifugal Fast Analyzer," presented at the 20th Conference on Analytical Chemistry in Energy and Environmental Technology, Gatlinburg, Tenn., Oct. 13, 1976.

Bostick, D. T.,[1] and W. D. Bostick, "The Kinetic Spectrophotometric Determination of Sulfate Using the Miniature Centrifugal Fast Analyzer," presented at the 20th Conference on Analytical Chemistry in Energy and Environmental Technology, Gatlinburg, Tenn., Oct. 13, 1976.

Bostick, W. D., R. C. Lovelace, and C. A. Burtis,[2] "Enzymatic Determination of Ammonia with a Miniature Centrifugal Fast Analyzer," *Water Res.* **10**, 887 (1976).

Bostick, W. D., and J. E. Mrochek, "Biochemical Markers in Cancer; Screening of Serum Enzyme Activity by Use of a Centrifugal Analyzer," presented at the Spring Meeting of the American Association of Clinical Chemists, Savannah, Ga., Mar. 10–12, 1977.

Bostick, W. D., and J. E. Mrochek, "Use of a Centrifugal Fast Analyzer (CFA) for the Evaluation of a Chemical Activation Procedure for Creatine Kinase MB Isoenzyme," presented at the Fall Meeting of the Southeastern Section of the American Association of Clinical Chemists, Gatlinburg, Tenn., Oct. 28–30, 1976.

Bostick, W. D., W. W. Pitt, and J. E. Mrochek, "Analytical Applications of Centrifugal Fast Analyzers," presented to the Department of Chemistry, University of Georgia, Athens, April 1976.

Burtis, C. A.,[2] "A Study of the Factors That Influence Sample Evaporation in the Clinical Laboratory," presented at the 28th National Meeting of the American Association of Clinical Chemists, Houston, Aug. 1–6, 1976.

Burtis, C. A.,[2] T. O. Tiffany,[3] and C. D. Scott, "The Use of a Centrifugal Fast Analyzer for Biochemical and Immunological Analyses," *Methods Biochem. Anal.* **23**, 189 (1976).

Burtis, C. A.,[2] and H. Veening,[4] "Automated Analysis," presented at the American Chemical Society Short Course, Chicago, Apr. 23–24, 1976.

Compere, A. L., and W. L. Griffith, "Continuous Fixed-Film Denitrification of High-Strength Industrial Nitrate Wastes," presented at the Annual Meeting of the Society for Industrial Microbiology, Jekyll Island, Ga., Aug. 16–20, 1976.

Compere, A. L., and W. L. Griffith, "Fermentation of Waste Materials to Produce Industrial Intermediates," *Dev. Ind. Microbiol.* **17**, 247 (1976).

---

1. Analytical Chemistry Division.
2. Center for Disease Control, Atlanta, Ga.
3. Pathology Associates, Inc., Spokane, Wash.
4. Bucknell University, Lewisburg, Pa.

Compere, A. L., W. L. Griffith, W. J. Boegly, Jr.,[5] I. Spiewak,[6] D. G. Thomas,[6] and S. A. Reed,[6] *MIUS Technology Evaluation – Water Supply and Treatment,* ORNL/HUD/MIUS-21 (April 1976).

Egan, B. Z., "Kinetics of Enzyme-Catalyzed Production of Hydrogen," presented at the ERDA Thermochemical Hydrogen Research Meeting, Germantown, Md., April 1976.

Egan, B. Z., and D. W. Holladay, "Use of Catechol Oxygenase for Determination of Catechol," *Anal. Lett.* **10**(3), 213 (1977).

Egan, B. Z., and C. D. Scott, "Enzyme-Catalyzed Production of Hydrogen," presented at the 172d National Meeting of the American Chemical Society, San Francisco, Aug. 29–Sept. 3, 1976.

Genung, R. K., and H. W. Hsu,[7] "Studies of Antigen-Antibody Intersections by Zonal Centrifugation Using Latex Beads as Carriers," presented at the Fall Meeting of the Southeastern Section of the American Association of Clinical Chemists, Gatlinburg, Tenn., Oct. 28–30, 1976.

Genung, R. K., and J. E. Mrochek, "Kinetic Assay for Gamma-Glutamyl Transpeptidase with the Centrifugal Fast Analyzer," presented at the Joint Southeast Florida–North Carolina Meeting of the American Association of Clinical Chemists, Atlanta, Ga., April 1976.

Griffith, W. L., and A. L. Compere, "Continuous Lactic Acid Fermentation Using a Fixed-Film System," presented at the Annual Meeting of the Society for Industrial Microbiology, Jekyll Island, Ga., Aug. 16–20, 1976.

Griffith, W. L., and A. L. Compere, "Method for the Isolation of Organisms Which Degrade Polyphenolic Compounds Including Lignins and Tannins," presented at the 76th Annual Meeting of the American Society for Microbiology, Atlantic City, N.J., May 2–7, 1976.

Holladay, D. W., C. W. Hancher, D. D. Chilcote,[8] and C. D. Scott, "Biodegredation of Phenolic Waste Liquors in Stirred-Tank, Columnar, and Fluidized-Bed Bioreactors," presented at the 69th Annual Meeting of the American Institute of Chemical Engineers, Chicago, Nov. 28–Dec. 2, 1976.

Jolley, R. L., "Characterization of Chloro-Organics: Compounds of Environmental Concern Produced by Chlorination of Water," presented as an Oak Ridge Associated University Traveling Lecture, Tennessee State University, Nashville, Nov. 12, 1976.

Jolley, R. L., "Discussion Leader Comments," presented at the Conference on Aquatic Pollutants and Biological Effects with Emphasis on Neoplasia, New York, Sept. 27–29, 1976.

Jolley, R. L., "Identification of Organic Constituents in Natural and Process Waters Using High-Resolution Liquid Chromatography," presented as an Oak Ridge Associated University Traveling Lecture, University of Alabama, Tuscaloosa, Dec. 2, 1976.

Jolley, R. L., "Identification of Organic Halogen Products," *Chesapeake Sci.* **18**(1), 122 (1977).

Jolley, R. L., "Nonvolatile Chloro-Organics in Secondary Effluents and Their Possible Biological Effects," presented at the Environmental Research Center Seminar, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 29, 1976.

Jolley, R. L., (ed.), *Proceedings of the Conference on the Environmental Impact of Water Chlorination,* CONF-751096 (1976).

Jolley, R. L., "Sources of Organic Materials in Water," Session chairman remarks presented at the Gordon Research Conference, Andover, N.H., June 28–July 2, 1976.

Jolley, R. L., G. Jones, Jr., W. W. Pitt, Jr., and J. E. Thompson, "Chlorination of Organics in Cooling Waters and Process Effluents," p. 115 in *Proceedings of the Conference on the Environmental Impact of Water Chlorination,* CONF-751096 (1976).

---

5. Energy Division.
6. Engineering Technology Division.
7. Department of Chemical Engineering, University of Tennessee, Knoxville.
8. Hanna Mining Co., Nashwauk, Minn.

Jolley, R. L., G. Jones, Jr., W. W. Pitt, Jr., and J. E. Thompson, "Determination of Chlorination Effects on Organic Constituents in Natural and Process Waters Using High-Pressure Liquid Chromatography," p. 233 in *Identification and Analysis of Organic Pollutants in Water,* ed. L. H. Keith, Ann Arbor Science, Ann Arbor, Mich., 1976.

Jolley, R. L., and W. W. Pitt, Jr., "Chloro-Organic By-Products from Sewage Effluent Chlorination," presented at the 1976 National Conference on Environmental Engineering, American Society of Civil Engineers, Seattle, Wash., July 12–14, 1976.

Jolley, R. L., and W. W. Pitt, Jr., "Chloro-Organic Pollutants: Aquatic Ecosystem Artifacts Produced During Water Chlorination," presented at the 27th Annual Meeting of the American Institute of Biological Sciences, New Orleans, May 30–June 4, 1976.

Jolley, R. L., and W. W. Pitt, Jr., "Nonvolatile Organics in Disinfected Wastewater Effluents: Characterization by HPLC and GG/MS," presented at the 173d National Meeting of the American Chemical Society, New Orleans, Mar. 20–27, 1977.

Jolley, R. L., and W. W. Pitt, Jr., "Organics in Natural and Polluted Water of Environmental Interest: Analysis by HPLC and GG/MS," presented at the Annual Meeting of the American Association for the Advancement of Science, Denver, Colo., Feb. 20–25, 1977.

Katz, S., W. W. Pitt, Jr., J. E. Mrochek, and S. Dinsmore, "Sensitive Fluorescent Monitoring of Carbohydrates in Column Chromatography," presented at the Symposium on High-Pressure Liquid Chromatography of Carbohydrates, Centennial Meeting of the American Chemical Society, New York, Apr. 4–9, 1976.

Lakings, D. B.,[9] T. P. Waalkes,[10] E. Borek,[11] C. W. Gehrke,[12] J. E. Mrochek, J. Longmore,[9] and R. H. Adamson,[9] "Composition, Associated Tissue Methyltransferase Activity, and Catabolic End Products of Transfer RNA from Carcinogen-Induced Hepatoma and Normal Monkey Livers," *Cancer Res.* **37**, 285 (1977).

Lee, N. E., and J. E. Mrochek, "A New Approach to Blood Grouping and Coombs 'Antiglobulin' Testing," presented at the 172d National Meeting of the American Chemical Society, San Francisco, Aug. 29–Sept. 3, 1976.

Mrochek, J. E., "Clinical Applications of the Centrifugal Analyzer," presented at the Workshop on Mechanisms Regulating Excretions of Modified Nucleosides, ORNL, Jan. 6, 1977.

Mrochek, J. E., and C. A. Burtis,[2] "Isoenzyme Analysis Based on Differences in Kinetic Parameters," presented at the Centennial Meeting of the American Chemical Society, New York, Apr. 8–9, 1976.

Mrochek, J. E., C. A. Burtis,[2] W. F. Johnson, M. L. Bauer,[13] D. E. Lakomy,[14] R. K. Genung, and C. D. Scott, "A New Portable Centrifugal Analyzer with Expanded Versatility," presented at the Ninth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, ORNL, Mar. 17–18, 1977.

Mrochek, J. E., S. R. Dinsmore, D. C. Tormey,[9] and T. P. Waalkes,[10] "Liquid Chromatographic Analysis of Protein-Bound Carbohydrates in Serum from Clinically Defined Breast Cancer Patients," presented at the 28th Southeastern Meeting of the American Chemical Society, Gatlinburg, Tenn., Oct. 27–29, 1976.

Mrochek, J. E., S. R. Dinsmore, D. C. Tormey,[9] and T. P. Waalkes,[10] "Protein-Bound Carbohydrates in Breast Cancer. Liquid Chromatographic Analysis for Mannose, Galactose, Fucose, and Sialic Acid in Serum," *Clin. Chem.* **22**, 1516 (1976).

Mrochek, J. E., R. L. Jolley, D. S. Young,[9] and W. J. Turner,[15] "Metabolic Response of Humans to the Ingestion of Nicotinic Acid and Nicotinamide," *Clin. Chem.* **22**, 1821 (November 1976).

Pitt, W. W., Jr., "Gradient-Elution Ion Exchange Chromatography. Part I. Digital Computer Solution of the Mathematical Model," *J. Chromatogr. Sci.* **14**, 396 (1976).

---

9. National Institutes of Health, Bethesda, Md.
10. Johns Hopkins University, Baltimore, Md.
11. University of Colorado Medical Center, Denver.
12. University of Missouri, Columbia.
13. Instrumentation and Controls Division.
14. University of Rochester, Rochester, N.Y.
15. Central Islip State Hospital, Central Islip, N.Y.

Pitt, W. W., Jr., R. L. Jolley, and S. Katz, "Separation and Analysis of Refractory Pollutants in Water by High-Resolution Liquid Chromatography," p. 215 in *Identification and Analysis of Organic Pollutants in Water,* ed. L. H. Keith, Ann Arbor Science, Ann Arbor, Mich., 1976.

Scott, C. D., "Some Advanced Techniques in Liquid Chromatographic Separations for the Biomedical Sciences," presented to the Department of Chemistry, University of Iowa, Iowa City, Apr. 22, 1976.

Scott, C. D., and R. K. Genung, "Serum Isoenzyme Analysis by Elution Electrophoresis," presented at the Spring Meeting of the American Chemical Society, New York, Apr. 8, 1976.

Scott, C. D., and C. W. Hancher, "Use of a Tapered Fluidized Bed as a Continuous Bioreactor," *Biotechnol. Bioeng.* **18**, 1393 (1976).

CHEMICAL ENGINEERING RESEARCH

Begovich, J. M., and J. S. Watson, *Flooding Characteristics of Goodloe Packing,* ORNL/TM-5212 (August 1976).

Canon, R. M., and E. L. Park, Jr.,[16] "Transition Boiling of Normal Pentane from a Horizontal Flat Gold Surface at One Atmosphere Pressure," *Int. J. Heat Mass Transfer* **19**, 696 (1976).

Scott, C. D., R. D. Spence, and W. G. Sisson, "A Continuous, Annular Chromatograph for Preparative Separations," presented at the 28th Meeting of the Southeastern Section of the American Chemical Society, Gatlinburg, Tenn., Oct. 27–29, 1976.

Scott, C. D., R. D. Spence, and W. G. Sisson, "Pressurized, Annular Chromatograph for Continuous Separations," presented at the International Symposium on Advances in Chromatography, Houston, Nov. 1–4, 1976; also in *J. Chromatogr.* **126**, 381 (1976).

COAL TECHNOLOGY

Cochran, H. D., Jr., "Coal Hydrocarbonization Studies," presented at a Graduate Seminar, University of Tennessee, Knoxville, Feb. 1, 1977.

Cochran, H. D., Jr., "Fluidized Beds in Coal Conversion," presented at a Special Training Seminar at Oak Ridge Associated Universities, Oak Ridge, Tenn., July 1976.

Forrester, R. C., III, "Comparison of One- and Two-Dimensional Pyrolysis Results," presented at the Third Technical Working Group of UCG Laboratory Research, Morgantown Energy Research Center, Morgantown, W.Va., June 3, 1976.

Forrester, R. C., III, "Recovery of Inaccessible Coal Reserves by In Situ Gasification," presented at the Eleventh Intersociety Energy Conversion Engineering Conference, State Line, Nev., Sept. 12–17, 1976; published in the *Proceedings.*

Forrester, R. C., III, "Status of 2-D Pyrolysis Studies at ORNL," presented at the Fourth Combined Working Group for UCG Modeling and Laboratory Research, Morgantown Energy Research Center, Morgantown, W.Va., Mar. 15, 1977.

Forrester, R. C., III, "Two-Dimensional Studies of Coal Pyrolysis: Preliminary Results," presented at the Second Annual Underground Coal Gasification Symposium, Morgantown, W.Va., Aug. 10–12, 1976; published in the *Proceedings,* MERC/SP-76/3 (1976).

Forrester, R. C., III, H. D. Cochran, Jr., and N. E. Bolton,[17] "Polycyclic Aromatic Hydrocarbons and the Oak Ridge National Laboratory's Experimental Coal Program: Minimizing the Hazards," presented at the Annual Meeting of the American Association for the Advancement of Science, Denver, Colo., Feb. 20–25, 1977.

16. University of Missouri, Rolla.
17. Health Division.

Forrester, R. C., III, and P. R. Westmoreland, "Two-Dimensional Pyrolysis Effects During In Situ Coal Gasification: Preliminary Results," presented at the 51st Annual Fall Meeting of the Society of Petroleum Engineers, New Orleans, Oct. 3–6, 1976.

Gambill, W. R., C. C. Littlefield,[18] R. H. Cooper, Jr.,[19] and J. E. Jones, Jr.,[6] *Exploratory Studies of the Application of Gas-Cooled Reactors to Coal Conversion,* ORNL/TM-5341 (January 1977).

Gibson, J. B., and F. J. Endelman, *Review and Evaluation of Residue Carbonization in the Consol Synthetic Fuel Process,* ORNL/TM-5346 (May 1976).

Holladay, D. W., C. W. Hancher, D. D. Chilcote,[8] and C. D. Scott, "Comparison of Three Standard Reactor Designs for Use as Bioreactors, with Each Containing Viable Microorganisms for Degrading Hazardous Compounds in Waste Liquors Produced During Coal Processing," presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, Nov. 14–18, 1976.

Holmes, J. M. (contributor), "Alternative Conversion Processes," pp. 3–29 in *Balanced Program Plan. Volume IV: Coal Conversion,* ORNL-5123, Special (May 1976).

Holmes, J. M., H. D. Cochran, Jr., M. S. Edwards, D. S. Joy, and P. M. Lantz, "Evaluation of Coal Carbonization Processes," p. 40 in *Coal Processing Technology,* vol. 3, ed. Chem. Eng. Prog., AIChE, New York, 1977.

Katz, S., and B. R. Rodgers, "A Laboratory Evaluation of Precoat Filtration Parameters for the Solvent Refined Coal Process," *Ind. Eng. Chem., Process Des. Dev.* **15**(3), 407 (1976).

Katz, S., and B. R. Rodgers, "Reformation of Inorganic Particulates Suspended in Coal-Derived Liquids and Improved Separation," presented at the 172d Meeting of the American Chemical Society, San Francisco, Sept. 3, 1976; also in *Liquid Fuels from Coal,* ed. R. T. Ellington, p. 173, Academic Press, New York, 1977.

McWherter, J. R., "Coal Research at ORNL," presented at the college faculty institute, Energy Production and the Environment, at Oak Ridge Associated Universities, Oak Ridge, Tenn., June 22, 1976.

Rodgers, B. R., "Agglomeration and Separation of Micron-Sized Particles from Coal Liquefaction Streams," presented at Case Western Reserve University, Cleveland, May 1976.

Rodgers, B. R., "Clean Energy from Coal," presented at an Energy-Environment Institute, Tennessee Technological University, Cookeville, Feb. 17, 1977; and at Cities Service Co., Engineers Club, Copper Hill, Tenn., Mar. 31, 1977.

Rodgers, B. R., "Coal Liquefaction – Removing the Bottleneck," presented to the Chattanooga Engineers Club, Chattanooga, Tenn., Nov. 1, 1976.

Rodgers, B. R., "Separation of Micron-Size Particles from Coal Liquids," presented at the University of Kentucky, Lexington, Feb. 14, 1977.

Rodgers, B. R., "The Effect of Solvents on Separation of Micron-Sized Particles from Coal Liquefaction Process Streams," *Hydrocarbon Process.,* p. 191 (May 1976).

Rodgers, B. R., F. L. Ball,[1] H. W. Dunn,[1] and M. H. Eager,[20] "Identification and Separation of Micron-Sized Inorganic Particles from Coal Liquids," presented at the Annual Meeting of the American Association for the Advancement of Science, Denver, Colo., Feb. 20–25, 1977.

Rodgers, B. R., and P. R. Westmoreland, "Agglomeration and Separation of Micron-Sized Particles from Coal Liquefaction Streams," presented at the 81st National Meeting of the American Institute of Chemical Engineers, Kansas City, Mo., Apr. 12–15, 1976.

Rodgers, B. R., and P. R. Westmoreland, "Removing Micron-Size Particles from Coal Liquids," p. 28 in *Coal Processing Technology,* vol. 3, ed. Chem. Eng. Prog., AIChE, New York, 1977.

---

18. UCC-ND Engineering.
19. Metals and Ceramics Division.
20. Y-12 Plant.

Scott, C. D., C. W. Hancher, D. W. Holladay, and G. B. Dinsmore, "A Tapered Fluidized Bioreactor for Treatment of Aqueous Effluents from Coal Conversion Processes," *Proceedings of the Symposium on Environmental Aspects of Fuel Conversion Technology, II,* EPA-600/2-76-149, p. 233 (June 1976).

Westmoreland, P. R. (coordinator), "Alternative Conversion Processes," pp. 3–29 in *Balanced Program Plan. Volume IV: Coal Conversion,* ORNL-5123, Special (May 1976).

Westmoreland, P. R., "Coal Conversion Technologies," presented to the Student Chapter of the American Institute of Chemical Engineers, Tennessee Technological University, Cookeville, Oct. 28, 1976.

Westmoreland, P. R., and R. C. Forrester III, "Pyrolysis of Large Coal Blocks: Implications of Heat and Mass Transport Effects for In Situ Gasification," presented at the 173d Meeting of the American Chemical Society, New Orleans, Mar. 20–25, 1977.

Westmoreland, P. R., and D. P. Harrison,[21] "Evaluation of Candidate Solids for High-Temperature Desulfurization of Low-Btu Gases," *Environ. Sci. Technol.* **10**(7), 659 (1976).

DEVELOPMENT OF THE THORIUM FUEL CYCLE

Ackley, R. D., and K. J. Notz, *The Distribution of Xenon between Gaseous and Liquid CO_2*, ORNL-5122 (October 1976).

Carter, W. L., K. J. Notz, and R. H. Rainey (contributors), *Assessment of the Thorium Fuel Cycle In Power Reactors,* ORNL/TM-5565 (January 1977).

Drago, J. P., and P. A. Haas, *Design and Test of a Thermosiphon Evaporator for Acid-Deficient Uranyl Nitrate,* ORNL/TM-5518 (November 1976).

Drago, J. P., and P. A. Haas, *Drying of Uranium-Loaded Cation Exchange Resin with Microwave Heating,* ORNL/TM-5508 (December 1976).

Drago, J. P., P. A. Haas, and D. L. Million, "Drying of Ion Exchange Resins for Resin-Based Preparation of Nuclear Reactor Fuels," presented at the 82d National Meeting of the American Institute of Chemical Engineers, Atlantic City, N.J., Aug. 29–Sept. 1, 1976.

Forsberg, C. W., "Separation of Krypton from Carbon Dioxide with Molecular Sieves," presented at the 14th ERDA Air Cleaning Conference, Sun Valley, Idaho, Aug. 2–4, 1976; published in the *Proceedings,* CONF-760822.

Forsberg, C. W., "Separation and Disposal of Actinides from Nuclear Wastes," presented at the Massachusetts Institute of Technology, Boston, Mar. 24, 1977.

Glass, R. W., and R. E. Barker, *A Computer Model for the KALC Process Studies in the ORGDP Off-Gas Decontamination Pilot Plant,* ORNL/TM-5457 (September 1976).

Glass, R. W., R. E. Barker, and J. C. Mullins,[22] *A Computer Program for the Calculation of Gas-Liquid Equilibria in the KALC System CO_2-N_2-CO-O_2-Xe-Kr,* ORNL/TM-5275 (December 1976).

Glass, R. W., H. W. R. Beaujean,[23] V. L. Fowler, T. M. Gilliam, D. J. Inman, and D. M. Levins,[24] "Experimental Studies on the Krypton Absorption in Liquid CO_2 (KALC) Process," presented at the 14th ERDA Air Cleaning Conference, Sun Valley, Idaho, Aug. 2–4, 1976.

Mullins, J. C.,[22] and R. W. Glass, *An Equilibrium Stage Model of the KALC Process,* ORNL/TM-5099 (August 1976).

Notz, K. J. and C. W. Greene, *Loading Ion Exchange Resins with Uranium for HTGR Fuel Kernels,* ORNL/TM-5647 (December 1976).

Notz, K. J. and A. B. Meservey, *The Solubility of Krypton in Liquid CO_2*, ORNL-5121 (June 1976).

---

21. Louisiana State University, Baton Rouge.
22. Clemson University, Clemson, S.C.
23. Bilfinger STR lc, Karlsruhe Durlach, Federal Republic of Germany.
24. Australian Atomic Energy Commission, Research Establishment, Sutherland, N.S.W., Australia.

Ryon, A. D., *"Demonstration of the KALC (Krypton Absorption in Liquid CO_2) Process: Campaign II at the ORGDP Off-Gas Pilot Plant,* ORNL/TM-5298 (July 1976).

Toth, L. M.,[25] J. T. Bell,[25] S. R. Buxton, H. A. Friedman,[25] D. W. Fuller,[25] and M. R. Billings,[25] *Chemistry of the KALC Process. The CO_2-I_2-CH_3I-H_2O System,* ORNL/TM-5656 (November 1976).

Vaughen, V. C. A., *On the Separation of Silicon Carbide–Coated Fertile and Fissile Particles by Gas Classification,* ORNL/TM-5091 (July 1976).

FUSION ENERGY STUDIES

Fisher, P. W., and J. S. Watson, "Cryosorption Vacuum Pumping of Deuterium, Helium, and Hydrogen at 4.2°K for Controlled Thermonuclear Reactor (CTR) Applications," presented at the 24th Remote Systems Technology Conference, Washington, D.C., Nov. 14–19, 1976.

Talbot, J. B., F. J. Smith,[25] J. F. Land,[25] and P. Barton,[26] "Tritium Sorption in Lithium-Bismuth and Lithium-Aluminum Alloys," *J. Less-Common Met.* **50**, 23 (1976).

Watson, J. S., J. T. Bell,[25] S. D. Clinton, P. W. Fisher, J. D. Redman,[25] F. J. Smith,[25] J. B. Talbot, and C. P. Tung,[27] "Current CTR-Related Tritium Handling Studies at ORNL," presented at the Second Topical Meeting on the Technology of Controlled Nuclear Fusion, Richland, Wash., Sept. 21–23, 1976; published in the *Proceedings,* CONF-760935-83 (1976).

Watson, J. S., and S. D. Clinton in *Oak Ridge Tokamak Experimental Power Reactor Study – 1976. Part 4: Nuclear Engineering,* ed. C. A. Flanagan,[28] ORNL/TM-5575 (December 1976).

Watson, J. S., and P. W. Fisher, "Vacuum Pumping for Controlled Thermonuclear Reactors," presented at the Ninth Symposium on Fusion Technology, Garmisch-Partenkirchen, Federal Republic of Germany, June 14–18, 1976.

Watson, J. S., V. Maroni,[29] C. Carston,[30] F. Coffman,[31] T. Galloway,[32] E. Johnson,[33] R. Riswall,[34] and L. Wittenberg,[35] "Study Session on Tritium," p. 128 in *Proceedings of Magnetic Energy Fusion Blanket and Shield Workshop – A Technical Assessment,* ERDA-76/171/1, CONF-760343 (August 1976).

HTGR TECHNOLOGY

Dyer, F. F.,[1] R. P. Wichner, W. J. Martin, and H. J. de Nordwall, *Distribution of Radionuclides in the Peach Bottom HTGR Primary Circuit During Core 2 Operation,* ORNL-5188 (March 1977).

Dyer, F. F.,[1] R. P. Wichner, W. J. Martin, L. L. Fairchild, R. J. Kedl,[6] and H. J. de Nordwall, *Postirradiation Examination of Peach Bottom HTGR Driver Fuel Element E06-01,* ORNL-5126 (April 1976).

Homan, F. J.,[19] E. L. Long, Jr.,[19] T. B. Lindemer, R. L. Beatty,[19] and T. N. Tiegs,[19] *Development of a Fissile Particle for HTGR Fuel Recycle,* ORNL/TM-5602 (December 1976).

Jones, J. E., Jr.,[6] I. Spiewak,[6] and W. R. Gambill, "Assessment of Very High-Temperature Reactors in Process Applications," presented at the 11th Intersociety Energy Conversion Engineering Conference, State Line, Nev., September 1976.

---

25. Chemistry Division.
26. Pennsylvania State University, University Park.
27. Atomic Energy Commission, Republic of China.
28. Westinghouse Electric Co.
29. Argonne National Laboratory, Argonne, Ill.
30. Los Alamos Scientific Laboratory, Los Alamos, N.M.
31. ERDA, Germantown, Md.
32. Lawrence Livermore Laboratory, Livermore, Calif.
33. Princeton Plasma Physics Laboratory, Princeton, N.J.
34. Brookhaven National Laboratory, Upton, L.I., N.Y.
35. Mound Laboratory, Miamisburg, Ohio.

Kania, M. J.,[19] T. B. Lindemer, M. T. Morgan, and J. M. Robbins,[19] *Irradiation Performance of HTGR Fertile Fuel in HFIR Target Capsules HT-12 through HT-15: Part I – Experiment Description and Fission Product Behavior,* ORNL/TM-5305 (February 1977).

Lin, K. H., "Radioactive Wastes from Reprocessing of HTGR Fuel – An Overview," presented at the 1976 International Conference of the American Nuclear Society, Washington, D.C., Nov. 15–19, 1976.

Lindemer, T. B., and R. L. Pearson, "Kernel Migration for HTGR Fuels from the Th-U-Pu-C-O-N System," *J. Am. Ceram. Soc.* **60**, 5 (1977).

Lindemer, T. B., "Interpretation of Oxygen Release During ThO_2 Fission," presented at the Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 3–5, 1976.

Notz, K. J., "Selected Studies in HTGR Reprocessing Development," presented at the American Institute of Chemical Engineers Symposium on Gas-Cooled Reactor Fuel Cycles, Atlantic City, N.J., Aug. 29–Sept. 1, 1976.

Osborne, M. F., E. L. Compere, and H. J. de Nordwall, *Studies of Iodine Adsorption and Desorption on HTGR Coolant Circuit Materials,* ORNL/TM-5094 (April 1976).

Pearson, R. L., and T. B. Lindemer, *Uranium Loss from BISO-Coated Weak-Acid-Resin HTGR Fuel,* ORNL/TM-5552 (February 1977).

Pearson, R. L., and T. B. Lindemer, "Vaporization of Uranium from High-Surface-Area, BISO-Coated, UC_2 Fuel Particles," presented at the Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 3–5, 1976.

Snider, J. W., and S. V. Kaye,[36] "Process Behavior and Environmental Assessment of ^{14}C Releases from an HTGR Fuel Reprocessing Facility," presented at a Topical Meeting of the American Nuclear Society–American Institute of Chemical Engineers, Sun Valley, Idaho, Aug. 5–6, 1976.

Spiewak, I.,[6] J. E. Jones,[6] W. R. Gambill, and E. C. Fox,[6] *Assessment of Very High-Temperature Reactors in Process Applications,* ORNL/TM-5242 (November 1976).

Wichner, R. P., *Effect of Steam Corrosion on Core Post Strength Loss: 1. Low, Chronic Steam Ingress Rates,* ORNL/TM-5534 (October 1976).

Wichner, R. P., *Effect of Steam Corrosion on HTGR Core Support Post Strength Loss: Part II. Consequences of Steam Generator Tube Rupture Event,* ORNL/TM-5550 (January 1977).

ISOTOPE SEPARATIONS

Caudill, H. H., H. R. Gwinn, and J. O. Younghanse, "Chemical Processing of Isotopic Mercury," presented to the Chemistry Section of the Tennessee Academy of Science, University of Tennessee, Chattanooga, Nov. 19–20, 1976.

Newman, E., W. A. Bell, Jr., W. C. Davis, L. O. Love, W. K. Prater, K. A. Spainhour, J. C. Tracy, and A. M. Veach, "Some New Techniques and Recent Developments in Isotope Separations at Oak Ridge," presented at the Ninth International Conference on Electromagnetic Isotope Separators and Related Ion Accelerators, Kiryat Anavim, Israel, May 10–13, 1976; published in *Nucl. Instrum. Methods* **139**, 87 (1976).

MISCELLANEOUS

Baes, C. F., Jr.,[25] H. E. Goeller, J. S. Olson,[37] and R. M. Rotty,[38] *The Global Carbon Dioxide Problem,* ORNL-5194 (August 1976).

Baes, C. F., Jr.,[25] H. E. Goeller, J. S. Olson,[37] and R. M. Rotty,[38] "Carbon Dioxide and Climate: The Uncontrolled Experiment," *Am. Sci.* **65**(3), 310 (1977).

36. Health and Safety Research Division.
37. Environmental Sciences Division.
38. Institute for Energy Analysis.

Beahm, E. C., and C. A. Culpepper,[39] "Basic Compatibility Studies of Advanced Fuels with 3*d* Transition Metals," presented at the American Nuclear Society 1976 International Conference, Washington, D.C., Nov. 15–19, 1976.

Beahm, E. C., C. A. Culpepper,[39] and O. B. Cavin,[19] "Laves Phases of Uranium and 3*d* Transition Metals," *J. Less-Common Met.* **50**, 57–71 (1976).

Besmann, T. M., and K. E. Spear,[26] "Kinetics of the Chemical Vapor Deposition of TiB_2," presented at the 78th Annual Meeting and Exposition of the American Ceramic Society, Cincinnati, Ohio, May 1–6, 1976.

Brooksbank, R. E., "Decommissioning Reprocessing Plants," presented at the International Symposium on the Management of Wastes from the LWR Fuel Cycle, Denver, Colo., July 11–16, 1976; published in the *Proceedings,* CONF-760701-1 (1976).

Campbell, D. O., "The Use of Ion Exchange with Nuclear Power Reactors," presented at the Georgia Institute of Technology, Atlanta, Oct. 25–29, 1976.

Cochran, H. D., Jr., R. G. Donnelly,[40] M. Modell,[40] and R. E. Baddour,[40] "Carbon Monoxide Oxidation on Platinum Catalysts," presented at the International Conference on Surface Chemicals and Catalysts, Puerto Rico, August 1976.

Feldman, M. J., "The Nuclear Power Park Concept – Its Value and Potential," *J. Br. Nucl. Energy Soc.* **15**(2), 123 (April 1976).

Feldman, M. J., "Current Energy Situation and Alternative Futures," presented at a seminar on Science, Technology, and Public Policy, Oak Ridge, Tenn., Mar. 23, 1977.

Gambill, W. R., H. H. Haselton,[41] S. L. Milora,[41] J. Kim,[41] C. C. Queen,[18] and W. L. Stirling,[41] "Neutral Beam Targets and Beam Stops," presented at the Meeting of the Plasma Physics Division of the American Physical Society, San Francisco, Nov. 15–19, 1976.

Goeller, H. E. (contributor), *Rational Use of Potentially Scarce Metals,* NATO Scientific Affairs Division, Brussels, 1976.

Goeller, H. E., "The Age of Substitutability," presented at the Monsanto Fellow Symposium, St. Louis, Mo., Oct. 20, 1976.

Goeller, H. E., "The Age of Substitutability: A Scientific Appraisal of Natural Resource Adequacy," presented at the Forum on the Economics of Natural Resource Scarcity, sponsored by Resources for the Future, Inc., Washington, D.C., Oct. 18–19, 1976; to be published in the *Proceedings.*

Goeller, H. E. (contributor), "Requirements for Fulfilling a National Materials Policy," *Proceedings of an Engineering Foundation Conference, New England College, Henniker, N.H., Aug. 11–16, 1976.*

Goeller, H. E. (panel participant), Symposium on The Next 200 Years, sponsored by The Hudson Institute, Rockefeller University, New York, May 4, 1976.

Goeller, H. E., and A. M. Weinberg,[38] "The Age of Substitutability," pp. 119–53 in *A Strategy for Resources,* North-Holland, Amsterdam, 1977.

Griffith, W. L., A. L. Compere, and W. J. Boegly,[37] "Modular Residential Utility Systems," presented at the American Society of Civil Engineers Meeting on Water Resources and Ocean Engineering, San Diego, Calif., April 1976.

Graham, H. B., "Standard for Design Criteria for Decommissioning of Nuclear Fuel Reprocessing Plants," presented at the 17th Annual Meeting of the Institute of Nuclear Materials Management, Seattle, Wash., June 23–25, 1976.

Kee, C. W., and L. E. McNeese, *MRPP – Multiregion Processing Plant Code,* ORNL/TM-4210 (September 1976).

39. Solid State Division.
40. Massachusetts Institute of Technology, Cambridge.
41. Fusion Energy Division.

Kocher, D. C.,[42] F. E. Bertrand,[42] E. E. Gross,[42] and E. Newman, "^{58}Ni (p,p') Reaction at 10 MeV: Study of the Analyzing Power for Inelastic Excitation of the Giant Resonance Region of the Nuclear Continuum and of Low-Lying Bound States," *Phys. Rev. C* **14**, 1395 (1976).

Lloyd, M. H., K. Bischoff,[43] K. Peng,[43] H. U. Nissen,[43] and R. Wessicken,[43] "Crystal Habit and Phase Attribution of U(VI) Oxides in a Gelation Process," *J. Inorg. Nucl. Chem.* **38**, 1141 (1976).

Lorenz, R. A., S. R. Manning, and W. J. Martin, "The Behavior of Highly Radioactive Iodine on Charcoal in Moist Air," presented at the 14th ERDA Air Cleaning Conference, Sun Valley, Idaho, Aug. 2–4, 1976.

Moore, F. L.,[1] and W. S. Groenier, "Removal and Recovery of Cyanide and Zinc from Electroplating Wastes by Solvent Extraction," *Plat. Surf. Finish.* **63**(8), 26 (1976).

Raman, S.,[42] R. L. Auble,[42] J. B. Ball,[42] E. Newman, J. C. Wells, Jr.,[42] and J. Lin,[42] "Levels in ^{144}Nd from the ^{143}Nd(d,p) and the ^{146}Nd (p,t) Reactions," *Phys. Rev. C* **14**, 1381 (1976).

Salmon, R., *PRP – A Discounted Cash Flow Program for Calculating the Production Cost (Product Price) of the Product from a Process Plant,* ORNL-5251 (March 1977).

Staff of the Pilot Plant Section (compilers), *A Guide to the Selection, Training, and Licensing or Certification of Reprocessing Plant Operators,* Vols. 1 and 2, ORNL/TM-5323 and ORNL/TM-5324 (June 1976).

Tedder, D. W., and D. F. Rudd,[44] "Parametric Studies in Industrial Distillation," presented at the 82d National Meeting of the American Institute of Chemical Engineers, Atlantic City, N.J., Aug. 29–Sept. 1, 1976.

Till, J. E.,[37] C. D. Barton,[37] and G. W. Parker, "Nuclear Energy: A Viable Alternative," *Aviat. Med. Bull.* (February 1977).

Wymer, R. G., "Fusion Reactors and Their Fuel Cycle: A Primer," presented at "Energy in Perspective: An Orientation Conference for Educators," Arizona State University, Tempe, June 9, 1976.

Wymer, R. G., "Technology of the Light-Water Reactor Fuel Cycle," presented at the University of Lowell, Lowell, Mass., Apr. 23, 1976; the Radiochemical Technology Training Program, UCC-ND Engineering, May 28, 1976; the Symposium on Energy Sources of the Future, Oak Ridge Associated Universities, Oak Ridge, Tenn., Aug. 5, 1976; and as an Oak Ridge Associated Universities Traveling Lecture at Fort Hays Kansas State College, Hays, Oct. 27, 1976, and at North Texas State University, Denton, Nov. 23, 1976.

MOLTEN-SALT REACTOR PROGRAM

Brown, C. H., Jr., J. R. Hightower, Jr., and J. A. Klein, *Measurement of Mass Transfer Coefficients in a Mechanically Agitated, Nondispersing Contactor Operating with a Molten Mixture of LiF-BeF$_2$-ThF$_4$ and Molten Bismuth,* ORNL-5143 (November 1976).

Lindauer, R. B., and J. R. Hightower, Jr., *Conceptual Design of a Continuous Fluorinator Experimental Facility (CFEF),* ORNL/TM-5253 (July 1976).

Savage, H. C., and J. R. Hightower, Jr., *Engineering Tests of the Metal Transfer Process for Extraction of Rare-Earth Fission Products from a Molton-Salt Breeder Reactor Fuel Salt,* ORNL-5176 (February 1977).

NUCLEAR REGULATORY COMMISSION PROGRAMS

Blanco, R. E., "Controlling the Radiological Impact in the Nuclear Fuel Cycle: A Cost/Benefit Analysis," presented at the 172d National Meeting of the American Chemical Society, San Francisco, August 1976.

Blanco, R. E., "Environmental Considerations and Regulations," presented at the UCC-ND Engineering Division Radiochemical Technology Training Program, Oak Ridge, May 25, 1976.

---

42. Physics Division.
43. E.I.R., Wurenlingen, Switzerland.
44. University of Wisconsin, Madison.

Blanco, R. E., "NRC Fuel Cycle Studies," presented to American Physical Society Groups at the Nuclear Fuel Cycle and Waste Management Conference, Oak Ridge, May 19–20, 1976.

Collins, J. L., M. F. Osborne, A. P. Malinauskas, R. A. Lorenz, and S. R. Manning, *Knudsen Cell–Mass Spectrometer Studies of Cesium-Urania Interactions,* ORNL/NUREG/TM-24 (June 1976).

Davis, W., Jr., *Carbon-14 Production in Nuclear Reactors,* ORNL/NUREG/TM-12 (February 1977).

Davis, W., Jr., "Costs and the Environmental Impact of Radioactive Waste Treatment in Reprocessing High-Temperature Gas-Cooled Reactor Fuel," presented at the Joint International Conference of the American Nuclear Society and the European Nuclear Society, Washington, D.C., Nov. 14–19, 1976.

Davis, W., Jr., "Models for Calculating the Effects of Isotopic Exchange, Radioactive Decay, and Recycle in Removing Iodine from Gas and Liquid Streams," *Nucl. Sci. Eng.* **61**, 11 (1976).

Davis, W., Jr., R. E. Blanco, B. C. Finney, G. S. Hill,[36] R. E. Moore,[36] and J. P. Witherspoon,[36] *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact in the Nuclear Fuel Cycle – Reprocessing of High-Temperature Gas-Cooled Reactor Fuel Containing U-233 and Thorium,* ORNL/NUREG/TM-4 (May 1976).

Davis, W., Jr., C. W. Kee, V. C. A. Vaughen, and M. L. Tobias,[6] *Calculating Fission Product Inventories in Peach Bottom FTE-4 Fuel Rods Using the ORIGEN Code,* ORNL/TM-5691 (January 1977).

Finney, B. C., "Radioactive Waste Treatment Costs and Environmental Impact for Reprocessing Light-Water Reactor Fuel," presented at the Joint International Conference of the American Nuclear Society and the European Nuclear Society, Washington, D.C., Nov. 14–19, 1976.

Finney, B. C., R. E. Blanco, R. C. Dahlman,[37] G. S. Hill,[36] F. G. Kitts, R. E. Moore,[36] and J. P. Witherspoon,[36] *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle – Reprocessing Light-Water Reactor Fuel,* ORNL/NUREG/TM-6 (January 1977).

Godbee, H. W., and A. H. Kibbey, "High-Level Radioactive Waste – What Is It? How Much Will There Be?", presented at the East Tennessee and Bluegrass Chapters of the Health Physics Society, Mammoth Cave National Park, Ky., Sept. 18, 1976.

Godbee, H. W., and A. H. Kibbey, *Source Terms for Radioactive Gaseous Effluents from a Model High-Level Waste Solidification Facility,* ORNL/NUREG/TM-67 (November 1976).

Godbee, H. W., and A. H. Kibbey, "The Future of High- and Low-Level Radioactive Waste Disposal Technology," presented at a Subsection Meeting of the American Society of Mechanical Engineers, Reading, Pa., Dec. 3, 1976.

Godbee, H. W., A. H. Kibbey, C. W. Kee, and J. O. Blomeke, "U.S. Nuclear Fuel Cycle: An Introductory Overview," presented at the Georgia Institute of Technology, Atlanta, Oct. 25–29, 1976.

Groenier, W. S., "Waste Treatment Cost/Benefit Analysis for Fabrication of Light-Water Reactor Fuel Containing Plutonium," presented at the 1976 International Meeting of the American Nuclear Society, Washington, D.C., Nov. 15–19, 1976.

Kibbey, A. H., and H. W. Godbee, "Management of Waste from the Nuclear Fuel Cycle," presented at the Georgia Institute of Technology, Atlanta, Apr. 2, 1976.

Lorenz, R. A., M. F. Osborne, J. L. Collins, S. R. Manning, and A. P. Malinauskas, *Behavior of Iodine, Methyl Iodide, Cesium Oxide, and Cesium Iodide in Steam and Argon,* ORNL/NUREG/TM-25 (July 1976).

Roddy, J. W., "Interactions in the Tri-*n*-butyl Phosphate-Water-Diluent System," presented at the 172d National Meeting of the American Chemical Society, San Francisco, Aug. 29–Sept. 3, 1976.

Roddy, J. W., R. E. Blanco, G. S. Hill,[36] R. E. Moore,[36] R. D. Seagren, and J. P. Witherspoon,[36] *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle – Fabrication of High-Temperature Gas-Cooled Reactor Fuel Containing Uranium-233 and Thorium,* ORNL/NUREG/TM-5 (September 1976).

Sears, M. B., "Airborne Effluent Control at Uranium Mills," presented at a Joint Topical Meeting of the American Nuclear Society and the American Institute of Chemical Engineers, Controlling Airborne Effluents from Fuel Cycle Plants, Sun Valley, Idaho, Aug. 5–6, 1976; published in the *Proceedings,* pp. 17-1 to 17-13.

Sears, M. B., "Radioactive Waste Treatment Costs and Environmental Impact for Milling of Uranium Ores," presented at the Joint International Conference of the American Nuclear Society and the European Nuclear Society, Washington, D.C., Nov. 14–19, 1976.

Wachter, J. W., "Model Plutonium Recycle Reactor for Environmental Analysis of the Mixed Oxide Fuel Cycle," presented at Hearings on Generic Environmental Statement on the Use of Recycle Plutonium in Mixed Oxide Fuel in LWRs, Washington, D.C., Dec. 2–7, 1976.

Weeren, H. O., Sects. 5.3 and 5.4 in *Alternative Processes for Managing Existing Commercial High-Level Radioactive Wastes,* NUREG-0043 (April 1976).

POWER REACTOR FUEL PROCESSING

Besmann, T. M., and T. B. Lindemer, "Thermodynamics of the Conversion of PuO_2 to $PuC_{0.88}$," presented at the 1976 Joint Fall Meeting of the American Ceramic Society, San Francisco, Oct. 31–Nov. 3, 1976.

Besmann, T. M., and T. B. Lindemer, "Thermodynamic Assessment of the Conversion of Plutonium Dioxide to Plutonium Monocarbide," presented at the University of Kansas, Lawrence, Nov. 18, 1976.

Besmann, T. M., and T. B. Lindemer, *Thermodynamics of the Conversion of Plutonium Dioxide to Plutonium Monocarbide,* ORNL/TM-5510 (July 1976).

Bond, W. D., "Chemical Aspects of Light-Water Reactor Fuel Reprocessing," presented at the 172d National Meeting of the American Chemical Society, San Francisco, Aug. 29–Sept. 3, 1976.

Burch, W. D., C. D. Watson, and W. E. Unger, "Techniques for Shearing and Dissolving LMFBR Fuels," presented at the International Atomic Energy Agency Advisory Group Meeting, Leningrad, Russia, May 17–21, 1976.

Burch, W. D., O. O. Yarbro, W. S. Groenier, and M. J. Stephenson,[45] "Retention of Gaseous Fission Products in Reprocessing LMFBR Fuels," presented at the International Atomic Energy Agency Advisory Group Meeting, Leningrad, Russia, May 17–21, 1976.

Campbell, D. O., and S. R. Buxton, "Hot-Cell Studies of Light-Water Reactor Fuel Reprocessing," presented at the 1976 International Conference of the American Nuclear Society, Washington, D.C., Nov. 15–19, 1976.

Campbell, D. O., and S. R. Buxton, "Recovery of Americium and Curium from Nuclear Fuel Processing Waste Solutions," presented at the 172d National Meeting of the American Chemical Society, San Francisco, Aug. 29–Sept. 3, 1976.

Campbell, D. O., and S. R. Buxton, "Recovery of Americium and Curium from Nuclear Reactor Waste Solutions," presented at the 12th Rare-Earth Research Conference, Vail, Colo., July 18–22, 1976.

Chilton, J. M., "The Sorption of Curium, Berkelium, Californium and Einsteinium on Cation Exchange Resin from Nitric Acid Solutions," presented at the 172d National Meeting of the American Chemical Society, San Francisco, Aug. 29–Sept. 3, 1976.

Clark, W. E., "Immobilization of I-129 as Barium Iodate with Portland Cement," presented at the 1976 Annual Meeting of the American Nuclear Society, Toronto, June 13–18, 1976.

Feldman, M. J., LMFBR Fuel Reprocessing," presented at WATTec – Energy in the Southeast – Social, Economic, and Technical Aspects, Knoxville, Tenn., Feb. 22–24, 1977.

Holland, W. D., C. O. Reiser,[46] R. B. Heimdahl,[47] and W. S. Groenier, *"Nuclear Fuel Dissolution and Rinsing Studies Using a Continuous Rotary Dissolver,* ORNL/TM-5566 (March 1977).

Horner, D. E., and D. J. Crouse, *Laboratory Development of Solvent Extraction Processes for Spent LMFBR Fuels,* ORNL/TM-5729 (January 1977).

---

45. Oak Ridge Gaseous Diffusion Plant.
46. Arizona State University, Tempe.
47. Bingham-Willamette Co., Portland, Ore.

Horner, D. E., J. C. Mailen, "Removal of Radioiodine from Gas Streams by Electrolytic Scrubbing," presented at the 1976 Annual Meeting of the American Nuclear Society, Toronto, June 13–18, 1976.

Horner, D. E., J. C. Mailen, and H. R. Bigelow,[48] "Solubility of PdI_2 in Nitrate and Perchlorate Solutions," presented at the 28th Annual Southeast Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Oct. 27–29, 1976.

Inman, D. J., "Sampling and Analysis of Simulated Nuclear Fuel Reprocessing Plant Off-Gases," presented at the 173d National Meeting of the American Chemical Society, New Orleans, Mar. 22, 1977.

Irvine, A. R., and F. J. Jones,[49] *LMFBR Spent Fuel Reprocessing: A Study of an Industrial-Scale Facility,* ORNL/TM-5723 (March 1977).

Klein, J. A., *Ruthenium Oxide Deposition and Scouring in a Rotary Kiln Voloxidizer,* ORNL/TM-5665 (January 1977).

Leuze, R. E., "An Overview of Light-Water Reactor Fuel Cycles," presented at the 172d Meeting of the American Chemical Society, San Francisco, Aug. 29–Sept. 3, 1976.

Lloyd, M. H., "Solution Instabilities and Solids Formation in LWR Reprocessing Solutions." presented at the 1976 International Conference of the American Nuclear Society, Washington, D.C., Nov. 15–19, 1976; published in the *Proceedings.*

Mailen, J. C., "Recent Advances in the Chemistry of Radioiodine Control Systems," presented at the 28th Annual Southeast Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Oct 27–29, 1976.

Mailen, J. C., "Use of Chemical Equilibrium Data to Calculate Iodox Column Operations," *Nucl. Technol.* **30**, 325 (September 1976).

Mailen, J. C., and D. E. Horner, "Removal of Iodine from Reactor Fuel Solutions as Insoluble PdI_2," presented at the 1976 Annual Meeting of the American Nuclear Society, Toronto, June 13–18, 1976.

Mailen, J. C., and D. E. Horner, "Removal of Radioiodine from Gas Streams by Electrolytic Scrubbing," *Nucl. Technol.* **30**, 317 (September 1976).

Shappert, L. B., N. C. Bradley,[13] W. L. Bryan,[13] K. K. Chipley,[18] J. H. Evans,[18] and R. D. Seagren, "The Full-Scale Cask Program at ORNL," presented at the International Atomic Energy Agency Seminar on the Design, Construction, and Testing of Packaging for the Safe Transport of Radioactive Materials, Vienna, Aug. 23–27, 1976; published as IAEA-SR-10/6.

Tallent, O. K., and J. C. Mailen, "Effects of Impurities on PuO_2 Dissolution in Nitric-Hydrofluoric Acid Solutions," presented at the 1976 Annual Meeting of the American Nuclear Society, Toronto, June 13–18, 1976.

Tallent, O. K., and J. C. Mailen, "Study of the Dissolution of Refractory PuO_2 in Nitric-Hydrofluoric Acid Dissolvents at 100°C," *Nucl. Technol.* **32**, 167 (1977).

Tallent, O. K., J. C. Mailen, and K. D. Williams, "Dissolution of Refractory PuO_2: New Techniques and Technology," presented at the 28th Annual Southeast Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Oct. 27–29, 1976.

Tennery, V. J.,[19] E. S. Bomar,[19] W. D. Bond, S. V. Kaye,[36] L. E. Morse, and J. E. Till,[36] *Potential Generation and Radiological Impacts of Gaseous ^{14}C Released During Reprocessing of Advanced LMFBR Fuels,* ORNL/TM-5538 (June 1976).

Tennery, V. J.,[19] L. E. Morse, E. S. Bomar,[19] R. D. Seagren, W. D. Bond, L. B. Shappert, G. S. Hill,[36] and J. E. Till,[36] *Environmental Assessment of LMFBR Advanced Fuels: A Radiological Analysis of Fuel Reprocessing, Refabrication, and Transportation,* ORNL-5230 (November 1976).

Vondra, B. L., Jr., "Nuclear Fuel Cycle (Breeder)," presented at the Oak Ridge Associated Universities, Oak Ridge, Tenn., Aug. 9, 1976.

---

48. Co-op student, University of Tennessee, Knoxville.
49. Bechtel Corp., San Francisco.

Watson, C. D., and S. D. Harris, *SRO/LWR Fuel Reprocessing and Recycle Support Program: A Scoping Study to Identify Unresolved Shearing and Related Head-End Problems,* ORNL/TM-5651 (October 1976).

Whatley, M. E., "Analysis of a Voloxidizer for Control of Tritium Release from Nuclear Fuel Reprocessing Plants," presented at the University of South Carolina, Charleston, Mar. 3, 1977.

Yarbro, O. O., W. S. Groenier, and M. J. Stephenson,[45] "Airborne Effluent Control for LMFBR Fuel Reprocessing Plants," presented at the American Nuclear Society–American Institute of Chemical Engineers Topical Meeting, Controlling Airborne Effluents from Fuel Cycle Plants, Sun Valley, Idaho, Aug. 5–6, 1976.

PROGRESS REPORTS

Burch, W. D., et al., *LMFBR Reprocessing Program Progress Report for Period January 1 to March 31, 1976,* ORNL/TM-5463 (June 1976).

Burch, W. D., et al., *LMFBR Fuel Reprocessing Program Process Report for Period April 1 to June 30, 1976,* ORNL/TM-5556 (August 1976).

Burch, W. D., et al., *LMFBR Fuel Reprocessing Program Progress Report for Period July 1 to September 30, 1976,* ORNL/TM-5668 (November 1976).

Burch, W. D., et al., *LMFBR Fuel Reprocessing Program Progress Report for Period October 1 to December 31, 1976,* ORNL/TM-5768 (February 1977).

Fontana, M. H.,[6] R. E. Adams,[6] T. S. Kress,[6] L. F. Parsly,[6] and G. W. Parker, *LMFBR Aerosol Release and Transport Program Quarterly Progress Report for January–March 1976,* ORNL/NUREG/TM-35 (August 1976).

Hightower, J. R., Jr., et al., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 22,* ORNL/TM-5041 (June 1976).

King, L. J., J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1975,* ORNL-5146 (October 1976).

Lorenz, R. A., J. L. Collins, S. R. Manning, and A. P. Malinauskas, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period January–March 1976,* ORNL/NUREG/TM-30 (July 1976).

Lorenz, R. A., J. L. Collins, S. R. Manning, O. L. Kirkland, and A. P. Malinauskas, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period April–June 1976,* ORNL/NUREG/TM-44 (August 1976).

Lorenz, R. A., J. L. Collins, and O. L. Kirkland, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period July–September 1976,* ORNL/NUREG/TM-73 (December 1976).

Lorenz, R. A., J. L. Collins, and O. L. Kirkland, *Quarterly Progress Report on Fission Product Release from LWR Fuel for the Period October–December 1976,* ORNL/NUREG/TM-88 (March 1977).

Mrochek, J. E., C. A. Burtis,[2] and C. D. Scott, *Biochemical Technology Program Progress Report for the Period January 1–June 30, 1976,* ORNL/TM-5446 (July 1976).

Newman, E., *Isotope Separations Section Progress Report for Quarter Ending December 31, 1975,* ORNL/TM-5345 (April 1976).

Newman, E., *Isotope Separations Section Progress Report for Quarter Ending March 31, 1976,* ORNL/TM-5465 (June 1976).

Newman, E., *Isotope Separations Section Progress Report for Quarter Ending June 30, 1976,* ORNL/TM-5625 (October 1976).

Scott, C. D., C. A. Burtis,[2] W. S. Groenier, W. W. Pitt, A. D. Ryon, C. D. Watson, and J. S. Watson, *Experimental Engineering Section Semiannual Progress Report (Excluding Reactor Programs) March 1, 1975, to August 31, 1975,* ORNL/TM-5291 (September 1976).

Vondra, B. L., et al., *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period January 1 to March 31, 1976,* ORNL/TM-5447 (May 1976).

Vondra, B. L., et al., *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period April 1 to June 30, 1976,* ORNL/TM-5547 (July 1976).

Vondra, B. L., et al., *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period July 1 to September 30, 1976,* ORNL/TM-5660 (November 1976).

Vondra, B. L., et al., *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period October 1 to December 31, 1976,* ORNL/TM-5760 (February 1977).

REACTOR SAFETY RESEARCH

Albrecht, H.,[50] M. F. Osborne, and H. Wild,[50] "The Release of Fission and Activation Products During Core Meltdown," presented at the CSNI Specialists Meeting on the Behavior of Water Reactor Fuel Elements under Accident Conditions, Spatind, Nord-Torpa, Norway, Sept. 13–16, 1976.

Kelly, M. J., T. S. Kress,[6] G. W. Parker, J. M. Rochelle,[13] and M. H. Fontana,[6] "Development and Application of the Capacitor Discharge Vaporization Technique for Fuel Aerosol Studies," presented at the Joint Meeting of the American Nuclear Society and the European Nuclear Society on Fast Reactor Safety and Related Physics, Chicago, Oct. 4–8, 1976.

Kelly, M. J., J. M. Rochelle,[13] and G. W. Parker, "Development of a Capacitor Discharge Vaporization Technique (CDV) to Provide Fuel Samples at HCDA Postulated Energy Conditions," presented at the International Meeting on Fast Reactor Safety and Related Physics, Chicago, Oct. 6–8, 1976.

Lorenz, R. A., J. L. Collins, A. P. Malinauskas, and S. R. Manning, "Fission Product Release from Simulated LWR Fuel," presented at the CSNI Specialists Meeting on the Behavior of Water Reactor Fuel Elements under Accident Conditions, Spatind, Nord-Torpa, Norway, Sept. 13–16, 1976.

Parker, G. W., "Problems in Size Determination of Highly Concentrated Aerosols," presented at the Ninth Aerosol Technology Meeting, Battelle Columbus Laboratories, Columbus, Ohio, Oct. 21–22, 1976.

SEPARATIONS CHEMISTRY

Campbell, D. O., "Separation of Lanthanides and Trivalent Acinides with Pressurized Ion Exchange," *Sep. Purif. Methods* **5**, 97 (1976).

Coleman, C. F., and R. E. Leuze, "Some Milestone Solvent Extraction Processes," presented at the 28th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Oct. 27–29, 1976.

McDowell, W. J., "Improvement in Sample Preparation for Alpha Liquid Scintillation Spectroscopy" (Letter to the Editor), *Talanta* **23**, 80 (1976).

McDowell, W. J., and C. F. Coleman, "Investigation of the Hydrates of Amine Sulfates by Dielectric Measurements," *J. Inorg. Nucl. Chem.* **38**, 871 (1976).

McDowell, W. J., O. L. Keller,[25] P. F. Dittner,[25] J. R. Tarrant,[25] and G. N. Case, "Nobelium Chemistry: Aqueous Complexing with Carboxylate Ions," *J. Inorg. Nucl. Chem.* **38**, 1207 (1976).

McDowell, W. J., P. T. Perdue,[36] and G. N. Case, "Purification of Di(2-ethylhexyl)phosphoric Acid," *J. Inorg. Nucl. Chem.* **38**, 2127 (1976).

McDowell, W. J., F. G. Seeley, and M. T. Ryan,[36] "Penetration of HEPA Filters by Alpha Recoil Aerosols," presented at the 14th ERDA Air Cleaning Conference, Sun Valley, Idaho, Aug. 2–4, 1976.

McDowell, W. J., and J. F. Weiss,[51] "Liquid Scintillation Alpha Counting and Its Application to Bone and Tissue Samples," presented at the International Conference on Liquid Scintillation Science and Technology, Banff, Alberta, June 14–17, 1976; also in *Health Phys.* **32**, 73 (1977).

---

50. GFK Karlsruhe, Federal Republic of Germany.
51. Comparative Animal Research Laboratory, University of Tennessee, Oak Ridge.

McDowell, W. J., and J. F. Weiss,[51] "Liquid Scintillation Alpha Counting and Spectrometry and Its Application to Bone and Tissue Samples," *Liquid Scintillation Science and Technology,* pp. 17–31, Academic Press, New York, 1976.

Perdue, P. T.,[36] D. J. Christian,[36] J. H. Thorngate,[36] W. J. McDowell, and G. N. Case, *Advances in the Sample Preparation and the Detector for a Combined Solvent Extraction–Liquid Scintillation Method of Low-Level Plutonium Measurement,* ORNL/TM-5166 (July 1976).

Ryan, M. T.,[36] and W. J. McDowell, *Observations of the Distribution and the Nature of Alpha-Active Particulate Material in a HEPA Filter Used for Plutonium-Containing Dust,* ORNL/TM-5765 (February 1977).

Seeley, F. G., and W. H. Baldwin,[25] "Extraction of Lithium from Neutral Salt Solutions with Fluorinated β-Diketones," *J. Inorg. Nucl. Chem.* **38**, 1049 (1976).

Shoun, R. R., W. J. McDowell, and B. S. Weaver, "Attempts to Optimize the Solubility and Extraction Characteristics of Some Bidentate Organophosphorus Compounds," presented at the Conference on Actinide Removal from Acidic Wastes, Rocky Flats Plant, Golden, Colo., May 4–5, 1976.

TRANSURANIUM-ELEMENT PROCESSING

Chattin, F. R., and L. J. King, "Remote Processing Practices and Equipment in the Transuranium Processing Plant after Ten Years of Operation," presented at the 24th Conference on Remote Systems Technology, Washington, D.C., Nov. 14–19, 1976; published in the *Proceedings.*

Collins, E. D., and J. E. Bigelow, "Chemical Process Engineering in the Transuranium Processing Plant," presented at the 24th Conference on Remote Systems Technology, Washington, D.C., Nov. 14–19, 1976; published in the *Proceedings.*

King, L. J., "Californium Production at the Transuranium Processing Plant," presented at the International Symposium on Californium-252 Utilization, Paris, Apr. 26–28, 1976.

Krichinsky, A. M., "Pilot-Scale Experience in the Ion Exchange Separation of ^{232}U Daughter Contamination from ^{233}U," presented at the Joint Fall Meeting of the Basic Science, Electronics, and Nuclear Divisions of the American Ceramic Society, San Francisco, Oct. 31–Nov. 3, 1976.

Williams, L. D.,[19] 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," presented at the 24th Remote Systems Technology Conference, Washington, D.C., Nov. 14–19, 1976; to be published in the *Proceedings.*

WASTE MANAGEMENT

Blomeke, J. O., "Waste Disposal," presented at the Nuclear Power Safety Seminar, Georgia Institute of Technology, Atlanta, Feb. 14–18, 1977.

Blomeke, J. O., "Waste Generation and Actinide Separation," presented to the American Physical Society Task Force on Nuclear Fuel Cycles and Waste Management, Oak Ridge, Tenn., May 20, 1976.

Blomeke, J. O., "Waste Management – Processing," presented at a UCC-ND Engineering Seminar, Oak Ridge, Tenn., June 4, 1976.

Blomeke, J. O., and W. D. Bond, "High-Level Waste Management Research and Development Program at Oak Ridge National Laboratory," *Adv. Chem. Ser.* **153**, 84 (1976).

Blomeke, J. O., "A Program to Establish the Technical Feasibility and Incentives for Partitioning," presented at the U.S. Nuclear Regulatory Commission Technical Workshop on Waste Partitioning as an Alternative in the Management of Radioactive Wastes, Seattle, Wash., June 8–10, 1976; published in the *Proceedings,* NR-CONF-001, p. 38 (June 1976).

Blomeke, J. O., "Concepts for Disposal of Radioactive Wastes in the United States," presented to the Council of Engineers and Scientists, Los Angeles, Apr. 27, 1976; and to the San Francisco Chapter of the American Nuclear Society, Apr. 28, 1976.

Blomeke, J. O., "Management of Radioactive Wastes," p. 255 in *Nuclear Power Safety,* Pergamon, New York, 1976.

Blomeke, J. O., "Partitioning and Transmutation in Perspective," presented at the Nuclear Waste Management Systems Overview Workshop, Scripps Institute of Oceanography, La Jolla, Calif., Jan. 24–25, 1977.

Blomeke, J. O., W. D. Bond, A. G. Croff, F. G. Kitts, R. E. Leuze, D. W. Tedder, and B. L. Vondra, in *Alternatives for Managing Wastes from Reactors and Post-Fission Operations in the LWR Fuel Cycle,* ERDA-76-43, vols. I–V (May 1976).

Blomeke, J. O., and C. W. Kee, "Projections of Waste to be Generated," presented at the International Symposium on the Management of Wastes from the LWR Fuel Cycle, Denver, Colo., July 11–16, 1976; published in the *Proceedings,* CONF-76-0701, p. 96 (July 1976).

Blomeke, J. O., and W. C. McClain,[52] "Oak Ridge Waste Management Programs: Geologic Isolation and Actinide Partitioning," presented at the First Pacific Basin Conference on Nuclear Development and the Fuel Cycle, Honolulu, Hawaii, Oct. 11–15, 1976; published in the *Proceedings,* p. 467, American Nuclear Society, Hinsdale, Ill., 1976.

Blomeke, J. O., and J. J. Perona,[53] "Source Terms for Airborne Effluents," presented at a Joint Topical Meeting of the American Nuclear Society–American Institute of Chemical Engineers on Controlling Airborne Effluents from Fuel Cycle Plants, Sun Valley, Idaho, Aug. 5–6, 1976; published in the *Proceedings,* CONF-760806-5, p. 1 (1976).

Bond, W. D., and R. E. Leuze, "Removal of Actinides from High-Level Wastes Generated in the Reprocessing of Commercial Fuels," pp. 423-32 in *Transplutonium Elements, 1975, Proceedings of the Symposium at Baden-Baden, September 13–17, 1975,* North-Holland, Amsterdam, 1976.

Croff, A. G., "Actinide Transmutation Studies: A Review," presented at the 1976 Annual Meeting of the American Nuclear Society, Toronto, June 13–18, 1976; published as CONF-760622-3 (1976).

Croff, A. G., "Radioactive Waste Treatment and Disposal," presented at the American Chemical Society Meeting, San Francisco, Calif., Aug. 30–Sept. 4, 1976.

Croff, A. G., "The Technological Impacts of Partitioning-Transmutation on the Nuclear Fuel Cycle," presented at the First Technical Meeting on the Nuclear Transmutation of Actinides, Ispra, Italy, Mar. 16–18, 1977.

Croff, A. G., *An Evaluation of Options Relative to the Fixation and Disposal of* ^{14}C*-Contaminated* CO_2 *as* $CaCO_3$, ORNL/TM-5171 (April 1976).

Kee, C. W., A. G. Croff, and J. O. Blomeke, *Updated Projections of Radioactive Wastes to Be Generated by the U.S. Nuclear Power Industry,* ORNL/TM-5427 (December 1976).

Leuze, R. E., "Actinide Partitioning from Nuclear Fuel Reprocessing Waste," presented at the Heavy Element Research Workshop, ORNL, May 24–25, 1976.

Leuze, R. E., and W. D. Bond, "Status of Reprocessing Methods for Actinide Partitioning," presented at the U.S. Nuclear Regulatory Commission Workshop on Radioactive Partitioning, Battelle Seattle Research Center, Seattle, Wash., June 8–10, 1976; published in the *Proceedings,* NR-CONF-001, p. 133 (1976).

Leuze, R. E., W. D. Bond, D. O. Campbell, and D. W. Tedder, "Conceptual Methods for Actinide Partitioning," presented at the Specialists Meeting on Partitioning-Transmutation, Ispra, Italy, Mar. 16–18, 1977.

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

Moore, J. G., "Some Studies on the Use of Cementitious Material in Radioactive Waste Management," presented at the Pennsylvania State University, University Park, Sept. 21, 1976.

Moore, J. G., "The Cement Technology Program at ORNL," presented at the Borehole Plugging Program Review Conference, Tucson, Ariz., Nov. 16–17, 1976.

52. Office of Waste Isolation.
53. University of Tennessee, Knoxville.

Moore, J. G., H. W. Godbee, and A. H. Kibbey, "Leach Behavior of Hydrofracture Grout Incorporating Radioactive Wastes," presented at the 1976 Annual Meeting of the American Nuclear Society, Toronto, June 13–18, 1976; *Nucl. Technol.* **32**(1), 39 (1977).

Weeren, H. O., *Shale Fracturing Injections at Oak Ridge National Laboratory – 1975 Series,* ORNL/TM-5545 (August 1976).

Wymer, R. G., "Radioactive Wastes: Sources, Treatment, and Disposal," presented at the Symposium on Energy Sources of the Future, Oak Ridge Associated Universities, Aug. 12, 1976.

SEMINARS

1976

April 7	Receivers Used in Calutron Separators	W. A. Bell
	Ion Source Characteristics and Development	A. M. Veach
April 14	Fission Product Interactions in Both Real and Synthetic Process Solutions	D. O. Campbell M. H. Lloyd
April 21	ALARA Studies	
	Milling Uranium Ores	M. Sears
	Fabrication of HTGR Fuel	J. W. Roddy
April 28	Effects of Alpha Aggregate Recoil on Filter Efficiency	W. J. McDowell F. G. Seeley
May 5	High-Burnup LWR Fuel Dissolution and Process Solution Stability	D. O. Campbell
May 12	Coal Conversion	J. H. Holmes George Peterson
May 19	Tritium Sorption from Liquid Metals	S. D. Clinton
	Tritium Release from Solid CTR Blanket Material	J. B. Talbot
May 26	Plans for the Engineering Phases of LMFBR Fuel Recycle	M. J. Feldman

1977

January 12	Cryosorption Pumping	P. W. Fisher
	Graphite Burning	R. M. Canon
January 26	Report on the Reactor Radwaste Management Workshop	R. E. Blanco
	Radwaste Problems at Reactor Stations	H. W. Godbee A. H. Kibbey W. E. Clark
February 2	SOLGAS: A Generalized Computer Program for Thermodynamic Calculations	T. M. Besmann
	Estimation of Gibbs Free-Energy Functions for Crystalline Compounds	T. B. Lindemer
February 9	Carbon-14 Production in Nuclear Reactors	W. Davis, Jr.
	Radioactive Waste Treatment Costs and the Environmental Impact for Conversion of Recycle Uranium to UF_6	J. W. Roddy

February 16	Hydroclones	J. B. Talbot
	Three-Phase Fluidization	J. M. Begovich
	Mechanically Agitated Contactors	C. H. Brown
February 23	KALC Engineering Studies	T. M. Gilliam
	Concentration of Krypton with Molecular Sieves	C. W. Forsberg
March 2	Transient Release from LMFBR Fuel	G. W. Parker
	Fission Product Release from Irradiated PWR Fuel Rods	J. L. Collins
March 9	LMFBR/LWR Fuel Reprocessing	
	Voloxidation	T. D. Welch
	Dissolution	B. E. Lewis
March 16	Chemistry of Hydrazine and Hydroxylamine in Fuel Reprocessing Systems	A. D. Kelmers[25]
	Organic Degradation Products and Fission Product Effects	L. Maya[25]
March 23	Scrubbing NO_x from Off-Gas	R. M. Counce
	Iodox Process Studies	B. A. Hannaford
March 30	Testing of Obsolete Spent Fuel Casks	R. D. Seagren

PATENTS

Campbell, D. O., "Recovery of Cesium and Palladium from Nuclear Reactor Fuel Processing Waste," U.S. Patent 3,979,498 (Sept. 7, 1976).

Horner, D. E., J. C. Mailen, and F. A. Posey,[25] "Electrolytic Trapping of Iodine from Process Gas Streams," U.S. Patent 4,004,993 (Jan. 25, 1977).

McDowell, W. J., and C. F. Coleman, "Liquid Film Target Impingement Scrubber," U.S. Patent 4,012,209 (Mar. 15, 1977).

Notz, K. J., "Process for Loading Weak-Acid Ion Exchange Resins with Uranium," U.S. Patent 3,995,009 (Nov. 30, 1976).

Scott, C. D., "Elution Electrophoresis," U.S. Patent 3,969,218 (July 13, 1976).

Tallent, O. K., "Method for Dissolving Plutonium Dioxide," U.S. Patent 3,976,775 (Aug. 24, 1976).

CHEMICAL TECHNOLOGY DIVISION

MARCH 31, 1977

D. E. FERGUSON, *DIRECTOR*
ALICE McWILLIAMS, *SECRETARY*
MILDRED GREGG,[1] *SECRETARY*

C. D. SCOTT, *ASSOCIATE DIRECTOR*
JO DeCARLO, *SECRETARY*

K. B. BROWN, *MANAGER*
SEPARATION SCIENCE AREA
MILDRED GREGG,[1] *SECRETARY*

EXPERIMENTAL ENGINEERING
R. E. LEUZE, *SECTION HEAD*
J. A. POSEY, *SECRETARY*
W. F. ENGLAND, *SECRETARY*

FUEL CYCLE DEVELOPMENT
A. O. RYON,[1] *MANAGER*

HTGR OFF-GAS PROCESSING
A. D. RYON[1]
T. M. GILLIAM
W. M. WOODS

TECHNICIANS:
V. L. FOWLER
D. J. INMAN

HTGR RECYCLE FUEL
P. A. HAAS, *GROUP LEADER*
R. D. SPENCE

TECHNICIAN:
R. D. ARTHUR

LMFBR FUEL REPROCESSING
B. A. HANNAFORD[1]

TECHNICIAN:
M. R. GIBSON

LWR FUEL REPROCESSING
D. W. HOLLADAY[1]
G. L. HAAG

IODINE WASTE STUDIES
B. A. HANNAFORD[1]
D. W. HOLLADAY[1]

TECHNICIAN:
C. F. BERTSCH[4]

EXXON SUPPORT
E. L. YOUNGBLOOD, *GROUP LEADER*
I. J. URZA[5]

TECHNICIAN:
W. E. ELDRIDGE

WASTE PARTITIONING
W. D. BOND, *GROUP LEADER*
C. W. FORSBERG
F. A. KAPPELMANN
S. KATZ
L. E. MORSE
F. M. SCHEITLIN

TECHNICIANS:
J. L. ANDERSON
G. D. DAVIS
R. I. HICKEY

ADVANCED TECHNOLOGY
J. R. HIGHTOWER, JR.,[1] *SECTION HEAD*
J. T. SHANNON, *SECRETARY*
B. K. BREEDEN, *SECRETARY*
O. V. GENTRY, *SECRETARY*
P. G. VALLIANT, *SECRETARY*

COAL CONVERSION PROGRAMS
J. R. HIGHTOWER, JR.,[1] *MANAGER*

HYDROCARBONIZATION PROGRAM PLANNING
H. D. COCHRAN, JR.

HYDROCARBONIZATION DEVELOPMENT
J. B. GIBSON

TECHNICIAN:
L. S. DICKERSON

HYDROCARBONIZATION BENCH-SCALE OPERATION
E. L. YOUNGBLOOD
C. H. BROWN, JR.
G. E. OSWALD
P. R. WESTMORELAND

TECHNICIANS:
J. BEAMS
J. C. ROSE

IN SITU GASIFICATION
R. C. FORRESTER III[1]

TECHNICIAN:
G. D. OWEN

PROGRAM DEVELOPMENT
V. A. DeCARLO
R. C. FORRESTER III[1]

TECHNICIANS:
R. L. ANDREWS
D. SELLINGER[4]

MIXING STUDIES AND FLOWSHEET SUPPORT
J. R. HIGHTOWER, JR.[1]
R. E. BARKER[1]
J. M. BEGOVICH[1]

TECHNICIANS:
S. M. GIBSON
G. S. MARTIN[4]
R. C. LOVELACE

BIOTECHNOLOGY AND ENVIRONMENTAL PROGRAMS
W. W. PITT, JR.,[1] *MANAGER*

ADVANCED ANALYTICAL SYSTEMS
J. E. MROCHEK
S. R. DINSMORE
N. E. LEE
W. D. BOSTICK
R. K. GENUNG
C. A. BURTIS[6]

TECHNICIAN:
J. B. OVERTON

BIOENGINEERING RESEARCH AND DEVELOPMENT
S. E. SHUMATE II
B. Z. EGAN
D. D. LEE
G. W. STRANDBERG

TECHNICIANS:
T. V. DINSMORE
J. P. EUBANKS
D. A. McWHIRTER
J. R. PARROTT, JR.
R. G. YATES[4]

BIOPROCESS DEMONSTRATION
C. W. HANCHER
I. B. ABDELRAZEK[7]
A. L. COMPERE
W. L. GRIFFITH
D. L. MILLION

TECHNICIANS:
G. B. DINSMORE
J. D. COHILL[4]

ENVIRONMENTAL MONITORING
W. W. PITT, JR.
D. D. SCHURESKO

TECHNICIAN:
G. JONES, JR.

ENVIRONMENTAL CONTROL TECHNOLOGY
J. A. KLEIN
R. E. BARKER[1]

ENVIRONMENTAL RESEARCH
R. L. JOLLEY

TECHNICIANS:
S. J. HARTMANN
J. E. THOMPSON

ENGINEERING SCIENCE PROGRAMS
J. S. WATSON,[1] *MANAGER*

CHEMICAL ENGINEERING RESEARCH
S. D. CLINTON
J. M. BEGOVICH[1]
R. M. CANON
B. R. RODGERS
J. B. TALBOT[1]

TECHNICIANS:
J. D. HEWITT
R. O. PAYNE
W. G. SISSON

FUSION ENERGY
J. S. WATSON[1]
S. D. CLINTON[1]
P. W. FISHER
S. W. SCHWENTERLY[8]
J. B. TALBOT[1]
C. P. TUNG[9]

TECHNICIAN:
F. L. ROGERS

H. B. GRAHAM,[3]
ADMINISTRATIVE ASSISTANT
JAN RENFRO, *SECRETARY*
LUCILLE KUYKENDALL,[3]
PROCUREMENT

MARTHA STEWART, *REPORTS EDITOR*
VIVIAN JACOBS, *REPORTS EDITOR*
CATHY SHAPPERT,[2] *REPORTS EDITOR*
DEBBIE STEVENS,[2] *REPORTS EDITOR*

RADIATION AND SAFETY CONTROL OFFICER
J. B. RUCH

SPECIAL ASSIGNMENT
H. E. GOELLER
A. T. GRESKY
W. R. GRIMES

QA COORDINATOR
J. E. KEETON[1]

R. G. WYMER, *ASSOCIATE DIRECTOR*
JEWELL ELLIS, *SECRETARY*

K. J. NOTZ, *MANAGER, HTGR PROGRAMS*
MILDRED PAYNE, *SECRETARY*

CHEMICAL DEVELOPMENT
A. P. MALINAUSKAS, *SECTION HEAD*
CAROL PROAPS, *SECRETARY*
BETTY DRAKE, *SECRETARY*
CHRIS FLANARY, *SECRETARY*
THELMA PATTON, *SECRETARY*

SEPARATIONS CHEMISTRY
C. F. COLEMAN, *MANAGER*
W. J. McDOWELL, *GROUP LEADER*
F. G. SEELEY
R. R. SHOUN
B. WEAVER[10]
C. T. BAHNER[10]
M. T. RYAN[11]
S. E. DORRIS[4]
E. J. BOUWER[12]

TECHNICIAN:
G. N. CASE

HOT-CELL OPERATIONS
V. C. A. VAUGHEN, *MANAGER*
J. H. GOODE,[1] *GROUP LEADER, SUPERVISOR, 4501*
C. L. FITZGERALD
C. E. LAMB
R. H. RAINEY
H. C. SAVAGE
R. G. STACY

TECHNICIANS:
E. C. HENDREN
D. J. KINGTON
R. J. SHANNON
J. R. TRAVIS
C. S. WEBSTER

FUEL REPROCESSING DEVELOPMENT
J. C. MAILEN, *MANAGER, ADVANCED BREEDER AND ALTERNATE FUEL CYCLES*
A. D. KELMERS,[13] *GROUP LEADER*
C. O. BOPP
G. I. CATHERS
D. E. HORNER
L. MAYA[13]
O. K. TALLENT, *TASK LEADER*
M. R. BENNETT[13]
W. E. CLARK
H. K. NICHOLS[14]

TECHNICIANS:
W. B. HOWERTON
D. Y. VALENTINE[13]
K. D. WILLIAMS

J. H. SHAFFER, *MANAGER, THORIUM UTILIZATION*
R. D. ACKLEY
E. E. McCOMBS
A. L. RICE[15]

TECHNICIANS:
C. W. GREENE
C. F. KECK
W. E. SHOCKLEY

REACTOR TECHNOLOGY
T. B. LINDEMER, *GROUP LEADER FUEL TECHNOLOGY*
E. C. BEAHM
T. M. BESMANN
R. L. PEARSON
R. P. WICHNER,[1] *GROUP LEADER FISSION PRODUCT BEHAVIOR*
F. F. DYER[16]
R. B. EVANS[17]
L. L. FAIRCHILD
W. J. MARTIN,[1] *SUPERVISOR, 4501*

REACTOR SAFETY
R. A. LORENZ, *GROUP LEADER LWR FISSION PRODUCT RELEASE*
M. F. OSBORNE[18]
J. L. COLLINS

TECHNICIANS:
O.L. KIRKLAND
R. L. TOWNS

G. W. PARKER, *GROUP LEADER, LMFBR SAFETY PROGRAM*
M. J. KELLY
G. E. CREEK[10]

TECHNICIAN:
A. L. SUTTON

R. P. WICHNER,[1] *GROUP LEADER LWR FISSION PRODUCT TRANSPORT*
S. K. WHATLEY

ACTINIDE SEPARATION AND ANALYSIS
D. O. CAMPBELL, *GROUP LEADER*
S. R. BUXTON
W. L. PATTISON

PILOT PLANT
R. E. BROOKSBANK, *SECTION HEAD*
BOBBIE HOYLE, *SECRETARY*
SUE ROBINSON, *SECRETARY*
BRENDA SMITH, *SECRETARY*
JANET URZA, *SECRETARY*
R. B. WATERS, *DRAFTSMAN*
W. A. LINDSEY, *SAFEGUARDS ENFORCEMENT*

SPECIAL PROJECTS

ALTERNATE FUEL CYCLE
R. B. LINDAUER
F. G. KITTS
J. R. GRAY[19]

NUCLEAR SAFETY JOURNAL, REPORTS PREPARATION
F. N. BROWDER[1]

NRC VAULT AUTOMATION STUDIES
W. T. McDUFFEE, *GROUP LEADER*
F. N. BROWDER[1]
W. R. HAMEL[20]
A. L. PRUITT[21]

CASK TESTING PROGRAM
R. D. SEAGREN, *GROUP LEADER*
W. D. BOX
M. C. JURGENSEN[6]

RADIOCHEMICAL OPERATIONS
J. R. PARROTT, SR., *MANAGER*
R. G. NICOL, *GROUP LEADER, OPERATIONS*
F. L. OALEY, *REACTOR FUELS PREPARATION*
W. A. SHANNON, *PURIFICATION SYSTEM*
C. W. MARTIN, *SITE PREPARATION, TRUST*

TRUST ENGINEERING
W. R. WHITSON
A M. KRICHINSKY

TECHNICIANS:
C. W. BOATMAN
J. M. BUTLER
D. M. HELTON
A. L. JOHNSON
R. F. KIRK
O. W. SCATES
B. W. STARNES
J. F. TALLEY

TRANSURANIUM PROCESSING PLANT
L. J. KING, *MANAGER*
J. E. BIGELOW, *TRANSURANIUM MATERIALS COORDINATOR*
F. R. CHATTIN, *GROUP LEADER, OPERATIONS*
R. G. ROSS
B. J. STRADER *(A SHIFT)*[22]
D. B. OWSLEY *(B SHIFT)*
R. C. SHIPWASH *(C SHIFT)*
C. E. WADDELL *(D SHIFT)*
G. A. WEST, *ENGINEERING*
E. D. COLLINS, *GROUP LEADER, TECHNICAL*
D. E. BENKER
L. C. WILLIAMS,[22] *GROUP LEADER, TARGET FABRICATION*

TECHNICIANS:
E. W. BROWN
W. J. BRYAN
E B. CAGLE
J. H. GROOVER
K. E. GUYMON
M. C. HILL
W. JENNINGS[22]
R. R. LAXSON
M. E. LITTLETON
S. L. RICH
L. R. ROACH
C. E. ROBERTS
S. E. SHELL
H. C. THOMPSON
A. V. WILDER
K. WILSON
G. E. WOODALL

PROCESS DEVELOPMENT
M. H. LLOYD, *MANAGER*
J. M. CHILTON
J. B. KNAUER
P. B. ORR

TECHNICIANS:
L. A. BYRO
S. A. McCOSH
D. H. NEWMAN
J. T. WIGGINS

ORNL TRANSPORTATION LOGISTICS STUDIES
L. B. SHAPPERT, *MANAGER*
O. S. JOY
M. HEISKELL

FUEL RECYCLE
W. D. BURCH,[1,23,24] *SECTION HEAD*
JUNE REDMOND,[24] *SECRETARY*
LOU GUINNELS, *SECRETARY*
KAYE MOORE, *SECRETARY*
MAY PEPPER, *SECRETARY*
KATHY ROBERSON, *SECRETARY*
KAREN THACKER, *SECRETARY*
VICKY WALLACE, *SECRETARY*
J. W. KIDD,[25] *DRAFTSMAN*
W. E. UNGER, *SENIOR TECHNICAL ASSISTANT*
W. G. STOCKDALE, *TECHNICAL ASSISTANT*

TECHNICAL AND ADMINISTRATIVE SUPPORT
W. D. BURCH,[1,23,24] *ACTING MANAGER*

PRELIMINARY SAFETY ANALYSIS
D. C. HAMPSON[1]

PROJECT CONTROL MANAGEMENT PLAN
D. C. HAMPSON[1]

OPERATIONS
D. E. DUNNING

TECHNICIANS:
A. L. BEETS
W. T. BOSTIC
E. C. BRANTLEY
E. R. JOHNS
J. F. LOCKMILLER
C. F. METZ
D. E. SPANGLER

PROCESS R&D
B. L. VONDRA,[1,26] *MANAGER*

SPECIAL STUDIES
D. J. CROUSE

SPECIAL ASSIGNMENT
R. L. BEATTY[27]

ENGINEERING RESEARCH
W. S. GROENIER, *MANAGER*
W. D. HOLLAND[28]

VOLOXIDATION
M E. WHATLEY[1]
B. B. SPENCER
T. D. WELCH

DISSOLUTION
R. M. COUNCE
B. E. LEWIS

FEED PREPARATION
J. G. MORGAN

SOLVENT EXTRACTION
M. E. WHATLEY[1]

ENGINEERING SYSTEMS
M. J. FELDMAN, *MANAGER*

HOT PILOT PLANT CONCEPTUAL DESIGN
O. O. YARBRO, *MANAGER*

FACILITY AND SITE DESIGN
J. R. WHITE
J. N. HERNDON

PROCESS AND EQUIPMENT DESIGN
E. D. NORTH
E. L. NICHOLSON
F. L. PEISHEL

ENGINEERING ANALYSIS
A. R. IRVINE

INTEGRATED PROTOTYPE EQUIPMENT TEST
J. M. CHANDLER, *MANAGER*

COMPONENT DEVELOPMENT
N. R. GRANT, *MANAGER*

DISASSEMBLY AND CUTTING
C. D. WATSON
M. E. CLIFTON
B. S. WEIL

DISSOLUTION
J. O. KIRKMAN

PRODUCT CONVERSION
J. D. SEASE[1]

RECEIVING AND STORAGE
S. A. MEACHAM[29]

REMOTE HANDLING AND MAINTENANCE
J. D. SEASE[1]
W. F. SCHAFFER

L. E. McNEESE, *ASSOCIATE DIRECTOR*
JAN THOMAS, *SECRETARY*

PROGRAM MANAGERS
R. E. BLANCO, *REGULATORY PROGRAM*
SUE DAMEWOOD, *SECRETARY*
J. O. BLOMEKE, *WASTE MANAGEMENT PROGRAM*
LINDA CROFF, *SECRETARY*
J. R. McWHIRTER, *COAL CONVERSION STUDIES*
MARY BROWN, *SECRETARY*

ENGINEERING COORDINATION AND ANALYSIS
R. W. GLASS, *SECTION HEAD*
BELINDA SMITH, *SECRETARY*
NANCY COCHRAN, *SECRETARY*
BETTY SELTZER, *SECRETARY*
DONNA WITHERSPOON, *SECRETARY*
K. F. STOOKSBURY, *STAFF ASSISTANT*

DRAFTING ROOM
R. P. EDWARDS,[25] *SUPERVISOR*
A. J. FARMER, *SPECIAL ASSISTANT*
SUPERVISOR
H. H. BRADFORD[25]
B. G. DeVALL
G. K. FORD[25]
B. F. HENRY[25]
G. H. KITCHINGS[25]
SANDRA KOPROWSKI[25]
J. L. LUCKETT
A. B. REID[25]

SPECIAL ASSIGNMENT
P. P. HAYDON, *FACILITIES COORDINATOR*

ORNL TRANSPORTATION AND LOGISTICS
D. S. JOY

COAL CONVERSION ENVIRONMENTAL STUDIES
S. G. DeCICCO

COAL CONVERSION EVALUATIONS AND PROCESS MODELING
R. SALMON
M. S. EDWARDS
G. J. MacKENZIE
J. P. MEYER
S. P. N. SINGH
W. C. ULRICH

COAL CONVERSION ANALYSES AND ASSESSMENTS
J. M. HOLMES
J. F. FISHER
W. R. GAMBILL

GENERAL FUEL CYCLE AND WASTE STUDIES
J. O. BLOMEKE
C. W. ALEXANDER
A. G. CROFF
G. H. JENKS[30]
C. W. KEE
H. F. SOARD
D. W. TEDDER
H. O. WEEREN, *HYDROFRACTURE*

HTGR FUEL RECYCLE
W. L. CARTER
K. H. LIN

TURF ENGINEERING
F. E. HARRINGTON
C. C. HAWS

PROCESS ANALYSIS AND EVALUATION
J. W. SNIDER

REGULATORY PROGRAMS
R. E. BLANCO, *MANAGER*
W. DAVIS
M. B. SEARS
J. W. WACHTER
E. J. FREDERICK
B. C. FINNEY
J. P. McBRIDE
H. W. GOODBEE
E. L. COMPERE
A. H. KIBBEY
J. W. RODDY

ISOTOPE SEPARATIONS
E. NEWMANN, *SECTION HEAD*
RITA CAMP, *SECRETARY*
ROBERTA DUNCAN, *SECRETARY*
RAMONA KEITH, *SECRETARY*

ENGINEERING COORDINATION
G. M. BANIC
W. C. DAVIS
J. E. KEETON
L. D. LOVE[10]

CHEMISTRY AND SPECIAL PREPARATIONS
H. R. GWINN, *GROUP LEADER*
J. O. YOUNGHANSE
R. L. BAILEY
J. G. BYRD
H. H. CAUDILL
L. E. McBRIDE
R. P. NORRIS
J. W. YORK
J. T. BARKER
J. H. PAEHLER

CALUTRON OPERATIONS
J. G. TRACY, *GROUP LEADER*
R. L. CALDWELL
D. R. HINES
G. J. FISHER
W. K. HENDERSON
B. G. JENKINS
O. M. GARRETT

DESIGN AND SERVICING
W. K. PRATER, *GROUP LEADER*
H. B. GREENE
H. T. MILTON
C. WILLIAMS

SEPARATOR R&D
W. A. BELL, *GROUP LEADER*
G. D. HOWELL
E. D. SHIPLEY[10]
A. M. VEACH

CEMENT TECHNOLOGY
J. G. MOORE, *GROUP LEADER*
H. E. DEVANEY
E. W. McDANIEL
M. T. MORGAN
G. C. ROGERS

TECHNICIANS:
P. C. ARWOOD
C. T. THOMPSON

[1] DUAL CAPACITY
[2] ON LOAN FROM INFORMATION DIVISION
[3] ON LOAN FROM FINANCE AND MATERIALS DIVISION
[4] CO-OP STUDENT
[5] GUEST SCIENTIST FROM EXXON COMPANY
[6] LEAVE OF ABSENCE
[7] GUEST SCIENTIST FROM EGYPT
[8] FUSION ENERGY DIVISION
[9] GUEST SCIENTIST FROM REPUBLIC OF CHINA
[10] CONSULTANT
[11] SUMMER PARTICIPANT
[12] ORAU SUMMER STUDENT EMPLOYEE
[13] ON LOAN FROM CHEMISTRY DIVISION
[14] YOUTH OPPORTUNITY EMPLOYEE
[15] SUMMER STUDENT EMPLOYEE
[16] ON LOAN FROM ANALYTICAL CHEMISTRY DIVISION
[17] DECEASED
[18] LEAVE OF ABSENCE – GTK KARLSRUHE
[19] ON LOAN FROM PROCESS ANALYSES SECTION, Y-12 PLANT
[20] ON LOAN FROM INSTRUMENTATION AND CONTROLS DIVISION
[21] ON LOAN FROM ORNL ENGINEERING
[22] ON LOAN FROM METALS AND CERAMICS DIVISION
[23] DIRECTOR, ORNL ADVANCED FUEL RECYCLE PROGRAM
[24] CENTRAL MANAGEMENT OFFICES
[25] UCC-ND ENGINEERING
[26] MANAGER, ALTERNATE FUEL CYCLE TECHNOLOGY
[27] ON ASSIGNMENT FROM ERDA WASHINGTON
[28] CONSULTANT, TENNESSEE TECHNOLOGICAL UNIVERSITY
[29] ON ASSIGNMENT FROM WESTINGHOUSE (SUBCONTRACT)
[30] ON LOAN TO OFFICE OF WASTE ISOLATION

INTERNAL DISTRIBUTION

1. Biology Library
2–4. Central Research Library
5. Laboratory Shift Supervisor
6. ORNL – Y-12 Technical Library Document Reference Section
7. MIT Practice School
8–25. Laboratory Records Department
26. Laboratory Records, ORNL R.C.
27. C. W. Alexander
28. S. I. Auerbach
29. J. A. Auxier
30. R. L. Bailey
31. G. M. Banic
32. J. T. Barker
33. R. E. Barker
34. E. C. Beahm
35. S. E. Beall
36. A. L. Beets
37. J. M. Begovich
38. W. A. Bell
39. Myer Bender
40. D. E. Benker
41. M. R. Bennett
42. T. M. Besmann
43. J. E. Bigelow
44. R. E. Blanco
45. J. O. Blomeke
46. W. D. Bond
47. C. D. Bopp
48. W. T. Bostic
49. W. D. Bostick
50. B. F. Bottenfield
51. W. D. Box
52. E. C. Bradley
53. R. E. Brooksbank
54. F. N. Browder
55. C. H. Brown
56. K. B. Brown
57. F. R. Bruce
58. W. D. Burch
59. S. R. Buxton
60. J. G. Byrd
61. R. L. Caldwell
62. D. O. Campbell
63. R. M. Canon
64. W. L. Carter
65. H. H. Caudill
66. J. M. Chandler
67. F. R. Chattin
68. J. M. Chilton
69. W. E. Clark
70. S. D. Clinton
71. H. D. Cochran
72. C. F. Coleman
73. E. D. Collins
74. J. L. Collins
75. W. C. Colwell
76. E. L. Compere
77. R. M. Counce
78. J. A. Cox
79. A. G. Croff
80. D. J. Crouse
81. F. L. Culler
82. J. E. Cunningham
83. F. L. Daley
84. W. Davis, Jr.
85. W. C. Davis
86. V. A. DeCarlo
87. S. G. DeCicco
88. M. S. Denton
89. H. E. DeVaney
90. S. R. Dinsmore
91. J. P. Drago
92. D. E. Dunning
93. M. S. Edwards
94. B. Z. Egan
95. L. L. Fairchild
96. G. G. Fee
97. M. J. Feldman
98. R. L. Fellows
99–299. D. E. Ferguson
300. L. M. Ferris
301. B. C. Finney
302. G. J. Fisher
303. J. F. Fisher
304. P. W. Fisher
305. C. L. Fitzgerald
306. R. C. Forrester

307. C. W. Forsberg
308. E. J. Frederick
309. William Fulkerson
310. W. R. Gambill
311. O. M. Garrett
312. R. K. Genung
313. J. B. Gibson
314. T. M. Gilliam
315. R. W. Glass
316. H. W. Godbee
317. H. E. Goeller
318. J. H. Goode
319. H. B. Graham
320. N. R. Grant
321. H. B. Greene
322. A. T. Gresky
323. W. L. Griffith
324. W. R. Grimes
325. W. S. Groenier
326. H. R. Gwinn
327. G. L. Haag
328. P. A. Haas
329. R. L. Hahn
330. D. C. Hampson
331. C. W. Hancher
332. B. A. Hannaford
333. F. E. Harrington
334. C. C. Haws
335. W. K. Henderson
336. J. N. Herndon
337. R. F. Hibbs
338. J. R. Hightower
339. H. N. Hill
340. D. R. Hines
341. D. W. Holladay
342. W. D. Holland
343. J. M. Holmes
344. D. E. Horner
345. G. D. Howell
346. A. R. Irvine
347. B. G. Jenkins
348. G. H. Jenks
349. R. L. Jolley
350. D. S. Joy
351. R. T. Jubin
352. F. A. Kappelmann
353–359. P. R. Kasten
360. S. Katz
361. S. V. Kaye
362. C. W. Kee
363. J. E. Keeton
364. O. L. Keller
365. M. J. Kelly
366. A. D. Kelmers
367. A. H. Kibbey
368. L. J. King
369. J. Q. Kirkman
370. F. G. Kitts
371. J. A. Klein
372. J. B. Knauer
373. A. M. Krichinsky
374. C. E. Lamb
375. E. Lamb
376. D. D. Lee
377. N. E. Lee
378. R. E. Leuze
379. B. E. Lewis
380. K. H. Lin
381. R. B. Lindauer
382. T. B. Lindemer
383. W. A. Lindsey
384. R. S. Livingston
385. M. H. Lloyd
386. R. A. Lorenz
387. A. L. Lotts
388. F. A. Maienschein
389. J. C. Mailen
390. A. P. Malinauskas
391. C. W. Martin
392. W. J. Martin
393. L. Maya
394. J. P. McBride
395. L. E. McBride
396. E. W. McDaniel
397. W. J. McDowell
398. W. T. McDuffee
399. L. E. McNeese
400. J. R. McWherter
401. J. P. Meyer
402. D. L. Million
403. H. T. Milton
404. A. D. Mitchell
405. J. G. Moore
406. J. G. Morgan
407. M. T. Morgan
408. L. E. Morse
409. J. E. Mrochek
410. E. Newman
411. J. P. Nichols
412. E. L. Nicholson
413. R. G. Nicol
414. R. P. Norris
415. E. D. North
416. K. J. Notz

417. P. B. Orr
418. M. F. Osborne
419. G. E. Oswald
420. D. B. Owsley
421. J. H. Paehler
422. G. W. Parker
423. J. R. Parrott, Sr.
424. W. L. Pattison
425. R. L. Pearson
426. F. L. Peishel
427. G. L. Peterson
428. W. W. Pitt
429. H. Postma
430. W. K. Prater
431. H. P. Raaen
432. R. H. Rainey
433. M. E. Ramsey
434. C. R. Richmond
435. H. D. Ringel
436. G. D. Robbins
437. J. W. Roddy
438. B. R. Rodgers
439. G. C. Rogers
440. M. W. Rosenthal
441. R. G. Ross
442. J. B. Ruch
443. A. D. Ryon
444. R. Salmon
445. H. C. Savage
446. W. F. Schaffer
447. F. M. Scheitlin
448. D. D. Schuresko
449–450. C. D. Scott
451. R. D. Seagren
452. M. B. Sears
453. F. G. Seeley
454. J. H. Shaffer
455. W. A. Shannon
456. L. B. Shappert
457. R. C. Shipwash
458. R. R. Shoun
459. W. D. Shults
460. S. E. Shumate
461. S. P. N. Singh
462. M. J. Skinner
463. J. W. Snider
464. H. F. Soard
465. R. D. Spence
466. B. B. Spencer
467. R. G. Stacy
468. D. Steiner
469. P. H. Stelson
470. M. G. Stewart
471. W. G. Stockdale
472. J. B. Storer
473. B. G. Strader
474. J. G. Stradley
475. G. W. Strandberg
476. J. B. Talbot
477. O. K. Tallent
478. D. W. Tedder
479. I. L. Thomas
480, J. G. Tracy
481. D. B. Trauger
482. W. C. Ulrich
483. W. E. Unger
484. J. E. Van Cleve
485. V. C. A. Vaughen
486. A. M. Veach
487. B. L. Vondra
488. J. W. Wachter
489. C. E. Waddell
490. C. D. Watson
491. J. S. Watson
492. H. O. Weeren
493. B. S. Weil
494. J. R. Weir
495. T. D. Welch
496. G. A. West
497. P. R. Westmoreland
498. M. E. Whatley
499. S. K. Whatley
500. J. C. White
501. J. R. White
502. W. R. Whitson
503. R. P. Wichner
504. M. K. Wilkinson
505. C. Williams
506. L. C. Williams
507. W. M. Woods
508–517. R. G. Wymer
518. O. O. Yarbro
519. J. W. York
520. E. L. Youngblood
521. J. O. Younghanse
522. A. Zucker
523. G. R. Choppin (consultant)
524. E. L. Gaden, Jr. (consultant)
525. C. H. Ice (consultant)
526. L. E. Swabb, Jr. (consultant)
527. K. D. Timmerhaus (consultant)

EXTERNAL DISTRIBUTION

528. C. B. Bartlett, Chief, Fuel Cycle Research Branch, Division of Safeguards, Fuel Cycle and Environmental Research, NRC, Washington, D.C. 20555
529. Bernard Baratz, Fossil Energy, Office of Program Planning and Analysis, ERDA, Washington, D.C. 20545
530. S. J. Beard, Manager, Fuel Reprocessing Engineering, Exxon Nuclear Company Inc., 777-106th Ave., N.E., Bellevue, Wash. 98009
531. R. M. Bernero, Assistant Director, Materials Safety and Standards, Division of Engineering Standards, NRC, Washington, D.C. 20555
532. W. P. Bishop, Assistant Director, Waste Management, Division of Fuel Cycle and Material Safety, NRC, Washington, D.C. 20555
533. J. A. Buckham, Allied General Nuclear Services, P. O. Box 847, Barnwell, S.C. 29812
534. J. L. Burnett, Division of Physical Research, ERDA, Germantown, Md. 20767
535. Leslie Burris, Jr., Director, Chemical Engineering Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, Ill. 60439
536. A. B. Carson, General Electric Company, 175 Curtner Ave., Mail Code 351, San Jose, Calif. 95100
537. C. E. Carter, Manager, Biomedical Programs, Division of Biomedical and Environmental Research, ERDA, Washington, D.C. 20545
538. R. B. Chitwood, Chief, Industrial Programs Branch, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
539. N. P. Cochran, Fossil Energy, Division of Major Facility Project Management, ERDA, Washington, D. C. 20545
540. F. E. Coffman, Division of Controlled Thermonuclear Research, ERDA, Germantown, Md. 20767
541. G. N. Cunningham, Director, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
542. R. E. Cunningham, Deputy Director, Division of Fuel Cycle and Material Safety, NRC, Washington, D.C. 20555
543. J. C. Dempsey, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
544. R. DiSalvo, Division of Reactor Safety Research, NRC, Washington, D.C. 20555
545. H. N. Dunning, Acting Director, Division of Petroleum, Natural Gas, and In Situ Technology, ERDA/FE, Washington, D.C. 20545
546. C. W. Eddington, Associate Director for Research and Development Programs, Division of Biomedical and Environmental Research, ERDA, Washington, D.C. 20545
547. R. L. Egli, Director, Reactor Division, ERDA-ORO, P. O. Box E, Oak Ridge, Tenn. 37830
548. W. Eister, Research and Development Branch, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
549. R. P. Epple, Division of Physical Research, ERDA, Germantown, Md. 20767
550. Mrs. I. Fegan, Library, United Kingdom Scientific Mission, British Embassy, 3100 Massachusetts Ave., N.W., Washington, D.C. 20008
551. David Garrett, Fossil Energy, Division of Major Facility Project Management, ERDA, Washington, D.C. 20545
552. H. D. Harmon, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, S.C. 29801
553. W. S. Harmon, Fossil Energy, Division of Major Facility Project Management, ERDA, Washington, D.C. 20545
554. W. J. Haubach, Division of Physical Research, ERDA, Germantown, Md. 20767
555. R. E. Isaacson, Atlantic Richfield Hanford Company, Richland, Wash. 99352
556. H. R. Johnson, Director, Office of Program Planning and Analysis, ERDA/FE, Washington, D.C. 20545
557. Hershul Jones, Fossil Energy, Division of Major Facility Project Management, ERDA, Washington, D.C. 20545

558. R. Jones, Chief, Materials Protection Standards Branch, Office of Standards Development, NRC, Washington, D.C. 20555
559. L. M. Joseph, Fossil Energy, Office of Program Planning and Analysis, ERDA, Washington, D.C. 20545
560. G. W. Kerr, Chief, Agreements and Exports Branch, Division of Materials and Fuel Cycle Facility Licensing, NRC, Washington, D.C. 20555
561. Jackson Kinzer, Program Manager, Chemical Processing, Atomics International Division, Rockwell Hanford Operations, P. O. Box 800, Richland, Wash. 99352
562. C. W. Knudsen, Fossil Energy, Office of Program Planning and Analysis, ERDA, Washington, D.C. 20545
563. R. W. Lambert, General Electric Company, Midwest Fuel Recovery Plant, Rt. 1, Box 219B, Morris, Ill. 60450
564. T. K. Lau, Fossil Energy, Division of Major Facility Project Management, ERDA, Washington, D.C. 20545
565. W. H. Lewis, Vice President, Nuclear Fuel Services, Inc., 6000 Executive Boulevard, Suite 600, Rockville, Md. 20852
566. J. L. Liverman, Assistant Administrator for Division of Environment and Safety, ERDA, Washington, D.C. 20545
567. H. Lowenberg, Assistant Director, Operations and Technology, Division of Fuel Cycle and Material Safety, NRC, Washington, D.C. 20555
568. J. B. Martin, Assistant Director, Fuel Cycle Safety and Licensing, Division of Fuel Cycle and Material Safety, NRC, Washington, D.C. 20555
569. H. H. Marvin, Director, Division of Solar Energy, ERDA, Washington, D.C. 20545
570. W. H. McVey, Chief, Technical Branch, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
571. S. Meyers, Director, Division of Fuel Cycle and Material Safety, NRC, Washington, D.C. 20555
572. G. A. Mills, Director, Division of Fossil Energy Research, ERDA/FE, Washington, D.C. 20545
573. R. B. Minogue, Director, Office of Standards Development, NRC, Washington, D.C. 20555
574. W. E. Mott, Division of Environmental Control Technology, ERDA, Washington, D.C. 20545
575. J. D. Navratil, Rockwell International, Rocky Flats Plant, P.O. Box 464, Golden, Colo. 80401
576. M. Neuworth, Director, Division of Coal Conversion and Utilization, ERDA/FE, Washington, D.C. 20555
577. D. A. Nussbaumer, Assistant Director for Materials, Agreements and Transportation, Division of Materials and Fuel Cycle Facility Licensing, NRC, Washington, D.C. 20555
578. E. S. Pierce, Division of Physical Research, ERDA, Germantown, Md. 20767
579. A. M. Platt, Battelle Memorial Institute, Pacific Northwest Laboratory, P. O. Box 999, Richland, Wash. 99352
580. J. L. Powell, Fossil Energy, Division of Major Facility Project Management, ERDA, Washington, D.C. 20545
581. L. L. Radcliff, ERDA-ORO, P.O. Box E, Oak Ridge, Tenn. 37830
582. Matthew Reilly, Fossil Energy, Division of Environmental and Socioeconomic Programs, ERDA, Washington, D.C. 20545
583. G. Rial, Director, Division of Major Facilities & Program Management, ERDA/FE, Washington, D.C. 20545
584. G. L. Rogosa, Division of Physical Research, ERDA, Germantown, Md. 20767
585. O. T. Roth, Technical Branch, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
586. L. C. Rouse, Chief, Fuel Processing and Fabrication Branch, Division of Fuel Cycle and Material Safety, NRC, Washington, D.C. 20555
587. Alfred Schneider, School of Nuclear Engineering, Georgia Institute of Technology, Atlanta, Ga. 30332
588. H. Schneider, Technical Branch, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.c. 20545

589. M. Silberberg, Division of Reactor Safety Research, NRC, Washington, D.C. 20545
590. G. P. Simon, Ionac Chemical Co., Birmingham, N.J. 08011
591. T. B. Simpson, Fossil Energy, Division of Major Facility Project Management, ERDA, Washington, D.C. 20545
592. C. V. Smith, Jr., Director, Office of Nuclear Material Safety and Safeguards, NRC, Washington, D.C. 20555
593. D. R. Spurgeon, Assistant Director for Fuel Cycle, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
594. G. Stapleton, Division of Biomedical and Environmental Research, ERDA, Washington, D.C., 20545
595. R. W. Starostecki, Chief, Fuel Reprocessing and Recycle Branch, Division of Fuel Cycle and Material Safety, NRC, Washington, D.C. 20555
596. D. K. Stevens, Assistant Director of Material Sciences, Division of Physical Research, ERDA, Germantown, Md. 20767
597. F. Dee Stevenson, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
598. K. G. Steyer, Chief, Fuel Process Systems Standards Branch, Division of Engineering Standards, NRC, Washington, D.C. 20555
599. M. J. Szulinski, Manager, Richland Office, Science Applications, Inc., 1385 George Washington Way, Richland, Wash. 99352
600. J. S. Theilacker, Manager, Advanced Reactor Division Operations, Westinghouse Electric Corporation, Waltz Mill Site, P. O. Box 158, Madison, Pa. 15663
601. J. G. Vlahakis, Fossil Energy, Office of Program Planning and Analysis, ERDA, Washington, D.C. 20545
602. D. K. Walter, Division of Building and Community Services, ERDA, Washington, D.C. 20545
603. P. C. White, Assistant Administrator for Fossil Energy, ERDA, Washington, D.C. 20545
604. C. E. Winters, Assistant to Vice President of Corporate Technology, Union Carbide Corporation, 1730 Pennsylvania Ave., N.W., Washington, D.C. 20006
605. F. E. Witmer, Division of Environmental Control Technology, ERDA, Washington, D.C. 20545
606. R. A. Wolfe, Division of Waste Management, Production and Reprocessing, ERDA, Washington, D.C. 20545
607. R. W. Wood, Manager, Physical and Technological Programs, Division of Biomedical and Environmental Research, ERDA, Washington, D.C. 20545
608. R. Zhradnik, Assistant Director, Division of Coal Conversion and Utilization, ERDA/FE, Washington D.C. 20545
609. Giacomo Calleri, Comitato Nazionale per l'Energia Nucleare, Programma EUREX, Saluggia (Vc), Italy
610. A. S. Kertes, Hebrew University, Jerusalem
611. Y. Marcus, Israel Atomic Energy Commission, Tel Aviv, Israel
612. P. Regnaut, C.E.N. Fontenay-aux-Roses, Boite Postale No. 6, Fontaney-aux-Roses, Seine, France
613. A. J. A. Roux, Director of Atomic Energy Research, South African Council for Scientific and Industrial Research, Box 395, Pretoria, South Africa
614. Jan Rydberg, Department of Nuclear Chemistry, Chalmers Tekniska Hogskola, Gibraltargatan 5 H., Goteborg, Sweden
615. Erik Svenke, Director, Department of Chemistry, Atomic Energy Company, Stockholm 9, Sweden
616. B. F. Warner, United Kingdom Atomic Energy Authority, Production Group, Windscale and Calder Works, Sellafield, Seascale, Cumberland, England
617. M. Zifferero, Comitato Nazionale per l'Energia Nucleare, Laboratorio Trattamento Elementi Combustibili, c/o Instituto di Chemica Farmaceutica e Tossicologica dell'Universita, Piazzale delle Scienze, 5, Rome, Italy

618. M. Claude Jean Jouannaud, Dept. of Nuclear Safety, CEA, B.P. No. 6, 92260 Fontenay-aux-Roses, Seine, France
619. Louis Gutierrez-Jadra, Director de Planta Pilotos e Industriales, Junta de Energia Nuclear, Ciudad Universitaris, Madrid(3), Spain
620. George Duyckaerts, Institut de Chimie, University of Liege, Sart Tilman, 4000 Liege, Belgium
621. Librarian, Department of Chemical Engineering and Chemical Technology, Imperial College, Prince Consort Road, London, S.W. 7, England
622. Guenther Wirths, NUKEM, Hanau, Germany
623. Giuseppe Orsenigo, CNEN, Via Belisario 15, Rome, Italy
624. Werner Muller, European Transuranium Institute, Euratom, Postfach 2266, 75 Karlsruhe, West Germany
625. F. Baumgartner, Heidelberg University, Karlsruhe, Postfach 947, West Germany
626. P. A. DeJonghe, Centre d'Etude de l'Energie Nucleaire, Mol, Belgium
627. Alfred Richard Boettcher, Director, Julich Nuclear Research Center, Julich, Germany
628. Hans W. Levi, Deputy Director, Hahn-Meitner-Institut fur Kernforschung, Berlin, Sektor Kernchemie, Glienicker Strasse 100, 1 Berlin 39, Germany
629. W. R. A. Goossens, Head, Chemical Technology, SCK-CEN, Mol, Belgium
630. H. A. C. McKay, Atomic Energy Research Establishment, Applied Chemistry Division, Building 220, Harwell, Didcot, Berks, England
631. C. J. Hardy, Australian Atomic Energy Commission, Lucas Heights, Sydney, Australia
632. E. Merz, JFA, D517, Julich, Postfach 365, West Germany
633. M. E. A. Hermans, N. V., KEMA, Arnhem, Netherlands
634. A. Facchini, Agipnucleare, Milan, Italy
635. Nobuo Mitsuishi, Department of Nuclear Engineering, Kyushu University, Hakozaki, Higashiku, Fukuoka, Japan 812
636. Y. J. Sousselier, Centre d'Etudes Nucleaires, Fontenay-aux-Roses, F-92 Chatillon-sous-Bagneux, France
637. M. H. Hagen, Federal Ministry for Research and Technology, Postfach 120 370, D-53, Bonn 12, Federal Republic of Germany
638. H. Krause, Nuclear Research Center Karlsruhe, Postfach-3640, D-75 Karlsruhe, Federal Republic of Germany
639. W. L. Lennemann, International Atomic Energy Agency, P. O. Box 590, A-1011 Vienna, Austria
640. N. S. Sunder Rajan, Bhabha Atomic Research Center, Bombay 400 085, India
641. N. J. Keen, Atomic Energy Research Establishment, Harwell, Didcot, Oxfordshire OX11 ORO
642. Todaya Hoshino, Power Reactor and Nuclear Fuel Development Corporation, 9-13 1-Chome, Akasaka, Minato-Ku, Tokyo
643. R. W. Stratton, EIR, 5303 Wurenlingen (Schweiz), Switzerland
644. Eidg. Institut fur Reaktorforschung, c/o Bibliothek, CH 5303 Wurlingen, Switzerland
645. Research and Technical Support Division, ERDA-ORO
646. Institute for Energy Analysis, P.O. Box 117, Oak Ridge, Tenn. 37830

647–800. Given distribution as shown in TID-4500 under Chemical Separations Processes for Plutonium and Uranium category (25 copies – NTIS)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1977-748-189/233