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ORNL-5172

Chemical Technology DIVISION

Annual Progress Report

PERIOD ENDING MARCH 31, 1976

MASTER

OAK RIDGE NATIONAL LABORATORY

DEPARTMENT OF ENERGY, OAK RIDGE, TENNESSEE 37831

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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 \$6.00; Microfiche \$2.25

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Contract No. W-7405-eng-26

**CHEMICAL TECHNOLOGY DIVISION
ANNUAL PROGRESS REPORT
For Period Ending March 31, 1976**

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Date Published: September 1976

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operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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Reports previously issued in this series are as follows:

ORNL-2382	Period Ending August 31, 1957
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ORNL-2788	Period Ending August 31, 1959
ORNL-2883	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
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ORNL-4682	Period Ending March 31, 1971
ORNL-4794	Period Ending March 31, 1972
ORNL-4883	Period Ending March 31, 1973
ORNL-4986	Period Ending March 31, 1974
ORNL-5050	Period Ending March 31, 1975

Preface

This progress report is a summary of the research and development efforts conducted in the Chemical Technology Division during the period April 1, 1975 - March 31, 1976. Further information regarding work in the various programs can be obtained from the topical reports and journal articles cited in the references.

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1. Development of Aqueous Processes for LMFBR and LWR Fuels

The work concerned with the development of aqueous processes for LMFBR fuels is not reported here this year, in compliance with regulations which stipulate that such information must be distributed solely under the category UC-79 - Liquid-Metal Fast Breeder Reactors. The results of our studies have been summarized in the *LMFBR Fuel Recycle Program Progress Report for Period January 1 to June 31, 1975*, ORNL TM-5107 (March 1976), *LMFBR Fuel Recycle Program Progress Report for Period July 1 to December 31, 1975*, ORNL TM-5477 (in preparation), and *LMFBR Reprocessing*

Program Quarterly Report for Period January 1 to March 31, 1976, ORNL TM-5463 (June 1976). Some areas of the work have also been discussed in documents of a topical nature.

The associated effort in LWR fuel reprocessing is being reported separately in a series of quarterly progress reports. The results of the investigations carried out during this report period have been summarized in the *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period January 1 to March 31, 1976*, ORNL TM-5447 (May 1976).

2. HTGR Fuel Recycle Development Program

The Chemical Technology Division's activities under the HTGR Fuel Recycle Development Program, which is part of the overall Thorium Utilization Program, include development work in head-end reprocessing and fuel fabrication, off-gas cleanup, and conceptual 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 January 1, 1974, to June 30, 1975*, ORNL-5128 (May 1976).

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. The work has been reported separately in MSR monthly documents, in the Molten-Salt Reactor Program semiannual progress reports,^{1,2} and in Chemical Technology Division quarterly progress reports.³⁻⁵ Because of the recent decision by ERDA to terminate the MSR

Program, no subsequent quarterly or semiannual progress reports will be issued in these series; however, several topical reports are in preparation.

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1. *MSR Program Semiannual Prog. Rep. Aug. 31, 1975*, ORNL-5078, p. 140.
 2. *MSR Program Semiannual Prog. Rep. Feb. 29, 1976*, ORNL-5132 (in preparation).
 3. J. R. Hightower, Jr., et al., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 22*, ORNL TM-5041 (in preparation).
 4. J. R. Hightower, Jr., et al., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 23*, ORNL TM-5252 (in preparation).
 5. J. R. Hightower, Jr., et al., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 24*, ORNL TM-5339 (in preparation).

4. HTGR Technology and Safety Programs

The work relative to HTGR technology and safety 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 are the *Gas-Cooled Reactor Programs, HTGR Base Program, Progress Report for the Period January 1, 1974, to June 30, 1975*, ORNL-5108 (in press) and *Gas-Cooled Reactor Programs, HTGR Safety Program, Progress Report for the Period January 1, 1974, to June 30, 1975*, ORNL-5183 (in preparation).

5. Waste Management

5.1 GEOLOGIC DISPOSAL EVALUATION PROGRAM

The Geologic Disposal Evaluation (GDE) Program has been continued to pursue the objective of evaluation of geologic formations and rock types as potential terminal storage repository sites for all categories of radioactive waste. Parallel development and engineering studies that support the geologic studies and that are preliminary to the construction of a repository have been continued at a somewhat reduced level as compared with previous years. The GDE Program was reorganized on February 19, 1976, as the Office of Waste Isolation, which will be responsible for managing the National Waste Terminal Storage Program.

Geology and Hydrology

The geologic and hydrologic studies have been changed in scope in the past year to focus on the following areas that have the greatest potential as regional terminal storage sites:

Northern Louisiana salt domes. Salinity concentrations have been determined for aquifers at Chester, Milams, Sikes, Pacton, Chestnut, Drakes, Arcadia, and Gibbsland domes. Geohydrologic cross sections and maps were prepared for each of these domes. Vacherie dome was examined by means of a seismic survey. The Louisiana District, Water Resources Division, U.S. Geologic Survey (USGS), is studying the regional groundwater regime of the North Louisiana Salt Dome Basin. The next phase of geologic exploration in this area will be a core hole that will be drilled on the Vacherie dome.

Paradox Basin—anticlinal salt. The geologic mapping of the Salt Valley anticline is completed, and core samples from five test holes in the salt are being analyzed.

Michigan Basin—bedded salt. The geologic maps and cross sections of the basin salt deposits have been revised to reflect new data. Two sites for test core holes through the salt formation were selected in northeastern Michigan.

Black Warrior Basin—mudstones and shales. A geologic investigation of the Black Warrior Basin of Alabama and Mississippi indicates that the Porter's Creek and the Yazoo formations are of suitable thicknesses [greater than 500 ft (152 m)] and occur at suitable depths [between 1000 and 3000 ft (305 and 914 m)] to warrant further investigation as potential repositories in shales.

Illinois Basin—shales. A geologic report is being prepared that will discuss the areas suitable for further detailed geologic investigation of three formations in the Illinois Basin: Maquoketa formation, New Albany shale, and Borden formation.

Midcontinent—Pierre shale. The preliminary maps and cross sections of the Pierre shale have been completed by the USGS, and three large target areas for further detailed studies have been designated on the east flank of the Denver Basin, the southeast flank of the Williston Basin, and the east flank of the Williston Basin.

Green River Basin—oil shales. A preliminary study of the hydrology of the Green River oil shale deposits of the Piceance Creek, Uinta, and Greater Green River basins was completed. The conclusions of the study are that the oil shale deposits are not attractive target sites for waste isolation, because the kerogen content of the rock is a potential hydrocarbon resource and the rocks are brittle, fractured, and transmit water readily in parts of the area under consideration.

Crystalline rocks. Atomic Energy of Canada, Limited, will undertake an intensive study of crystalline rocks (especially granites) of the Canadian Shield area. The results of this study will be available to us through a cooperative agreement between the United States and Canada with respect to the problems of disposal of nuclear waste.

Developmental Studies

The borehole plugging program consists of the following: (1) a cement-concrete research effort; (2) an engineering analysis of the instrumentation that is

available or that might be developed for in situ measurement of the physical properties of borehole plugs and hole wall rock; (3) an engineering analysis of the research and development program necessary to demonstrate, using an in situ test, the down-hole compaction of natural materials for borehole plugging; (4) the compilation of a state-of-the-art technology document for all techniques for plugging boreholes; and (5) laboratory and mathematical modeling of salt dissolution around a borehole through a salt bed.

Boreholes that have been or will be drilled in prospective waste repository sites must be resealed. These plugs of a high-density, low-permeability material must form leakproof bonds with the wall rock and have lifetimes comparable to the surrounding rock formations. Feasibility studies indicated that one of the more practicable solutions to the problem lies in the use of cementitious materials such as the various commercial cements and cement-aggregate mixtures. Therefore, a cement technology research effort was initiated to determine the mixtures that can best serve to plug boreholes in various geologic formations. Initial studies will be directed toward the development of accelerated methods of testing the permeability and durability of concretes, using pozzolanic (fly ash) cement mixtures and hydrothermal cements. Pozzolanic cements have low permeability, high resistance to ground- and seawater, and have been shown by the experience of 2000 years to possess excellent durability.¹ Feasibility studies showed that tobermorite ($5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$), or a solid solution of this phase containing Al_2O_3 , could be synthesized hydrothermally. There is evidence that tobermorite has long-range thermodynamic stability and is likely to be compatible with expected shale, sandstone, and limestone wall rock materials.

Stored-Energy Studies

The stored-energy studies on salt were completed, and a final summary report was drafted.² The conclusion reached was that the storage of radiation energy in salt will not present any barrier to the safe operation of a salt mine repository.

The stored-energy studies on solidified waste, conducted in a cooperative program with Battelle

Northwest Laboratories, were completed and a report was issued.³ The main concerns with stored energy in solidified high-level wastes addressed in this work are: (1) its rapid release may cause temperature rises that could be excessive with respect to the effects of high temperatures on the integrity of the waste container and on the physical and chemical properties of the solid wastes, and (2) an explosive release of mechanical energy accompanying a sudden temperature rise in the wastes might breach the containment. Maximum heavy-particle radiation doses employed correspond to those which would accumulate in solidified waste during a period of about ten years following reprocessing of mixed uranium-plutonium oxide fuels. Extrapolations of the experimental results to higher doses lead to the conclusion that the saturation amount of stored energy would be 50 cal/g or less in each of the waste forms studied: borosilicate glasses, calcines, and hot-press compacts. No serious adverse effects on the waste container or on the physical and chemical properties of the wastes are likely as a result of the maximum temperature rises accompanying the sudden release of 50 cal/g of stored energy.

A report was issued reviewing the theoretical and experimental information of gamma radiation effects in geologic formations of interest in waste disposal.⁴

Thermal Analysis

A thermal analysis of a fuel cladding repository pilot plant in salt was completed.⁵ The design criteria provide for retrievability of the wastes and ready access to the rooms for several years, a condition that restricts the maximum floor temperature to less than 110°F (43.3°C) and probably to the order of 100°F (38°C). For this study, waste canisters were assumed to be 15 ft (4.6 m) long [active length of 13 ft (4.0 m)] and made from standard 12-in. (30.5-cm) steel pipe, with the hulls compacted to about 70% theoretical density. A reasonable arrangement for the canisters is emplacement in 20-in.-diam (50-cm) holes drilled in several rows in the salt comprising the floor of an excavated room. The empty space would be filled

1. F. M. Lea, *The Chemistry of Cement and Concrete*, 3d ed., Chemical Publishing Co., New York, 1971.

2. G. H. Jenks and C. D. Bopp, *Storage and Release of Radiation Energy in Salt in Radioactive Waste Repositories*, ORNL-5088 (in preparation).

3. F. P. Roberts, G. H. Jenks, and C. D. Bopp, *Radiation Effects in Solidified High-Level Waste. Part I. Stored Energy*, BNWL-1944 (January 1976).

4. G. H. Jenks, *Gamma Radiation Effects in Geologic Formations of Interest in Waste Disposal. A Review and Analysis of Available Information and Suggestions for Additional Experimentation*, ORNL TM-4827 (September 1975).

5. H. C. Claiborne, *Thermal Analysis of a Fuel Cladding Repository Pilot Plant in Salt*, ORNL TM-5221 (April 1976).

with sand, which should facilitate retrievability. It was assumed that the canisters were filled with pressurized water reactor fuel hulls (which had a heat generation rate of 0.35 kW per canister in the case of one-year-old wastes) and that the material loadings were the same for all of the canisters regardless of the age of the waste.

A number of two-dimensional thermal calculations for a unit cell were made to determine the effects of pitch, burial depth, waste age, and canister stacking on the maximum mine floor temperature. These calculations indicated that considerably less burial area is required for ten-year-old waste as compared with one-year-old waste. A concept utilizing a 4-ft (1.2-m) pitch was studied from an excavation viewpoint. The results show that the waste must be aged about seven years in order for the maximum floor temperature not to exceed 100°F (38°C) when single canisters are buried so that the top of each canister is 15 ft (4.6 m) below the surface of the floor. In the case of two canisters stacked vertically with a 5-ft (1.5-m) sand-filled separation distance, at least a 4.5-ft (1.4-m) pitch and an age of ten years are required for a burial depth of 5 ft (1.5 m).

For selected maximum floor temperatures, the required excavation of salt per waste canister (rooms plus canister holes) varies as some inverse function of waste age, burial depth, and the number of canisters stacked vertically in an array mode. The required excavation per canister is greatly affected by the choice of parameters, particularly the age of the waste. For example, if a maximum floor temperature of 100°F (38°C) is selected, the required room excavation (for the conditions examined) ranges from 200 ft³ (5.7 m³) per canister for ten-year-old waste contained in two vertically stacked canisters and buried to a depth of 15 ft (4.6 m) over the top canister, to 650 ft³ (18 m³) per canister for one-year-old waste in single canisters buried 5 ft (1.5 m) deep.

Engineering Assessment Studies

A number of studies related to geologic disposal were initiated during the past year. Engineering studies and analyses are needed to assess the technological feasibility of the many potential waste disposal systems so that promising concepts can be identified and developed into viable waste disposal systems. One approach to sorting out and identifying these promising waste disposal systems involves the examination and evaluation of each element in a three-dimensional matrix with the geologic formations and rock types along one axis, the types and

categories of radioactive waste along a second axis, and the waste emplacement concepts along the third axis. The three components were classified, defined, and investigated independently and then brought together to identify the most promising combinations of rock type, waste type, and emplacement concept. This study essentially completed the phase I preliminary investigations section of the overall GDE program plan."

Dome salt study. A program was initiated to develop the engineering information needed to perform preconceptual evaluations of various types of repositories that appear feasible for salt domes. Current efforts are directed toward the following: (1) evaluating and adapting for dome salt the concepts developed for a mine-type waste repository in bedded salt capable of handling high-level, intermediate-level, and transuranium (TRU) wastes; (2) developing a concept using solution-mixed cavities as the receptacles for intermediate-level and TRU wastes; (3) developing a concept using a matrix of large-diameter, deep holes as receptacles for intermediate-level and TRU wastes; and (4) evaluating the thermal problems involved in placing high-level waste in a repository located in a salt dome.

Deep-rock melt study. Three specific deep-rock melting waste disposal concepts were reviewed to identify areas of concern regarding their technical feasibility. These concepts provide for the self-melting of waste in situ; for example, the Sandia concept is to deposit the material as a solid at the bottom of a drilled hole, the Lawrence Livermore Laboratory concept is to deposit liquid waste in a cavity underground, and the University of New Mexico concept is to enclose the waste in an "indestructible" capsule in a drilled hole.

Extensive analytical and experimental analyses will be required to resolve the problems associated with thermal expansion in the rock melt zone and the surrounding heated rock formation before technical feasibility can be demonstrated for the deep-rock melt concepts. If 10% rock expansion is assumed during the rock melting phase, the molten rock volume will appear to be many times in excess of the volume of the large access holes. As a result, possible land upheaval, breaching of the processing equipment, vertical cracks propagating to the top surface of rock formation, and possible contamination of an

6 W. C. McClam, I. F. Lomenack, and R. S. Lounie, *Geologic Disposal Evaluation Program: Semiannual Report for Period Ending March 31, 1974*, ORNL-5052 (July 1975).

existing water table could present formidable problems. Major areas of concern for the capsule concept are the capsule material and the methods of loading, cooling, and emplacing such a device in a very deep hole. ERDA programmatic directives require a waste retrievability option that is not readily compatible with deep-rock melt concepts. Because of this requirement and the fact that basic technical feasibility has not been demonstrated for these concepts, all efforts in this concept area have been terminated.

In situ field tests in salt. An in situ field test program for both bedded and dome salt was initiated: (1) to confirm and validate Project Salt Vault results for salt domes; (2) to provide additional data not obtained during PSV; and (3) to obtain information required for the design of a pilot-plant facility with waste retrieval capability.

Information related to the method of emplacing waste canisters in salt and related to physical and chemical interactions between the salt formation and test unit components is required to assure both the integrity of the canister and the retrievability of the waste at any time during pilot-plant operations. The facilities are designed to minimize the number and size of test installations required to obtain the desired experimental information within an operating period of one to one and one-half years.

5.2 UPDATING OF THE ORIGIN COMPUTER CODE

During FY 1976, a concerted effort was begun to update the ORIGIN computer code and the associated data bases that were compiled during the late 1960s and early 1970s. The fission product decay, cross-section, and yield data have been updated and extended using information in the ENDF B-IV compilation.⁷ The number of fission product nuclides considered has been increased from 461 to 825, allowing for a more accurate simulation of fission product decay behavior, particularly at short decay times.⁸ The fission product cross-section data were

updated by the incorporation of ENDF B-IV cross sections weighted with a Clinch River Breeder Reactor (CRBR) neutron spectrum. The independent fission product yields given in ENDF B-IV have also been incorporated into the new ORIGIN fission product library, replacing the old fission product yields (which were mostly chain yields).

The light-nuclide library, which contains decay and cross-section data for structural materials, activation products, and impurities, has also been updated.¹⁰ The number of nuclides in this library was increased from about 240 to 674. This size increase allows the production rate of more trace contaminants to be calculated and therefore aids in determining the environmental impact of various nuclear fuel cycle facilities. The light-nuclide cross sections were also updated using the values published by the National Neutron Cross-Section Center.¹¹

These data libraries, along with a redimensioned version of the ORIGIN computer code, are now available as a package from the Radiation Shielding Information Center at ORNL.¹² Also available in this package is a memorandum describing methods whereby ORIGIN subroutines may be used by other computer codes to perform depletion and decay calculations.

There are several ongoing efforts under way to update the ORIGIN code that have not yet been completed. The major project under way involves updating the actinide cross-section library. Basic actinide cross-section data have been obtained from three compilations^{13,14} and will be used to calculate ORIGIN cross sections for the following nuclear reactors: (1) uranium-enriched PWR, (2) plutonium-enriched PWR, (3) uranium-enriched BWR, (4) plutonium-enriched BWR, (5) HTGR, (6) CRBR, (7) early oxide fuel LMFBR, (8) advanced oxide fuel LMFBR, (9) carbide fuel LMFBR, (10) nitride fuel LMFBR, and (11) MSBR.

7. R. L. Bradshaw and W. C. McClain, *Project Salt Vault: A Demonstration of the Disposal of High Activity Solidified Wastes in Underground Salt Mines*, ORNL-4555 (1971).

8. ENDF B-IV Fission Product Library Tapes 414-419 (December 1974), available from National Neutron Cross-Section Center, Brookhaven National Laboratory.

9. G. W. Morrison, C. R. Weishin, and C. W. Kee, "Decay Heat Analysis for an LMFBR Fuel Assembly Using ENDF B-IV Data," presented at the Conference on Nuclear Cross-Section Technology, Washington, D.C., Mar. 5-7, 1975.

10. C. W. Kee, *A Revised Light Element Library for the ORIGIN Code*, ORNL TM-4896 (May 1975).

11. S. F. Mughabghab and D. I. Garber, *Neutron Cross Sections*, 3d ed., vol. 1, BNL-325 (June 1973).

12. M. J. Bell, *ORIGIN: The ORNL Isotope Generation and Depletion Code*, Computer Code Package CCC-217, ORIGIN, Radiation Shielding Information Center (May 1973).

13. R. W. Benjamin, V. D. Vanderveide, T. C. Gorrell, and F. J. McCrosson, *A Consistent Set of Transplutonium Multigroup Cross Sections*, DP-MS-74-61 (March 1975).

14. R. J. Howerton, *The Lawrence Livermore Laboratory Evaluated Nuclear Data Library (ENDL) Translated into the ENDF/B Format*, UCID-16727 (March 1975).

The reactor physics calculations used to obtain the ORIGEN cross sections will involve one-dimensional static calculations and point depletion calculations, followed by two-dimensional depletion calculations on selected reactors for verification purposes. The input fuel and structural material compositions and the irradiation conditions for each of these reactors are also being updated using the latest available information. Translator computer codes are being written that will allow machine-readable nuclear data bases¹⁵ to be converted directly to an ORIGEN-readable form.

Finally, some modifications are being made to the ORIGEN code itself. The computational speed of ORIGEN has been increased by a relatively simple modification in one of the calculational subroutines. ORIGEN has been variably dimensioned to make it more adaptable to different problem sizes. Options have been included to give the user greater control over the potentially voluminous ORIGEN output. Lastly, the ORIGEN code has been substantially rewritten to allow for the simulation of much more complex nuclear fuel cycle flowsheets. This last modification has been made at the expense of increased ORIGEN input complexity; it is being tested and is not yet documented or available for use.

5.3 STUDIES OF ORNL LIQUID WASTE MANAGEMENT

Studies have continued on two aspects that bear on the future management of ORNL intermediate-level wastes (ILW). An engineering design and analysis of alternatives to hydrofracturing these wastes and chemical laboratory studies of improved grouts for use in hydrofracturing have been completed.

Alternative Methods for Management of ORNL Liquid Waste

The shale fracturing process is a proven, economical method for the permanent disposal of ILW solution at ORNL. Over the past eight years, about 1.3×10^6 gal (4.9×10^6 liters) of waste solution containing 5.5×10^5 Ci of radionuclides has been mixed with cement and injected into the impermeable shale beds that underlie the ORNL area. However, recent national emphasis in waste disposal technology has been to store wastes in retrievable forms, thereby maintaining the maximum flexibility in the

choice of future disposal options. The waste disposed of by the shale fracturing process is essentially nonretrievable as a matter of deliberate choice. For this reason, this process is in conflict with the current philosophy and, despite its obvious advantages, may be discontinued in the future. Should this occur, an alternative method for handling the waste solution generated at ORNL will be required—a method that can utilize largely existing technology to convert the waste solution into a solid, noncombustible material with low leachability, suitably packaged for storage until some method of disposal is selected.

A study was made to determine the most promising process(es) for the conversion of various ORNL waste streams to suitable forms for temporary on-site storage and for ultimate shipment off-site to be disposed of by whatever means is chosen. The desirable characteristics of the waste forms include low leachability, structural strength, minimum volume, and noncombustibility. Since these wastes have low heat generation rates, heat dissipation is not a problem and good thermal conductivity is not required. The characteristics desired for a chosen process would include operational simplicity, compatibility with alkaline nitrate solutions, low operating cost, and a minimum of required development. Eleven suggested alternative processes were investigated for possible application to future management of ORNL waste. Abbreviated flowsheets of the most promising of these methods are summarized for reference in Fig. 5.1. All processes are based on the same weekly load (one-fortieth of the annual load), and all volumetric outputs are indicated in this flow diagram in terms of 55-gal (208-liter) drums so that comparison of different processes will be simplified.

The shale-cement process is an outgrowth of the shale fracturing process. This process was suggested by the discovery that radionuclides incorporated in a matrix of cement and other additives are not easily leached from this matrix. In this process the waste solution or sludge is mixed with a cement base mix and pumped into drums to set. The drummed waste is then moved into a shielded storage vault. Facilities for the recovery of specific drums from the vault for periodic inspection are provided. A shipping facility is also included in the design study.

The cesium strip process is being developed at Savannah River and Hanford for possible application to the processing of their waste solutions. In this process, radionuclides are removed from the waste solution by ion exchange. The decontaminated waste solution is concentrated and disposed of, and concentrated fission products are eluted from the ion

15. M. J. Martin, *Nuclear Decay Data for Selected Radionuclides*, ORNL-5114 (January 1976).

* BASED ON 1 22" diam x 34" DRUM (55 gal NE1)
 ** DILUTE 5:1 FOR TRANSFER

Fig. 5.1. Processes for waste fixation.

exchange columns, fixed in a glass or cement matrix, and stored. This process would handle the waste solution only; the sludge would have to be processed by an alternative method, assumed here to be the shale-cement process. Two methods for the disposal of the decontaminated waste solution were considered: mixing with cement in a surface trench, and disposal by the shale fracturing process. The first of these methods could be used only if very good decontamination were achieved for all radionuclides.

The glass fixation process considered in this study is a combination of several somewhat similar processes that have been at least partly demonstrated. In this process the waste solution or sludge is pumped into a stainless steel pot and converted to a glass at 950°C. The filled pot is then disconnected, cooled slowly, and moved to a storage vault. An empty pot is connected to the pot line to receive the next charge.

Engineering studies of these three processes were made. These studies resulted in preliminary facility

designs and cost estimates.¹⁶ The design of each facility included a vault for the storage on-site of a five-year accumulation of processed ILW and sludge, and a shipping facility where the stored waste could be loaded in carriers for off-site shipment to a permanent storage area.

A comparison of the salient features of these three waste fixation processes is shown in Table 5.1. The equivalent features of the shale fracturing process are also compared.¹⁷ Estimated capital costs, research and development costs, and annual operating costs for each of these waste handling methods are shown in Table 5.2.

16. H. O. Weeren, F. T. Binford, and J. O. Blomeke, *Study of Alternative Methods for the Management of Waste Solution and Sludge at Oak Ridge National Laboratory*, ORNL TM-5208 (January 1976).

17. H. O. Weeren, *An Evaluation of Waste Disposal by Shale Fracturing*, ORNL TM-5209 (February 1976).

Table 5.1. Advantages, disadvantages, and status of current technology of alternatives for management of intermediate-level waste at ORNL.

Alternative process	Advantages	Disadvantages	Current technological status
Shale fracturing product	Low-leaching solid product. No off-site shipping. Immediate placement in geologic formation. Process has been field tested using intermediate-level radioactive waste. Not susceptible to natural acts on earth's surface, e.g., glaciation, denudation, flood, tornados. Very low operating and capital costs.	Waste is not retrievable. Not possible to change to alternative form.	Full-scale demonstration for neutralized intermediate-level radioactive wastes at ORNL.
Shale cement	Low-leaching solid product. Key portions of process use state-of-the-art technology. Good retrievability. Easily transported.	Large volume of waste-grout mixture must be stored. Difficult to change to alternative form if necessary. Technology has not been demonstrated.	Process is in the conceptual stage.
Cement strip	Low-leaching solid product. Good retrievability. Easily transported.	Difficult to change to alternative form if necessary. Technology has not been demonstrated. Need to store or dispose of large volume of residual salt.	Process is under active laboratory development with concurrent conceptual design of facilities for application to neutralized radioactive waste.
Conversion to glass	Low-leaching solid product. Glass product would be thermally and radiolytically stable. Good retrievability. Easily transported.	Technology has not been demonstrated. Difficult to change to alternative form if necessary. High operating and capital costs. Complex high-temperature process.	Glass product has been produced on a laboratory scale from neutralized radioactive waste. Has been demonstrated on pilot scale for acidic high-level waste.

Table 5.2. Cost comparison^a for waste fixation processes

	Shale cement	Cesium strip	Cesium strip with shale fracture	Glass	Shale fracture
Estimated capital cost, \$10 ⁶	14.9	15.0	17.0	21.8	5.4
Annual operating cost, \$10 ⁶	0.6	1.1	1.1	3.5	0.1
Annual shipping cost, \$10 ⁶	1.6	1.0	1.0	1.0	
Research and development cost, \$10 ⁶	1.2	2.1	2.1	3.0	0.7

^aIn 1975 dollars.

Leaching Studies of Hydrofracture Grouts

Additional studies were completed to determine the leachability of cesium and strontium from simulated hydrofracture grout.¹⁹ In these studies we used either the test method proposed by the International Atomic Energy Agency or a modified technique that exposed smaller specimens having a higher surface:volume ratio to a larger volume of leachant. The results showed that the amount of cesium or strontium leached from the grout varied directly with the degree of drying during curing and inversely with the time of curing. The leachability also depends on the composition of the leachant and varies in the following order: distilled water > tap water > grout water. Concentrating the waste by a factor of up to 4 (prior to incorporation into a grout) had little effect on the leach rate of either strontium or cesium.

The credibility of the laboratory results was substantiated by a short-term continuous leach test made on a fragment of a core sample of actual hydrofracture grout. The modified effective diffusivities (10^{-11} to 10^{-12} cm²/sec, equivalent to a leach rate of 10^{-3} g/cm²/day⁻¹) calculated from these limited data were comparable to those obtained from laboratory studies utilizing Grundite clay.

These tests also confirm the effect of various clays on the leachability of cesium and the relationship of leachant renewal frequency to the leach rate.

5.4 PROJECTIONS OF RADIOACTIVE WASTES FROM THE NUCLEAR FUEL CYCLE

In order to obtain waste management data based on more current power projections and more detailed calculational procedures, new projections were made

of the volumes and characteristics of wastes to be shipped and stored through the year 2000.²⁰ The new projections considered PWRs and BWRs separately, and the reference PWR and BWR models used for the ORIGEN calculations were based on more detailed fuel isotopic charge-discharge data²¹ than were the models for previous projections.²² A recent forecast ["Low Growth," February 1975 (Revised)] of the ERDA Office of Planning and Analysis was used as a basis. In this forecast, processing of spent fuels is assumed to begin in 1978, and plutonium recycle to LWRs begins in 1981. Large commercial LMFBRs are introduced in 1993, but the HTGR does not achieve market penetration. The contribution of each reactor type to the total installed nuclear capacity is shown in Fig. 5.2.

Projections were made for the ten types of wastes described previously²³ and for the isotope ¹³⁷Cs. A summary of these projections for the year 2000 is given in Table 5.3. Most of the volumes and activities are smaller than reported previously because of the lower power levels projected; however, several changes in the bases used to estimate waste generation rates were also of some consequence. These changes included the following:

1. The volume of solidified high-level waste generated per metric ton of LWR fuel reprocessed was increased from 2 ft³ (0.057 m³) to 3 ft³ (0.085 m³).
2. The volume of compacted cladding waste was increased from 2.1 ft³ (0.059 m³) per metric ton of

19 C. W. Kee, A. G. Croft, and J. O. Blomcke, *Updated Projections of Radioactive Wastes to be Generated by the U.S. Nuclear Power Industry*, ORNL TM-5427 (in press).

20 Pacific Northwest Laboratories, *Theoretical Analysis of Plutonium Buildup and Uranium Depletion in Pressurized Water and Boiling Water Power Reactors*, Report Y49024 to IAEA Division of Nuclear Power Reactors (July 1968).

21 *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1974*, ORNL-4966, pp. 11-12.

22 *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1975*, ORNL-5050, pp. 18-19.

18 J. G. Moore, *Development of Cesium/Strontium Grouts for the Incorporation of Radioactive Wastes. Part 2: Continuation of Cesium and Strontium Leach Studies*, ORNL-5142 (in press).

Fig. 5.2 Installed nuclear capacity in the United States as projected by the ERDA Office of Planning and Analysis: Low Growth Case of February 1975 (Revised).

reprocessed LWR fuel to 2.29 ft³ (0.065 m³) per metric ton of PWR fuel and 2.92 ft³ (0.083 m³) per metric ton of BWR fuel.

3. The volume of iodine was based on incorporating iodine as barium iodate in cement at an iodine concentration of 5.3 kg ft³ (187 kg m³) rather than as pellets of KI.
4. The volume of LWR tritium was estimated on the basis of 63,000 and 16,600 gal (240,000 and 40,000 liters) of tritiated water being bled annually from the primary circuit of each 1000-MW PWR and BWR respectively.
5. The volume of nontransuranium solid wastes was based on the generation of 15,000 ft³ (425 m³) per year at each 1000-MW power station, and on the generation of 68,000 ft³ (1930 m³) per ton of plutonium processed at fuel fabrication and reprocessing plants. The ¹⁴C levels resulting from an (n,p) reaction with ¹⁴N and an (n,α) reaction with ¹⁶O were calculated from the assumption of 25 ppm of nitrogen impurity being present in LWR and LMFBF oxide fuels.

Table 5.3. Fuel cycle waste projected for the year 2000

Category	Annual generation			Accumulated inventory in the United States					
	Volume (10 ³ m ³)	Activity (MBq)	Annual shipments	Volume (10 ³ m ³)	Activity (MBq)	Thermal power (kW)	Metric tons of materials	Tonnages (m ³) of HL/G ^a	Water
High-level waste, solidified	1.0	28,000	210 ^b	10.5	78,000	372,000	774	3.8 × 10 ¹²	2.5 × 10 ¹⁰
Transuranium wastes									
Lodding bath	0.6	260	550 ^c	8.3	980	3,800	55	9.0 × 10 ¹⁰	2.2 × 10 ¹¹
Intermediate-level solids	4.2	3 ^d	2,000 ^e	45	6	50	0.22	1.7 × 10 ¹⁰	6.1 × 10 ¹²
Low-level solids	14	14	900 ^f	125	20	11 ^g	9.6	7.0 × 10 ¹⁰	1.2 × 10 ¹²
Non-transuranium wastes									
Spent pins	0.03 ^h	82	110 ⁱ	0.32 ^j	560	840	0	1.9 × 10 ¹¹	
Lubric	0.014	0.0004	16 ^k	0.14	0.0036	0.002	0	1.8 × 10 ¹⁰	6.0 × 10 ¹⁰
Cathode-14		0.006			0.009			5.9 × 10 ¹¹	7.3 × 10 ¹⁰
LWR tritium (gases)	74	0.35	5,000 ^l	860	2.9	0.090	0	1.4 × 10 ¹¹	9.2 × 10 ¹⁰
Fission product oxides	0.1	4.8	300 ^m	1.0	38	1.3	0	1.9 × 10 ¹⁰	1.3 × 10 ¹⁰
Non-fissionable solids	190	0 ⁿ	14,000 ^o	1,900	2.6	7.6	-0	1.9 × 10 ¹¹	2.9 × 10 ¹⁰
(Re tailings)	24,000	0.20		250,000	3.8	93	54,000	5.3 × 10 ¹⁰	1.6 × 10 ¹¹

^a Volume, meters of air or water required for dilution to Radiation Control, extraction Guides (RC/G) values (Appendix B, Table II, of 10 CFR 20).

^b Solidified immediately and shipped ten years after generation.

^c Rail shipments are assumed.

^d Shipped one year after generation.

^e Truck shipments are assumed.

^f Pressured at 2200 psi (1.5 × 10⁷ 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. It functions integrally with the researchers and not merely as a supplier. 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. In addition to the normal production functions, various programs are pursued in cooperative ventures with other research laboratories to assist them in their work. Special isotopes are provided at their request, and hot-cell space can be made available for certain experimental programs with large quantities of material when such an approach is feasible. 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].

Status and Progress

During the first four years that TRU was in operation, the materials processed were obtained from irradiations made for the TRU program at the Savannah River Plant (SRP) and at the HFIR, and all recovered transuranium elements (plutonium through fermium) were distributed to researchers. During the next three years, operations at TRU were expanded to include the processing of materials irradiated at SRP as part of the Californium-1 (Cf-1) campaign. This was an irradiation and processing campaign designed to obtain ^{252}Cf for use in a market evaluation program being sponsored by the ERDA Division of Nuclear Fuel Cycle and Production (DNFCP). There has been no further request to process Cf-1 materials during the past three years, therefore, participation in the DNFCP program has been limited to the purification and shipment to SRP of ^{252}Cf recovered from targets irradiated in the HFIR. Operations have been at about one-half of TRU's capacity for fabricating and processing HFIR targets. However, the amounts of transuranium elements produced in HFIR targets have been maintained at a meaningful level by irradiating isotopically heavier curium, most of which was recovered from the Cf-1 campaigns at TRU.

The primary role of TRU as supplier of research materials has continued. 82 shipments were made this year to researchers throughout the country.

Production and Processing

During this report period, two campaigns were made, and a total of 20 HFIR targets were processed.

1. L. E. King, L. E. Riegelson, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June 30, 1975*, ORNL 5284 (March 1976).

2. L. E. King, L. E. Riegelson, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1975*, ORNL 5346 (in press).

Sixteen of these targets had been prepared from Cf-I curium. Key isotopes in the campaign products are listed in Table 6.1.

Product finishing operations include (1) final purification and packaging of the transcurium elements; (2) separation, purification, and packaging of daughter products (^{240}Cm , ^{242}Cf , and ^{252}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 target campaigns 48, 49, and 50, some of the products from previous campaigns, and various rework materials. The amounts of materials undergoing product finishing operations included 10 g of ^{243}Am , 443 g of curium, 76 mg of ^{240}Bk , 1061 mg of ^{242}Cf , 4.7 mg of ^{252}Es (mixed isotopes), and about 1.6 pg of ^{257}Fm . We also recovered and purified 263 μg of ^{252}Es (the daughter product of ^{242}Cf), 8.3 mg of ^{242}Cf (the daughter product of ^{240}Bk), and 136 mg of ^{240}Cm (the daughter product of ^{242}Cf).

Fabrication of Targets

Twenty-six targets were fabricated in order to recycle curium to the HFIR. Of these targets, 2 contained curium from regular TRU stock, 14 contained Cf-I curium, and 10 contained curium recovered from previous irradiation of Cf-I curium in the HFIR.

Processes and Equipment

Flowsheets used at TRU remain unchanged. The condition of plant equipment at TRU is generally good and is continually maintained. When replacements are necessary, modifications are usually included to provide improved capability and performance.

This year we replaced the equipment rack in cubicle 6 containing equipment for decontamination of the transplutonium actinides from rare-earth fission products and for separation of curium from the heavier elements by means of the LiCl-based anion exchange process. The old rack had been in service for a period of seven years and had been used to process actinide solutions containing more than 1.3 kg of ^{240}Cm and 2.3 g of ^{242}Cf .

Also, we replaced the two equipment racks in cubicle 5 which were used for separation of the transcurium elements by means of high-pressure ion exchange and purification of ^{240}Bk by means of a batch solvent extraction process (Berkex). By eliminating obsolete, multipurpose vessels and piping, we were able to fit the new equipment onto a single rack. The new rack contains a pressure-pot feed system, which should be more reliable than a pump for transferring radioactive solutions to the loading column. A pump will still be used for transfer of nonradioactive eluent solutions.

Table 6.1. Amounts of materials recovered in major campaigns in the Transcurium Processing Plant during the period April 1, 1975, through March 31, 1976

	Campaign 49	Campaign 50	Total recovered
Completion date	6/75	2/76	
Material processed	6 Cf-I Cm-HFIR targets, 4 TRU Cm-HFIR targets plus rework	10 Cf-I Cm-HFIR targets plus rework	20 HFIR targets plus rework
Amount recovered			
^{243}Am , g ^a	1.3	2.0	3.3
^{240}Cm , g ^a	27(62) ^b	50(107) ^b	77(169) ^b
^{240}Bk , mg	27	29	56
^{242}Cf , mg	240	277	517
^{252}Es , mg	1.3	1.7	3.0
^{257}Fm , pg	0.4	0.5	0.9

^aAmericium and curium are not usually separated from each other.

^bThe amount shown in parentheses is total curium.

Curium Composition and Californium Production

The rates at which californium and other transuranium elements are produced during the neutron irradiation of curium depend on the isotopic composition of the curium. Figure 6.1 is a diagram of the primary isotope path followed in transmuting curium into berkelium, californium, and einsteinium by neutron irradiation. As neutrons are absorbed, ^{244}Cm is transmuted successively into ^{245}Cm , ^{246}Cm , ^{247}Cm , ^{248}Cm , and then to ^{249}Cm , which decays rapidly by beta emission to ^{249}Bk . The ^{249}Bk is converted to ^{249}Cf by either of the paths shown, involving both a neutron absorption and a beta emission in one order or the other. Then more neutron absorption forms ^{250}Cf , which decays by beta emission to ^{250}Bk .

The arrows pointing down to the right in Fig. 6.1 indicate that a significant fraction of the atoms of the isotope fission when they absorb a neutron instead of going on to the heavier isotope. That produces fission products instead of desired products and consumes curium nonproductively.

In the curium part of the growth chain in the HFIR, only about 14% of the ^{244}Cm atoms go on to ^{249}Cm (the other 86% are destroyed in fission), and only 25% of the ^{249}Cm atoms are converted to ^{249}Bk .

Only about 10 g of actinides can be put into an HFIR target because of limitations on heat removal during irradiation. If the 10 g of curium in an HFIR target contains a larger fraction of ^{244}Cm and ^{246}Cm , transcurium elements will be produced faster than if the curium is predominantly ^{245}Cm . The ^{244}Cm and ^{246}Cm have such high fission cross sections that these isotopes constitute only a small percentage of the curium we handle.

Figure 6.2 shows the buildup of ^{252}Cf in two targets, one in which the curium contains about 95% ^{244}Cm , and one in which the curium contains more of the heavier isotopes (about 62% ^{244}Cm , 30% ^{246}Cm , and 3.2% ^{248}Cm). This heavy curium composition is about the average composition of the curium we recovered from the Cf-I campaign. The squares in Fig. 6.2 indicate the irradiation periods that have been used prior to removal of the targets from the HFIR for processing. Irradiation of curium containing 30% ^{246}Cm and 3.2% ^{248}Cm for only one-third as long as for the same amount of total curium containing 95% ^{244}Cm produces three times as much ^{252}Cf . This is the reason we are producing so much of the transcurium elements today, even though fewer HFIR targets are actually being processed.

There is nothing basically different between the Cf-I curium and the curium produced in the HFIR. Curium becomes enriched in the heavier isotopes

Fig. 6.1. Transmutation path from ^{244}Cm to ^{253}Es .

Fig. 6.2. Heavy curium makes ^{252}Cf faster.

during irradiation. Longer irradiations such as those given the Cf-I curium at SRP or repeated cycles of irradiations such as we give curium in HFIR targets result in heavier curium.

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. Special projects include nonroutine productions, special preparations, special irradiations in the HFIR, and fabrication of neutron sources from ^{252}Cf .

Fabrication of Neutron Sources from ^{252}Cf

Some of the californium recovered at TRU is incorporated into neutron sources, which are subsequently loaned to researchers. Seven sources containing from 15 μg to 22 mg of ^{252}Cf were fabricated this year; two of these were doubly encapsulated in type 304L stainless steel in a standard TRU configuration (NSD).⁴ Four sources were prepared as standard singly encapsulated sources (NSS) and then welded into stainless steel outer capsules furnished by the customer (Bettis Atomic Power Laboratory). While these sources are not identical in configuration to the standard model

NSDs, they should be equally rugged. 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. Seven sources that contain from 35 to 1116 μg of ^{252}Cf are now in this category. During the report period, two sources were returned and three were reassigned.

Sources Reprocessed

Three neutron sources were retired from service and reprocessed to recover a calculated 3.9 mg of ^{248}Cm , which had grown into the sources during an average life of 4.5 years. No direct measurement of the ^{248}Cm recovery was obtained, since the source pellets were combined for processing with a number of other items containing ^{248}Cm .

Special Product Development

A series of special irradiations was initiated to investigate the feasibility of producing curium rich in ^{249}Cm . In this case, curium containing a few thousand ppm of ^{249}Cm would be excellent, and curium containing about 50 ppm of ^{249}Cm might conceivably be acceptable.

Eight target pellets, each containing approximately 100 μg of ^{248}Cm , were fabricated by means of a special technique that ensures even distribution of the target isotope throughout the pellet.⁵

Four of the pellets were put into two special HFIR targets (T-79 and T-80). In each target, one pellet was located at a position corresponding to the reactor midplane, and the other pellet was located about 8 in. lower, corresponding to a position in the reactor in which the flux is about one-half of that at the midplane. The targets were irradiated for one and two reactor cycles, respectively, and the pellets were

4. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1972, ORN-4794, p. 38.

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*, ORN-4965 (November 1974), p. 14.

3. W. D. Burch, J. E. Bigelow, and L. J. King, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June 30, 1971*, ORN-4718 (January 1972), p. 13.

dissolved and processed separately to purify the curium from the other actinides sufficiently to permit isotopic analyses of the curium. The results are given in Table 6.2. Although there is considerable scatter in the results, the ^{246}Cm contents indicate that the ^{246}Cm capture cross section is 12 to 24 b, nearly an order of magnitude higher than previously supposed. This information, in conjunction with data for longer exposures made earlier, indicates that the total absorption cross section of ^{246}Cm is from 90 to 180 b, which is also much higher than previously supposed. This means that a ^{246}Cm concentration of 1000 ppm

probably is not achievable, but that a usable concentration (>50 ppm) might be.

Two of the pellets were placed at the midplane positions of two HFIR targets (one pellet per target), and the remaining space in each target was filled with standard curium pellets, which have no connection with this experiment. We are merely utilizing the space in the targets for the normal TRU production program, because the targets will be irradiated for four and eight cycles respectively. The two remaining ^{246}Cm pellets are being stored for use if further investigation is warranted.

Table 6.2. Isotopic compositions of curium in four irradiated ^{246}Cm pellets

	Pellet No.			
	P1	P2	P3	P4
Cycles of irradiation	1	1	2	2
Neutron flux, neutrons $\text{cm}^{-2} \text{sec}^{-1}$	3×10^{15}	1.5×10^{15}	5×10^{15}	1.5×10^{15}
Nuclide, at. %				
^{244}Cm	1.416	1.263	2.14	0.847
^{245}Cm	0.020	0.018	0.028	0.013
^{246}Cm	3.44	3.29	4.14	3.19
^{247}Cm	0.082	0.064	0.119	0.078
^{248}Cm	95.04	95.37	93.57	95.87
^{250}Cm	0.0007	0.0003	0.0015	0.0005

7. Isotopic Separations

The Isotope Separations Program became a section of the Chemical Technology Division on July 1, 1975. This program, which was instituted in 1945 following the cessation of the large-scale electromagnetic separation of uranium isotopes, is the major supplier of enriched stable and radioactive isotopes for ERDA's multidisciplinary research programs. Enriched isotopes are distributed either on a loan basis to ERDA-approved users from a Research Materials Collection (RMC) or on a sales basis to more than 350 customers throughout the world. The current separations program is primarily concerned with maintaining a viable sales inventory for research and commercial interests in areas such as atomic frequency devices, lasers, Mossbauer instrumentation, mass spectrometry, spikes, and nuclear medicine. During the past year, 121 new loans were made from the RMC, amounting to more than 5.3 kg of enriched stable isotopes. During the same period, 2754 sales of material were made whose value was more than \$1.4 million.

The separations facility, located in the Y-12 area, has 39 operable separators of three basic types. The primary production unit is the conventional 61-cm-radius 180° beta calutron, which has been modified with more versatile ion sources and receivers since its original use with uranium. The second type of separator is a 255° double-focusing spectrometer with an inhomogeneous magnetic field of index $n = 0.5$. The dispersion of this unit is approximately one and one-half times that of the conventional 180° separators. However, this unit has slightly less ion throughput. Six of these units and three groups of eight beta-type separators are arranged in four magnetically isolated sections. Isotopes of four or more elements can therefore be separated concurrently. Eight additional beta-type separators, located within a radioactively contained facility in an area adjacent to a "hot," controlled laboratory, are available for radioisotopic separations, including the heavy elements. The third type of separator is a 180° sector device which differs from the other two in that

the source and object are external to the magnetic field. This type is a 180° focusing, inhomogeneous, $n = 0.8$ device with a 61-cm orbit radius. The dispersion of this separator is approximately seven times the dispersion of the conventional 180° separators. Its primary use is in obtaining extremely high enrichment in a single pass (especially low-natural-abundance isotopes) and in the fabrication of surface-deposited enriched targets and ion implantation studies.

7.1 STABLE-ISOTOPE SEPARATIONS

Isotopic separations of chlorine, mercury, thallium, tin, and ytterbium were carried out in either the 180° or 255° electromagnetic isotope separators in order to provide quantities of ^{37}Cl , ^{196}Hg , ^{202}Hg , ^{203}Tl , ^{112}Sn , and ^{168}Yb . Although the primary mode of operation involved 24 separators on a 5-day, 24-hr basis, other modes of operation were used, including a short interval in which only six separators were operated on a 5-day, 8-hr basis. Most of the nuclides mentioned are source materials used for the production of high-specific-activity radiopharmaceuticals in nuclear medicine. A number of other isotopes, separated concurrently, are potentially available for inclusion in the sales or RMC inventories.

During the year, 50 new lots of isotopes of 13 different elements were added to the inventory to fill sales or loan requirements. In addition, 61 lots of isotopes that had been returned after loan from the RMC were reprocessed and returned to inventory.

Some new techniques, such as in situ fluorination of the platinum-group metals with chlorine trifluoride and the use of germanium monoxide charge material, led to the highest isotopic purity of palladium, ruthenium, and germanium isotopes attained in the program to date. Isotopic purities and ion outputs for palladium and ruthenium are presented in Tables 7.1 and 7.2. These tables provide a comparison of the ClF_3 method with earlier methods of separation.

Table 7.1. Comparison of palladium ion output and assays using standard and in situ fluorination

	Standard fluorination	In situ fluorination with ClF_3
Average total ion output, mA	2.6	22.6
Mass assays, at. %		
^{102}Pd	75.45	77.89
^{104}Pd	89.75	95.25
^{105}Pd	94.51	97.38
^{106}Pd	96.66	98.48
^{108}Pd	98.11	98.88
^{110}Pd	96.98	97.73
Charge material	Pd^0	$\text{Pd} + \text{ClF}_3$
Charge consumption, g/hr	0.15	1.9

^aHigh-temperature ion source (not electron bombardment).

Table 7.2. Comparison of ruthenium ion output and assays using standard and in situ fluorination

	Standard fluorination ^a	In situ fluorination with ClF_3
Average total ion output, mA	7.3	22.45
Mass assays, at. %		
^{96}Ru	98.07	97.92
^{98}Ru	89.00	89.34
^{99}Ru	98.8	98.11
^{100}Ru	97.24	97.55
^{101}Ru	97.73	97.82
^{102}Ru	99.53	99.35
^{104}Ru	99.7	99.35
Charge material	RuF_5	$\text{Ru} + \text{ClF}_3$
Charge consumption, g/hr	0.9	1.4

^a255° separators.

7.2 RADIOACTIVE SEPARATIONS

The radionuclides ^{41}Ca and ^{205}Pb have relatively long half-lives (8×10^4 and 3×10^7 years respectively); both decay by electron capture, and both have interesting nuclear properties because of their proximity to doubly magic nuclei. Significant quantities of these isotopes have been produced recently by irradiating isotopically enriched target materials for approximately three years in the High Flux Isotope Reactor (HFIR) at ORNL. Following the chemical recovery from their respective target containers and appropriate radioactive decontamination steps, both nuclides have been further enhanced by calutron separation. The assays of the material before and following the irradiation, and after

the separation, are shown in Table 7.3. Prior to making the separations, research and developmental efforts were made to test new charge systems and ion sources. The results of the developmental effort were higher process efficiencies and greater enhancement than were achieved in previous normal separations.

Calcium-41 was produced by the (n,γ) reaction in the HFIR, using 6.2 g of >99.998% enriched ^{40}CaO . Particular attention was given to the depletion of ^{44}Ca in the sample to less than one part in 10^5 to reduce the production of unwanted ^{45}Ca . Following the irradiation the sample contained 1.53% ^{41}Ca . The postirradiation material was blended with powdered lanthanum metal and pelletized so that calcium metal would be made in situ in the ion source. The charge material was cycled through the separator twice with an appropriate charge recovery after each cycle. A total of 26 mg of ^{41}Ca was obtained; 19 mg had an enrichment greater than 80%, and the remaining 7 mg had an isotopic abundance of 63%.

Lead-205, which was to be used in nuclear measurements and for mass spectrometry spike analyses, was obtained by irradiating 10.7 g of PbO enriched to 70.94% in ^{204}Pb in the HFIR. The lead sample contained 2.73% ^{205}Pb after chemical recovery and radioactive decontamination. In order to make the most efficient use of the limited charge, the lead sample was cycled through the separator three times with complete charge recoveries after each cycle. Separate enriched product samples of ^{205}Pb were reclaimed after each cycle as follows: 41.9 mg at 78.88%, 16.0 mg at 76.75%, and 23.3 mg at 78.74%. To date, 60.9 mg of the original 81.2 mg have been distributed to various research institutions.

Table 7.3. Mass analyses of ^{41}Ca and ^{205}Pb samples

Isotope	Before irradiation (at. %)	After irradiation (at. %)	After separation (at. %)
^{40}Ca	>99.998	98.28	18.22
^{41}Ca	0	1.53	81.69
^{42}Ca	<0.0005	0.157	0.04
^{43}Ca	<0.0003	0.004	<0.01
^{44}Ca	<0.0012	0.26	0.05
^{46}Ca	<0.0003		<0.01
^{48}Ca	<0.0003		<0.01
^{204}Pb	70.94	68.19	13.70
^{205}Pb	0	2.73	78.88
^{206}Pb	12.68	13.09	4.68
^{207}Pb	6.42	5.97	1.22
^{208}Pb	9.96	10.02	1.53

7.3 ION DEPOSITION

The 180° Oak Ridge Sector Isotope Separator, a high-resolution milliamperage-output machine interfaced with an on-line computer for control and surveillance, is used to produce isotopically enriched nuclear targets of both the surface deposition and ion implantation types. Since enhancement factors of up to 4×10^3 can be achieved, the separator is particularly attractive and cost-effective for making highly enriched targets from isotopes of low natural abundance. Targets are prepared by placing the backings (typically carbon or aluminum foils) at the collector position in the separator and depositing the specified ion species directly on them. The energy of an ion at impact (and hence the deposition depth) is controlled by applying a suitable potential at the collector. Ion energies ranging from a few electron volts to several hundred kilo-electron volts can be achieved. High-energy implants (>80 keV) are made by selecting a multiply charged ion beam of the desired isotope. Energies of 350 keV have been obtained for ^{22}Ne by collecting the pentavalent ion with a total accelerating voltage (source plus collector potential) of 70 kV. Surface deposition targets are prepared at low-impact energies, usually below 200 eV. Table 7.4 shows the targets prepared in the separator this year. These target deposits typically have a line shape that measures 1.5 mm by 1 cm on the backing foil and thicknesses of 20 to 100 $\mu\text{g}/\text{cm}^2$. However, the deposited line can be as long as 8 cm, and the width can be altered, within limits, by applying a sweep voltage in the collector region.

Surface deposits that are 25 to 100 $\mu\text{g}/\text{cm}^2$ thick and have an isotopic purity of 95% or greater are highly attractive in the field of heavy-ion reaction studies. Those targets currently in demand are primarily the rare-earth and the platinum metal groups.

Table 7.4. Ion-deposited targets prepared during report period

Nuclide	Natural abundance (at. %)	Thickness ($\mu\text{g}/\text{cm}^2$)	Enrichment ^a (at. %)	Target backing ^b ($\mu\text{g}/\text{cm}^2$)
^{150}Sm	7.44	25	>99	90
^{115}Sn	0.35	75	>99	90
^{186}Os	1.49	50	>99	75
^{192}Pt	0.78	50	>99	75
^{194}Pt	32.9	25	>99	75

^aBased on contamination factors obtained in earlier separations.

^bCarbon.

7.4 PROCESS IMPROVEMENT

255° Ion Source

The 255° double-focusing separator, which were constructed in six calutron vacuum systems and corresponding magnetic coils, have served a vital role for several years. With decreases in the total number of separators in continuous operation, the productivity of the 255° separator becomes more significant. These separators are important because of their increased mass dispersion, which is beneficial in the separation of isotopes with masses of 100 or greater. For this mass range, in comparison with the 61-cm-radius calutrons, the 255° separators provide samples having enhancement factors that are increased by $1\frac{1}{2}$ to 2, but at a rate approaching 60 to 70% of calutron productivity. The trade-off of ion output for isotopic purity is programmatically sound, and we are attempting to improve the ion output level of the 255° separators as one method of controlling rising unit costs for separated isotopes.

To better understand the problem, one must briefly trace the developmental phases through which these separators have passed. Initially, the system was equipped with a straight ion exit slit with an appropriately curved receiving slit. Subsequently, this configuration was reversed to simplify receiver component construction. Straight receiving pockets and a 30-cm-radius ion exit slit were adapted and are being used. No appreciable change in ion output was noted when the modification was incorporated. In actual operation the ion output for each configuration appears to be limited by sudden and complete breakdown of voltages in the ion source accelerating region. This condition is contrary to that experienced in calutrons where the drain current usually increases slowly with increasing ion output until the voltage breakdown point occurs.

We are investigating whether this voltage breakdown is triggered by conditions arising from the mismatch of the curvature of the magnetic field lines (101-cm-radius) at the arc position and the curvature of the ion exit slit. The mismatch is shown in the insert in Fig. 7.1.

Experiments with a 101-cm-radius ion-exit-slit geometry and with a 30-cm-radius geometry of reduced length show that the ion output can be improved to calutron levels if the ion-exit-slit length and area are chosen more carefully than are required in calutron work. In general, ion output maximizes at a slit length of about 7.6 cm for the 30-cm-radius geometry and a constant ion-exit-slit area. For the 101-cm-radius geometry with the same restrictions, output is essentially

Fig. 7.1. Result of ion-exit-slit changes in the 255° separator.

independent of length. In either case, both size and area are critical to the element being processed. This feature is depicted by data for Sn^+ and Cl^+ , as shown in Fig. 7.1. Neither system has been investigated sufficiently to establish the maximum ion current; however, the trend is sufficient to show the necessity for optimization of geometry for each element or charge. Beam focus for either tin or chlorine is highly sensitive to pressure, and calcium pumping is used routinely to reduce system pressure.

In the course of the investigation, an ion source was modified and utilized to collect ^{122}Sn in a standard receiver. The ion exit slit was centered in the arc chamber and reduced to 0.32 by 7.6 cm. The electron collimating slot was moved forward, thus allowing the arc to contact the inner surface of the ion exit slit. In addition, the depth of the arc chamber was reduced to 0.7 cm, with the filament positioned so that electrons collimated by the 101-cm-radius magnetic field would

coincide with the ion-exit-slit center, and the gap between the electrode and the ion exit slit was reduced by about 0.3 to 1.1 cm. This system provided a total Sn^+ beam equal to that achieved in calutron work, or approximately twice that achieved in prior 255° work. At the same time, the sample purity for ^{122}Sn was increased from 95% to 98.3%. The results of this work are compared with previous separations in Fig. 7.2. These purities for the 255° separator correspond to isotopic enhancement factors of 240 and 1160 respectively. Similar 255° sources are in use in a germanium enrichment program where the separators are providing ^{73}Ge at greater than 90% purity and at outputs exceeding calutron levels. The feed compound is germanium tetrachloride, a liquid whose high vapor pressure creates contamination problems in the separator. To minimize the collection of these neutral contaminants, calcium vapor pumping is applied to the beam region. The effectiveness of reducing the tank pressure

Fig. 7.2. Comparison of ion output and isotopic purity for tin.

in this manner is shown in Fig. 7.3. The collected Ge^+ current decreases logarithmically with increasing pressure, whereas the valley current between peaks (here the $^{72,73}\text{Ge}^+$ valley) increases much more rapidly than the peak falls. The ratio of peak current to valley current is an indirect index of enrichment capability; thus, operation at the lowest possible pressure is indicated for objectives of both ion output and product purity. Under normal operating conditions, the beam quality index (peak-to-valley ratio) for germanium beams in 255° equipment indicates that it is possible to attain more than 95% ^{73}Ge ; in practice, even with a calcium-pumped system, normal contaminants limit the purity to about 93%.

180° Ion Source

In those separations where only a limited supply of feed exists, the goal is to attain a maximum process efficiency consistent with an acceptable isotopic enrichment. During the past year we have approached this goal in a new way by miniaturizing both the calutron arc chamber and the charge container. A stainless steel insert is fitted into an existing arc chamber cavity, and a small stainless steel charge container is slipped into the existing heater cavity. This modification, which is simple and inexpensive, does not destroy or preclude reuse of calutron equipment on which it is utilized. Pertinent features of the modification are depicted in

Fig. 7.4. The structural materials in contact with the charge vapor have been changed to stainless steel or nickel to minimize losses by absorption, and the interior surface area has been markedly reduced. The

Fig. 7.3. Relationship of Ge^{+} current to $^{72}\text{Ge}^{+}$ peak and to $^{72-73}\text{Ge}^{+}$ valley positions with changing tank pressure.

ion exit slit dimensions were reduced to maintain beam focus, the electron collimating slot was moved into contact with the ion exit slit, and a collimating slot-vapor baffle combination was inserted to create a drift region which may be maintained at an elevated pressure. The pressure in this region minimizes the charge vapor normally lost through the electron collimating slot.

This ion source has been used in two separations involving small charges, the most typical being described here. A significant quantity of high-purity ($>99.8\%$) ^{124}Te containing less than 0.15% ^{126}Te was required by Brookhaven National Laboratory for the experimental cyclotron production of high-purity ^{123}I . Sample specifications dictated the use of a pre-enriched charge feed with corresponding emphasis on process efficiency and the use of techniques to reduce neutral contamination. The charge material for the separation consisted of 12.2 g of elemental tellurium containing 78.9% ^{124}Te that had been obtained in a prior calutron enrichment program. The material was vaporized from the stainless steel charge container into the special double-section arc chamber to achieve a process efficiency of 11.3%. This efficiency is a factor of 4 greater than that obtained in conventional sources.

An additional innovation for this separation was a specially designed three-part water-cooled aluminum receiver assembly that caught the main part of the ^{124}Te beam well behind the faceplate. A diagram of the receiver is shown in Fig. 7.5. As can be seen, all beams except ^{124}Te are caught in the normal way. This beam, having an angular convergence of $\pm 10^\circ$, enters the appropriate defining slot. "Skimmers" in pocket segment B clip the beam to $\pm 6^\circ$, and the central portion

Fig. 7.4. Arc chamber modifications.

ORNL - DWG 75-6000

Fig. 7.5. Rounded pocket receiver.

continues toward eventual collection in segment A. The portion of the beam undergoing charge exchange near the defining slot and the low-energy ions resulting from faceplate scattering entering the slit cannot reach

segment A and are retained in segments B and C. The effectiveness of such collector segmentation can be determined by comparing the assays of material recovered from each segment (see Table 7.5). Approximately one-half of the collected isotope exceeded the desired specifications, whereas the remainder was contaminated with the unwanted nuclide.

Table 7.5. Assays of high-purity ^{124}Te

Isotope	Assay (%)		
	Pocket A	Pocket B	Pocket C
120	<0.002	<0.04	<0.02
122	<0.003	0.00	0.05
123	0.006	0.04	0.04
124	99.87	97.12	99.35
125	0.095	2.60	0.43
126	0.020	0.11	0.04
128	<0.010	0.04	0.03
130	<0.008	0.05	0.04
Weight, mg	300	430	43

8. Preparation of $^{235}\text{UO}_2$

ORNL's contract with Bettis Atomic Power Laboratory (BAPL) to prepare $^{235}\text{UO}_2$ involves: (1) purifying several hundred kilograms of ^{235}U (presently stored in the facility) at the rate of approximately 20 kg of ^{235}U per week, (2) converting the purified uranyl nitrate to ceramic-grade UO_2 powder at the rate of about 22 kg of ^{235}U per week, (3) packaging and shipping the UO_2 to BAPL for blending with thorium and pressing into pellets, and (4) recovering ^{235}U from the $^{235}\text{UO}_2$ scrap generated at ORNL and the $^{235}\text{UO}_2$ - ThO_2 scrap generated at BAPL. The production of UO_2 powder was increased to 120 kg/month by beginning operation on a six-day week as of February 1, 1976.

8.1 RECOVERY OF ^{235}U FROM WASTE UO_2 AND SCRAP UO_2 - ThO_2 PELLETS

During this report period, the oxide dissolver was operated to recover 221.0 kg of ^{235}U in 67 dissolutions. The source of the material was (1) UO_2 stored since receipt from the Savannah River Plant in 1970 (148.0 kg), (2) ammonium diuranate rejected as a result of overheating in the microwave oven, (3) ammonium diuranate and UO_2 accumulated from cleanup of the glove boxes after each week's operation, (4) one and one-half lots of powder originally prepared within specifications but allowed to age excessively at BAPL, and (5) one-half lot of powder rejected because of dubious appearance.

All of the pure UO_2 was dissolved in slightly more than the stoichiometric amount of nitric acid at 80°C so that the resulting solution, on analysis for impurities, could be sent directly to storage or processed through the ion exchange system for purification. The product from the dissolution of ammonium diuranate and UO_2 that had been spilled or used in analytical tests was purified in the solvent extraction system before being returned to storage. Ten of the dissolutions were essentially "cleanout" operations made in an effort to account for all uranium charged previously.

We received 46 shipments (13.3 metric tons) of binary (UO_2 - ThO_2) scrap generated at BAPL. This

scrap, which contained 293 kg of uranium and 11.2 metric tons of thorium, included 45 kg of uranium and 1.3 metric tons of thorium in the form of baked grinder sludge. Two hundred seventy-three dissolutions were made in the scrap dissolver to recover the thorium and ^{235}U from this material. The amount of scrap charged to the dissolver in each case varied from 50 to 250 kg of mixed oxide. The dissolvent, which had the composition 12 M HNO_3 , 0.04 M F^- , 0.1 M $\text{Al}(\text{NO}_3)_3$, was held at 105°C until the thorium concentration reached 1.0 to 1.2 M. The resulting solutions were accumulated for use as feed to the solvent extraction system.

8.2 ^{235}U PURIFICATION SYSTEMS

Twenty-one runs were conducted in the solvent extraction system to purify 544 kg of uranium. These runs were made to recover and purify the uranium present in various types of scrap, recycle material from the ion exchange system, and recycle material from previous solvent extraction runs. Uranium losses to the raffinate ranged from 0.3 to 1%, averaging 0.66%. The thorium content of the uranium product ranged from 500 to 1500 ppm.

Approximately 765 kg of uranium was purified in 37 runs made in the ion exchange equipment. Nonrecoverable losses totaled 0.02%. In addition, 345 kg of uranium that had been stored for five years was processed through the ion exchange column in six runs to remove thorium. The product solution was then returned to storage to allow the ^{228}Th daughters to decay; at various intervals, selected volumes of this solution were withdrawn and purified to provide feed for the conversion facility.

8.3 CONVERSION OF ^{235}U FROM NITRATE SOLUTION TO CERAMIC-GRADE DIOXIDE POWDER

During the year, a total of 772 kg of ceramic-grade UO_2 powder (36 lots) was prepared and 733 kg (34.5

lots) was transferred to BAPL in 47 shipments. Non-recoverable losses totaled 0.16%. One and one-half lots (26.9 kg of UO_2) were recycled, at the request of BAPL, after storage for an extended period. One lot of material (25.7 kg of uranium) was recycled after the conversion was 50% complete because suspended carbon particles were detected in the nitrate feed solution. Investigation revealed that the source of this carbon was worn Graphstar bearings in the pump used to recirculate the ion exchange product before it was

fed to the conversion facility. This was the first time, in the preparation of 80 lots of material, that we failed to meet the operating schedule requested by BAPL.

The material is processed through the conversion facility in 1.0- to 1.1-kg (uranium) batches. During this report period, we rejected three batches as a result of ignition in the microwave oven, one batch because of incomplete drying in the oven, and one-fourth batch because of failure of the ammonium diuranate granulator.

9. Separations Chemistry Research and Development

The work reported here, pertaining to both nuclear and nonnuclear sources of energy, is divided between the parallel activities of descriptive chemistry and process development. Descriptive chemistry includes studies of the reactions of substances to be separated and of separations agents, sufficient to identify and measure the controlling variables in particular separations applications, and investigation of potential new separations agents and methods, sufficient to evaluate their usefulness. In process development, selected methods are developed into complete processes and tested at the scale needed to evaluate their effectiveness and/or economics and to predict their large-scale performance. While there is considerable interdependence and overlap between these two activities, descriptive chemistry is involved principally in Sects. 9.1, 9.4, 9.5, and 9.7, and process development in Sect. 9.2, 9.3, and 9.6.

9.1 NEW SEPARATIONS AGENTS

The search for new separations agents has continued to concentrate on the problem of selectively removing plutonium and the transplutonium actinides from acidic fuel reprocessing wastes (2 to 6 *M* HNO₃). At present, the most promising compounds for this purpose appear to be the carbamylmethylenephosphonates and the diphosphonates (see Table 9.1). We have succeeded in purifying by molecular distillation the two carbamylmethylenephosphonates previously obtained,¹ and five other new compounds were synthesized and have been purified in the same way. Purification by molecular distillation appears to remove the impurity that interferes with stripping the plutonium and transplutonium compounds with water. The offending impurity (or impurities) has not yet been identified, but work toward this objective has begun.

1. *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1975, ORNL-5050*, p. 28.

One important reason for varying the size and placement of the alkyl groups on the compounds listed in Table 9.1 is to try to determine the arrangement of substituents giving the most desirable combination of extraction power, strippability, diluent compatibility, and aqueous insolubility. We appear to be close to obtaining an acceptable combination of these characteristics for the carbamylmethylenephosphonates in some diluents (Table 9.1). However, the diphosphonates tested to date have been less promising. Additional variations of both compounds are being synthesized for testing.

A number of macrocyclic polyethers, called crown ethers, have been examined as possible selective extractants for metal ions. Tests have been made with alkali and alkaline-earth metals (with which the crown ethers are reported to form complexes) and with representatives of the lanthanide and transplutonium elements. A wide variety of scouting tests were made in an effort to find possible areas of usefulness for the crown ethers as extractants of complexers. These are summarized in Table 9.2.

In addition to the tests tabulated, mixtures of crown ethers with various concentrations of di(2-ethylhexyl) phosphoric acid (HDEHP) were tried as extractants for calcium from chloride and nitrate systems. Distribution ratios were not greater than those expected for HDEHP alone and varied little with HDEHP concentration, indicating no contribution to the extraction by the crown compounds.

Other experiments were done in which crown ether solutions were used to solubilize dry² alkali metal and alkaline-earth salts. When the individual chloride salts were contacted with 0.1 *M* dicyclohexyl-18-crown-6 in benzene, the order of concentration in the organic phase was Ca > Li > Sr > Na > K > Ba > Mg > Rb > Cs, and with 15-crown-5 the order found was Na > Li > K > Rb > Ba > Ca > Cs > Sr > Mg. When

2. Although anhydrous salts were used, no special effort was made to test for, or remove, traces of water. Additional tests are planned using carefully dried components.

Table 9.1. Experiments for removing alpha emission from nuclear wastes

Compound	Compatibility (at 30%) with diluents		Aqueous solubility	Am distribution coefficient from 6 <i>M</i> HNO ₃ ^a
	<i>n</i> -Dodecane	DEB		
Carbamoylmethylene phosphonates				
$\begin{array}{c} \text{R-O} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{P} \\ \diagdown \quad \diagup \\ \text{R-O} \end{array} \text{---CH}_2\text{---} \begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \quad \text{R}' \end{array}$				
Diisobutyl <i>N,N</i> -diethyl ^f	Third phase	OK	High	10
Dibenzyl <i>N,N</i> -diethyl ^f	Third phase	OK	Moderate	10
Di(2EH) <i>N,N</i> -di(isobutyl) ^f	OK		Very low	0.7
Di(2EH) <i>N,N</i> -diethyl ^f	Third phase	OK	Very low	1.5
				9.8 ^g
				19.4 ^g
				8.2 ^g
Dibenzyl <i>N,N</i> -di(isobutyl) ^f	OK		(Very low)	1.6
				3.7 ^g
				5.8 ^g
Carbamoyl phosphonate				
$\begin{array}{c} \text{O} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{R-O} \quad \text{P} \\ \diagdown \quad \diagup \\ \text{R-O} \quad \text{C} \end{array} \text{---} \begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \quad \text{R}' \end{array}$				
Di(2EH) <i>N,N</i> -diethyl ^f	OK			0.7
Diphosphonates				
$\begin{array}{c} \text{O} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{R-O} \quad \text{P} \\ \diagdown \quad \diagup \\ \text{R-O} \end{array} \text{---} (\text{CH}_2)_n \text{---} \begin{array}{c} \text{O} \quad \text{OR}' \\ \diagup \quad \diagdown \\ \text{P} \\ \diagdown \quad \diagup \\ \text{OR} \end{array}$				
Tetra(2EH) ethylene	OK			0.12
Tetra- <i>n</i> -octyl ethylene	OK			0.46
Tetra- <i>n</i> -butyl ethylene	Third phase	OK		0.18
Tetra- <i>n</i> -butyl methylene		OK	High	4.0

Abbreviations: 2 EH = 2-ethylhexyl; isobu = isobutyl; DEB = diethylhexanoate.

^a 30% solution in DEB, except as noted.

^b Available compounds purified by molecular distillation.

50% solution in DEB.

40% in decalin.

³⁰ 7% solution in Kermac 470B, a proprietary solvent of mixed aromatic and aliphatic hydrocarbons.

¹30% solution in pentamethylheptane.

the dry chlorides of each group were mixed and contacted with various crown ether solutions, the order of solubilization was found to be: C-3 (see Table 9.2), $K \approx Na > Li > Rb > Cs$ and $Ca > Mg > Sr > Ba$; C-4, $Rb > Li > Cs > K > Na$ and $Ca > Mg > Sr > Ba$; C-5, $Na > K \approx Li > Rb > Cs$ and $Ca > Mg > Sr > Ba$; C-6, $Li > K \approx Rb > Cs > Na$ and $Ca > Sr > Mg > Ba$. When both groups were mixed and contacted with dicyclohexyl-18-crown-6, the order found was

Li > Sr > Ca > Rb > K > Na > Cs > Ba > Mg. The extraction values and orders observed are not consistent with the earlier reported orders of complexing²⁴ in indicating a selectivity for the alkali metals dependent on the size of the hole in the crown

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

4. H. K. Frensdorff, *J. Am. Chem. Soc.* **93**, 6006 (1971).

Table 9.2. Extraction coefficients D_c for metal ions by crown ether solutions

Aqueous solution ^a	Organic solution							
	C-2	C-3	C-3 plus TOPO	C-4 (18-crown-6)	C-5 (Dibenz-18-crown-6)	C-6 (Dicyclohexyl-18-crown-6)	C-6 plus TOPO	C-7 (15-crown-5)

	0.01 M in CHCl ₃	0.01 M in CHCl ₃	each 0.01 M in CHCl ₃	0.1 M in benzene	0.01 M in benzene	0.1 M in benzene	each 0.1 M in benzene	0.1 M in benzene
0.1 M HNO ₃ ^b	Sr } < 10 ⁻⁴ Ce } Am } Cs 0.007		Am 0.006			Am < 10 ⁻⁴	Ce 0.14 Eu 0.31 Am 0.32	
2 M HNO ₃ ^b	Sr } < 10 ⁻⁴ Ce } Am } Cs 0.035		Eu } < 10 ⁻⁴ Am }			Am < 10 ⁻⁴	Ce 0.0006 Eu 0.011 Am 0.011	
Neutral nitrate	Ca < 10 ⁻⁴ K 0.22	K } < 10 ⁻⁴ Ca }				K < 10 ⁻⁴		
Hydroxide	Na 0.95 K 2.58 Ca 1.86 Sr 2.65 Ba 2.05	Na } < 10 ⁻⁴ K } Ba } Ca 0.1 Sr 0.001	Sr < 10 ⁻⁴	Na } < 10 ⁻⁴ K } Sr } Ba }	Na } < 10 ⁻⁴ K } Sr } Ba }	K } < 10 ⁻⁴ Ba }	Na } < 10 ⁻⁴ K } Sr 0.008	
Neutral chloride	Ca < 10 ⁻⁴ K 0.21	K } < 10 ⁻⁴ Ca }				K < 10 ⁻⁴	K < 10 ⁻⁴	
4 M LiClO ₄ ^b						Zn } < 10 ⁻⁴ Eu } Ca 0.12 Am 0.0007		
Thiocyanate, 2 M						Li 0.20 Na 0.023 K 0.035 Ca 0.009		

Abbreviations: = ethylene; = methylene; = CH₂; = cyclohexylene; = benzo; = naphthalene.

TOPO = tri-*n*-octylphosphine oxide

^a0.01 to 0.1 M except as otherwise noted.

^bTest cations at tracer levels.

C-6 loadings from 38 to 94%, and C-7 loadings from 11 to 28% from thiocyanate solutions.

ether. All the compounds tested in this way except C-7 are six-oxygen rings, supposedly of the same hole size, but several orders of preference for the alkali metals and alkaline-earth metals are observed. These data suggest that other factors, as yet unidentified, are affecting the extraction and complexing of metal ions by the crown ethers.

A wide range of chemicals are produced in coal processing, including thiocyanates, hydrogen sulfide, sulfurous acid, and a number of hydroxy aromatics (phenolics). Recovery of these substances from aqueous process streams is desirable because of their value, to allow recycle of the water, and to help reduce their releases to the environment. (Final

Table 9.3. Extractants for coal-derived aqueous pollutants (initial concentration, 1000 ppm; ^{14}C -traced)

Extractant ^a	Extraction coefficient at pH 6	
	Phenol	KSCN
Amines:		
1-Nonyldecyl	42	
Amberlite LA-1	6.7	
Adogen 364	7.2	1.45
Adogen 464	b	
Organophosphates:		
Tributyl phosphate	60	
Trihexyl phosphate	290	3.3
50% in dodecanol	160	
HDEHP 5.8 M in DEB ^c	5.2	

^aUndiluted except as noted.

^bEmulsion formed.

^cDEB = diethylbenzene.

cleanup by sorption or biodegradation for release of the water to the environment would probably be necessary.) Brief scouting tests to probe the applicability of solvent extraction for removing these compounds have so far utilized reagents already available in the ORNL separations program. The examples in Table 9.3 include anion exchangers (various classes of alkylamines), a cation exchanger (HDEHP), and neutral phosphate esters. These already include extraction coefficients high enough to suggest practical application. Trihexyl phosphate, for example, is an excellent extractant for phenol and has very low aqueous-phase solubility.

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

Recent increases in the price of processed uranium concentrates and increased concern for environmental quality have made the use of nitric acid much more attractive than it has been in the past for the recovery of radium and thorium from uranium ores and leached tailings. Consequently, a renewed effort is being initiated to study the recovery of uranium, ^{230}Th , ^{226}Ra , ^{210}Pb , and ^{210}Po from uranium ores and sulfate-leached tailings by a nitric acid leach process. A conceptual flowsheet includes multistage leaching of the solids with about 3 M HNO_3 , efficient water washing of the leached solids, and recovery of HNO_3 and water by distillation. Recovery of uranium could

be accomplished by tributyl phosphate (TBP) extraction from the HNO_3 leach solution prior to the distillation step.

Preliminary results from a three-stage leach of a composite tailings sample (obtained from an abandoned uranium mill at Salt Lake City, Utah) with 3 M HNO_3 at 85°C indicated that, although greater than 98% of the sulfate was removed after the first leach and wash, approximately 4% of the radium remained in the tailings after the third leach (~35 pCi/g). Since 11% of the uranium content also remained in the leached tailings, it is possible that a small but significant fraction of the radionuclides is contained within a refractory portion of the tailings.

9.3 SEPARATION OF ALPHA EMITTERS FROM FUEL REPROCESSING WASTE

Work has continued on testing and developing the tentative flowsheet previously reported,⁵ which uses oxalate precipitation to separate the trivalent lanthanides and transplutonium actinides from Purex waste and which uses the Talspeak⁶ process to separate the actinides from the lanthanides. The principal modifications include improvements in the methods for oxalate decomposition and for nitric acid recovery, steps to remove zirconium from the Talspeak feed to avoid precipitation when it is adjusted to pH 3, and steps to remove other residual fission products that might interfere with separation of the actinides from the rare earths or contaminate the actinide product stream.

9.4 WASTE STREAM PROCESSING STUDIES

The purpose of this program is to provide certain fundamental information that is required for the satisfactory treatment of waste streams in nuclear fuel reprocessing plants. A number of problems have already become apparent in studies⁷ of processes for removing long-lived actinides from wastes, and

5. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1975, ORNL-5050, p. 30.

6. Boyd Weaver and F. A. Kappelmann, *Talspeak: A New Method of Separating Americium and Curium from the Lanthanides by Extraction from an Aqueous Solution of an Aminopolyacetic Acid Complex with a Monoacidic Organophosphate or Phosphonate*, ORNL-3559 (August 1964); "Preferential Extraction of Lanthanides over Trivalent Actinides by Monoacidic Organophosphates from Carboxylic Acids and from Mixtures of Carboxylic and Aminopolyacetic Acids," *J. Inorg. Nucl. Chem.* 30, 263-72 (1968).

7. W. D. Bond and R. E. Leure, *Feasibility Studies of the Partitioning of Commercial High-Level Wastes Generated in Spent Nuclear Fuel Reprocessing: Annual Progress Report for FY-1974*, ORNL-5012 (January 1975).

certain basic information is required to solve these problems. Additional problems will likely become apparent as process development studies continue.

Initially, the program involves only studies related to the removal of actinides from high-level waste streams from fuel reprocessing plants. During the past year, efforts were primarily concerned with investigations of plutonium behavior in nuclear fuel reprocessing solutions to determine the nature of inextractable species and mechanisms by which these species are formed. In additional work, we completed a study of the kinetics of the reduction of Np(V) to Np(IV) in nitric acid solution by ferrous nitrate.

Plutonium Behavior in Fuel Reprocessing and Waste Solutions

Due to anticipated difficulties in achieving high plutonium recoveries (99.99%) during reactor fuel reprocessing, studies were continued to investigate reactions that can result in plutonium losses and to determine the basic mechanisms involved. These studies included the investigation of plutonium losses associated with colloids and precipitates of zirconium and molybdenum and also associated with decreasing Pu(IV) distribution coefficients with successive extraction stages. This work involved glove-box studies with synthetic feeds and hot-cell tests with irradiated UO_2 .

Studies of solids formation in synthetic waste solutions indicate that precipitates due to zirconium hydrolysis and zirconium-molybdenum or plutonium-molybdenum compound formation can provide mechanisms for significant plutonium losses. The compound variables that affect the rate of solids formation and the quantity of solids produced have been identified, formation rates were determined for various conditions of interest, and solids have been characterized by electron microscopy and x-ray diffraction.

At elevated temperatures, zirconium oxynitrate in nitric acid solution can hydrolyze to form colloids and precipitates. The four principal variables that affect zirconium hydrolysis were found to be acid concentration, zirconium concentration, solution temperature, and total ionic strength. In general, the rate of zirconium hydrolysis increases with increasing temperature and zirconium concentration and decreases with increasing acid concentration and ionic strength. When zirconium hydrolyzes in solutions of low HNO_3 concentrations (1.5 M or less), colloidal solutions of zirconia are formed that carry about 5×10^{-1} mg of plutonium per zirconium. At

higher acid concentrations, zirconia precipitates as an amorphous solid that carries 1×10^{-4} mg of plutonium per mg of zirconium. Zirconium hydrolysis can occur even in concentrated HNO_3 ; however, hydrolysis does not occur above 6 M HNO_3 when the zirconium concentration is 0.2 M or less. At moderate conditions the rates are slow, requiring weeks or months for equilibrium conditions to occur, and rate curves are S-shaped rather than linear. For example, when a zirconium salt solution (10 g of zirconium per liter of 2 M HNO_3) is heated at 105°C, little or no hydrolysis occurs during the first five days. This is followed by a rather rapid rate of hydrolysis until about 75% of the zirconium is hydrolyzed, and then the rate decreases rapidly. About 2% of the zirconium remains ionic after 50 days of aging.

Experiments to date indicate that zirconium hydrolysis and attendant plutonium losses in reactor fuel reprocessing solutions can be prevented or minimized if the acid strength is maintained at 3 M or greater, the zirconium concentration is not allowed to exceed 5 g/liter, and the solution temperature is maintained at 60°C or less.

A second plutonium loss mechanism that results from solution instability involves formation and precipitation of a zirconium-molybdenum compound. This material promises to be far more troublesome in fuel reprocessing and waste solutions than precipitated zirconia, because it carried much higher concentrations of plutonium (0.02 mg of plutonium per mg of $\text{Zr} + \text{Mo}$), and precipitates can form at virtually all conditions proposed for fuel reprocessing plants. Under some conditions, small crystallites are formed that plate out and adhere to surfaces in contact with the solution.

This compound can be tentatively assigned the formula $\text{ZrMo}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. Chemical analysis shows that it contains two moles of molybdenum per mole of zirconium; although crystallographic data for this form have not been previously reported, x-ray diffraction and thermogravimetric studies indicate that it is a hydrated form of a high-temperature preparation that has been reported to be ZrMo_2O_7 .

Precipitates of this compound can form at all HNO_3 concentrations up to 9 M at very low metal concentrations (1 g of molybdenum to 5 g of zirconium per liter), and the amount of plutonium carried does not vary significantly with acid concentration in this range. Precipitation rates are slow, and the rates are functions of the same four variables that affect zirconium hydrolysis; however, unlike zirconium hydrolysis, the precipitation rate increases with increasing ionic strength.

It is significant that there have been no indications of molybdenum compound with any metal ion other than zirconium, with only one exception. At the conditions of interest, insoluble molybdates do not form with such elements as cesium, barium, strontium, or the trivalent rare earths. The single exception is tetravalent plutonium, which does not form insoluble molybdates in HNO_3 solutions of low concentration ($<2\text{ M}$). This compound also contains two moles of molybdenum per mole of plutonium. There are no previously reported crystallographic data for any plutonium-molybdenum compound; however, preliminary analysis suggests that this material is isostructural with or very similar to a uranium molybdate reported to be $\text{U}(\text{MoO}_4)_2 \cdot x\text{H}_2\text{O}$. A $\text{U(VI)}\text{-Mo}$ compound has also been reported, but we have not been able to form a comparable compound with Pu(VI) . The plutonium molybdate forms and precipitates readily in 1 M HNO_3 at elevated temperatures. Formation decreases with increasing acid concentration, and only trace amount precipitate from 3 M HNO_3 at the metal concentrations of interest. When zirconium is present in solution, the plutonium-molybdenum compound is not formed to a significant degree.

The report last year indicated that small plutonium losses occur when highly purified tetravalent plutonium in 3 M HNO_3 is extracted with 30% TBP-dodecane. In seven consecutive extraction stages, plutonium distribution coefficients decreased from 14 to 0.2. After four batch extraction contacts with equal volumes of aqueous and organic phases, about 0.02% remained in the aqueous phase, and nearly half of this material was inextractable in subsequent stages. We have recently demonstrated in hot-cell tests that this phenomenon also occurs for radioactive feeds prepared from highly irradiated UO_2 . Plutonium extraction data for a typical run are shown in Fig. 9.1. This behavior was duplicated in two subsequent experiments. Figure 9.1 shows the plutonium concentration, in $\text{counts min}^{-1} \text{ ml}^{-1}$, that remains in the aqueous raffinate for seven consecutive extraction stages. The straight line illustrates the extraction behavior that would be obtained with a constant plutonium distribution coefficient of 14. In the first two stages, the plutonium distribution coefficient was less than 1, as the result of uranium saturation in the organic phase. After most of the uranium was extracted, plutonium extraction was normal except for a very small amount of plutonium which appears to be inextractable. The reason for this behavior is not known, but results are very similar to those for extraction from pure nitric acid. This behavior

appears to be some function of the extraction process itself, since the inextractable plutonium from pure nitric acid behaves like normal Pu(IV) in both anion and cation exchange loading and eluting behavior.

Oxidation-Reduction Kinetics of Neptunium

Studies on the oxidation-reduction kinetics of neptunium were completed. A paper has been prepared for submission to the *Journal of Inorganic and Nuclear Chemistry*. The abstract follows:

"The Oxidation-Reduction Kinetics Involved in the $\text{Np(V)} + \text{Fe(II)} \rightarrow \text{Np(IV)} + \text{Fe(III)}$ System in Nitric Acid Solutions," by W. D. Bond, Y. Jao, and J. R. Peterson. *Abstract*: The rate law for the overall reaction may be expressed as $d[\text{Np(V)}]/dt = k_1[\text{Np(IV)}][\text{Fe(III)}][\text{H}^+]^2 - k_2[\text{Np(V)}][\text{Fe(II)}][\text{H}^+]^2$. The forward rate constant, k_1 , and the reverse rate constant, k_2 , with the nitrate ion influence being included, are $15.7\text{ M}^{-1}\text{min}^{-1}$ and $1.71\text{ M}^{-1}\text{min}^{-1}$, respectively, at 25°C in 1.0 M nitrate solutions with ionic strength equal to 1.5. The proposed reaction mechanism for the forward reaction involves two activated complexes—one of which contains at least two protons. The reverse reaction involves either an activated complex containing three hydroxyl groups or one of its hydroxyoxygenated equivalents. The apparent activation energy of the forward reaction is 10 kcal/mole and that of the reverse reaction is 35 kcal/mole. The ionic strength effects on the specific rate constants are consistent with a Debye-Hückel treatment of the chemical equilibria involved in the formation of activated complexes. The nitrate ion influence on the specific rate constants could be quantitatively taken into account by a parallel pathway mechanism after assuming that one of the activated complexes of both the forward and of the reverse reactions contained a nitrate ion.

9.5 ASH REMOVAL FROM SOLVENT-REFINED COAL

Hydrogenation of coal slurried in a coal-derived hydrogen-donor oil without the use of a catalyst is one of the most promising methods of converting coal into a clean fuel or refinery feed. The most serious problem in this process is removal of the micron-sized ash from the resulting viscous oil.^{9,10} The standard separation methods of filtration and centrifugation are not really effective or economical. Thus, other possible methods of de-ashing solvent-

8. University of Tennessee, Knoxville.

9. D. E. Griggs and J. A. Sterling, *Studies on the Separation of Coal Extract from Mineral Matter Residue in the Solvent Refining of Coal*, NSF-RA-N-74-262, University of Michigan, Department of Chemical Engineering, (December 1974).

10. 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).

Fig. 9.1. Plutonium extraction behavior from feed prepared by dissolution of irradiated UO₂. Feed adjusted to 3 M HNO₃ was contacted with equal volumes of TBP-dodecane.

refined coal should be examined. Processes for the use of molten zinc chloride as a hydrogenation catalyst have been developed;^{11,12} in these, the ash remains in the molten-salt phase. However, removal of the ash from the salt is difficult. Later work¹¹ has shown that a mixture of ZnCl₂ and KCl allows the ash-char residue to concentrate in a slag comprising only about 10% of the total melt, thus simplifying rework of a molten-salt catalyst. Tests suggested by these effects are in progress, and preliminary results show promise of providing an effective way of scavenging ash from the viscous tarlike oil.

9.6 PHYSICAL SEPARATIONS

Penetration of High-Efficiency Air Filters by Alpha Recoil Aggregates

The phenomenon of alpha creep has been known for years, at least since 1927;¹⁴ recently, workers at Lowell Technological Institute determined that this phenomenon may affect the retention of alpha particulate materials by high-efficiency particulate aerosol (HEPA) filters.¹⁵ Their tests with ²¹²Pb (and alpha-emitting daughters) indicated that recoil aggregate particles of 100 to 100,000 atoms were produced from a plated source of this material and that these particles penetrated HEPA filters much more effectively than would be expected from the rated filter efficiency.

We have confirmed the results of the Lowell Technological Institute workers and have extended the tests to include the alpha-emitting nuclides ²³⁵Es and ²³⁹Pu. The radionuclides were either plated on metal supports or placed on a 47-mm Gelman type A filter disk as oxide or oxychloride. The source was then positioned in an apparatus designed to flow air over the source and through four or five subsequent filters. In every case where the source was alpha-active material, significant migration of the nuclide through the series of filters was observed. No migration was observed when beta-gamma-active material was used instead of alpha-active material.

The observed migration of this alpha-active material is consistent with a description of small aggregates of atoms dislodged from the "massive" surface as alpha-active particulate material and then repeatedly dislodged from positions on the filter fibers by subsequent alpha recoils. A mathematical model for this process has been written, and the collected data allow evaluation of parameters in this model so that we are able to calculate expected penetration and release by alpha aggregate recoil under various conditions. The data and these calculations indicate that releases by this process can, in some cases, be much greater than those expected from normal filter inefficiency and may thus account for many instances of ineffective filtration previously attributed to mechanical failure of the filter system. Rates of release change with time, generally increasing for one to two half-lives and then decreasing because of radioactive decay. Calculations show that total release through four filters for one year for 1 Ci (0.06 g) of ²³⁹Pu on the first filter would be approximately 10 μ Ci. The release rate for this system at the end of one year would be producing an air concentration approaching the 10 CFR 20 limit of 10^{-12} μ Ci/cc at a flow rate of 1000 cfm.

If a constant weight of nuclide is considered to be deposited on the first of four filters, calculations of the release through the filter system in 300 days for 10 g of hypothetical nuclides of various half-lives show a curve increasing as half-life decreases, from about 1 μ Ci for a 25,000-year half-life to about 50,000 μ Ci for a 150-year half-life, and then decreasing sharply as half-life decreases further.

Our present understanding of the release of alpha activity through HEPA filters indicates that methods of preventing release through the alpha recoil process may be relatively easy. Frequent removal of the source material from the filter system should solve the problem. Such removal could be accomplished by changing the first filter (or a more economical roughing filter) at appropriate intervals or by precleaning the air by some method other than filtration that continuously removes the activity from the system. Additional study to better define this problem and devise solutions is under way.

Perfusion Impactor

In the course of investigation of the chemistry of ²³⁹No (Sect. 9.7), work was done to develop a method of continuously collecting the cyclotron-produced nuclide in a small volume of aqueous solution. The nuclide was produced at the rate of about 500

11. U.S. Department of the Interior, *Final Report Development of CSF Coal Liquefaction Process*, OCR-RDR-39, vol. V (April 1973).

12. C. F. Trilling, *Molten-Salt Process for the Gasification of Coal*, CONF-740473-P2, pp. 215-35.

13. L. Berg and J. S. Malsam, "Coal Hydrogenation Using a Potassium Chloride Zinc Chloride Molten-Salt Mixture as a Catalyst," U.S. Patent 3,736,250 (May 29, 1973).

14. C. Chamie, *Compt. Rend.* 184, 1243 (1927).

15. M. T. Ryan, F. W. Skrabie, and G. Chabot, *Health Phys.* 29, 796-98 (1975).

atoms min and swept out of the bombardment cell with a helium flow of 5 to 6 liters min. A device was developed in which a radioactive aerosol in such a gas stream could be collected with 99 to 100% efficiency in 0.025 ml of water per minute, thus giving a concentration factor of about 2×10^4 for the nuclide. The device consists of an impactor where the impaction surface is a porous material through which a suitable solvent is continuously perfused. The impaction surface is thus a liquid film so that the device is continuously self-cleaning, and the collected material can be removed from the device without interrupting its operation.

9.7 DISTRIBUTION EQUILIBRIA, KINETICS, AND MECHANISMS

The contributions of this program to the studies of the chemistry of nobelium, using cyclotron-produced ^{254}No ($t_{1/2} = 223$ sec), have been completed.¹⁶⁻¹⁸ The adaption of separations chemistry techniques to the rapid handling and to the small volumes needed for this work allowed determination that the chemical nature of nobelium is similar to strontium and barium, and evaluation of the following: valence (II); ionic radius (1.1 Å); single ion heat of hydration (~355 kcal g-atom); complex formation constants with citrate (152), oxalate (48), and acetate (~0); and reduction potential [$\text{No}^{2+} + 2e^- = \text{No(Hg)}$, 1.6 V].

Liquid Scintillation Alpha Spectrometry

There continues to be a growing interest on this alpha-assay method and the associated separations techniques. At present, seven groups are known to be using these procedures on a routine basis; about 30 others have asked for detailed information (besides many reprint requests), but we have no follow-up information as to whether they are now using it. Most

recently, a group from the University of Tennessee Comparative Animal Research Laboratory has developed, with our assistance, a method for assay of plutonium in the bone, tissue, and excreta of experimental animals. A paper has been submitted *Health Physics*. The abstract follows:

"Liquid Scintillation Alpha Counting and Spectrometry and Its Application to Bone and Tissue," by W. J. McDowell and J. F. Weiss. *Abstract:* Three methods for determination of alpha-emitting nuclides using liquid scintillation counting are compared, and the pertinent literature is reviewed. Data showing the application of each method to the measurement of plutonium concentration in tissue and bone samples are presented. Counting with a commercial beta-liquid scintillation counter and an aqueous-phase-accepting scintillator is shown to be accurate only in cases where the alpha activity is high (several hundred counts min or more), only gross alpha counting is desired, and beta-gamma emitters are known to be absent from the sample or present at low levels compared with the alpha activity. Counting with the same equipment and an aqueous-immiscible scintillator containing an extractant for the nuclide of interest (extractive scintillator) is shown to allow better control of alpha peak shift due to quenching, a significant reduction of beta-gamma interference, and, usually, a low background. The desirability of using a multichannel pulse-height analyzer in the above two counting methods is stressed. The use of equipment and procedures designed for alpha liquid scintillation counting is shown to allow alpha spectrometry with an energy resolution capability of 200 to 300 keV full-peak-width-at-half-peak-height and a background of 0.3 to 1.0 count min, or as low as 0.01 count min if pulse-shape discrimination methods are used. Methods for preparing animal bone and tissue samples for assay are described.

16. R. J. Silva, W. J. McDowell, O. L. Keller, Jr., and J. R. Tarrant, *Inorg. Chem.* 13, 2233-37 (1974).

17. W. J. McDowell, O. L. Keller, Jr., P. F. Dittner, J. R. Tarrant, and G. N. Case, *J. Inorg. Nucl. Chem.* 30, 1207-10 (1976).

18. R. E. Meyer, W. J. McDowell, P. F. Dittner, R. J. Silva, and J. R. Tarrant, *J. Inorg. Nucl. Chem.* 30, 1171-73 (1976).

19. University of Tennessee Comparative Animal Research Laboratory.

10. Biomedical Technology

10.1 ADVANCED ANALYTICAL TECHNIQUES

Advanced analytical systems employing chromatographic separations are being developed for the analysis of specific molecular constituents in physiologic fluids. These systems are important chiefly because they can provide specific and sensitive analyses for individual molecular species in a complex biochemical matrix.

Engineering Development

Three analytical concepts and an automated blood preparation system are under development. The analytical concepts include high-resolution liquid chromatography, centrifugal elution chromatography, and elution electrophoresis.

High-resolution liquid chromatographic systems. The development of chromatographic systems for the analyses of protein-bound carbohydrates in serum is still in progress. Previous work¹ has led to the development of an appropriate system and the necessary methodology for analyses of the neutral protein-bound carbohydrates mannose, sucrose, and galactose in sera. Current developmental work is directed toward the analysis of protein-bound *n*-acetylneuraminic (sialic) acid in serum. The system used is virtually identical to that designed for the determination of neutral carbohydrates, except that elution with a concentration gradient of borate¹ is replaced by isocratic elution with ammonium acetate acetic acid buffer (pH 4.4). Good resolution of the peak representing sialic acid is realized within 3.5 hr (see Fig. 10.1), and regeneration of the chromatographic column is avoided by using an eluent of constant concentration.

Centrifugal elution chromatographic system. We have developed a new, removable-column rotor that greatly enhances the experimental flexibility and operation of the prototype system for centrifugal elution chromatography.^{2,3} The new rotor assembly accepts up to

eight chromatographic columns and consists of a plastic center insert for partitioning the sample and eluent stream among the separate flow channels. A flow channel consists of a chromatographic column followed by a flow-through cuvet. The final element is a retainer clip with center screw, which is used to compress and secure the assembly within the rotor.

Unsatisfactory flow characteristics in the form of bed compression were observed for gel-packed chromatographic columns. This necessitated replacement of the gel with an inorganic support which had more rigidity than the gels. A technique developed for covalently attaching proteins to alumina via cyanogen bromide activation of the support⁴ was used to attach anti-(human)IgG covalently to 70- to 100-mesh alumina. Chromatographic columns prepared with this immunosorbent exhibited good dimensional stability under centrifugally forced flow of liquid.

Elution electrophoresis. Initial feasibility of the concept of elution electrophoresis was reported earlier;⁵ however, achieving reproducibility and ease of operation, which are necessary for the application of the concept to clinical measurements, proved to be difficult. A series of fundamental investigations was performed in order to attain the desired reproducibility and simplicity of operation.

Investigations of the electrophoretic mobility of bovine serum albumin (BSA) in a bed of particulate packing (such as is typically maintained in the elution electrophoresis system⁵) were performed. The results

2. C. D. Scott et al., *Experimental Engineering Sect. Semiannual Prog. Rep. (Excluding Reactor Programs)*, Mar. 1 to Aug. 31, 1974, ORNL/TM-4777 (July 1975).

3. C. D. Scott, W. W. Pitt, Jr., and W. F. Johnson, "Centrifugal Elution Chromatography with Eluate Monitoring," *J. Chromatogr.* 99, 35 (1974).

4. C. A. Burtis, J. E. Mroczek, and C. D. Scott, *Biochemical Technology Program Prog. Rep. July 1 to Dec. 31, 1975*, ORNL/TM-5167 (January 1976), pp. 237-40.

5. C. D. Scott, N. E. Lee, and A. W. Perkins, "Automated Elution Electrophoresis. A Potential Clinical Tool," *Clin. Chem.* 21, 1217 (1975).

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

Fig. 10.1. isocratic elution of a normal human serum hydrolyzed under mild conditions to liberate salicylic acid.

indicate that, for the conditions presented, mobility was not apparent at low voltages (<600 V) or for short run times (<30 min). Figures 10.2 and 10.3 demonstrate that both higher voltages and longer run times involve increased current flow within the column. This phenomenon is related directly to the system cooling capacity, with higher temperatures resulting in in-

creased solution conductivity. Since cooling water was recycled through an ice bath, inlet cooling water temperature was accepted as a representative average temperature. (The temperature drop across the column was negligible during each run.)

The apparent mobility accompanying higher voltages and longer run times may be electrophoretic motion enhanced by temperature (because of temperature effects of BSA properties or interaction between BSA and packing), or it may be a convective motion resulting from the higher temperatures. Additional experimentation will be required to relate the phenomenon to acceptable operating conditions for elution electrophoresis.

System for preparing blood samples. Genetic mutation is commonly monitored by the determination of variant cellular isoenzymes, using electrophoretic techniques coupled with the staining of specific proteins. Statistically meaningful results necessitate the analyses of large numbers of blood samples that, in turn, require a large commitment of technical manpower to prepare the necessary cellular hemolysates for analysis. A system automating this procedure is under development and is designed to perform the following functions: (1) separate whole blood into plasma and cell fractions; (2) wash the cells, collecting samples of plasma and washed cells; and (3) facilitate the preparation of a lysed cell sample for electrophoretic analysis.^{6,7}

A prototype system (shown in Fig. 10.4) incorporates external connections for fluid, air, and vacuum for washing and sample transfer. The rotor and sample collection ring are shown in Fig. 10.5. A rotary seal affixed to the center of the rotor (see Fig. 10.5) facilitates the dynamic introduction of cell-washing liquids and hemolyzing solution.

One of the problem areas associated with the preparation of hemolysate samples by an automated system is the complete removal of stroma. This cell debris, if not completely sedimented, causes streaking and incomplete resolution of electrophoretic bands. The standard against which system-prepared samples have been compared is a final high-speed (18,000-rpm) spin in a Sorvall centrifuge. Figure 10.6 shows an electrophoretogram for lactate dehydrogenase on acrylamide gel, using hemolysates prepared on the automated system with and without additional high-speed centrifu-

6. C. D. Scott et al., *Experimental Engineering Sect. Semi-annu. Prog. Rep. (Excluding Reactor Programs)*, Sept. 1, 1973, to Feb. 28, 1975, ORNL/TM-4602 (December 1974).

7. C. A. Burtis et al., *Biochemical Technology Program Semiannu. Prog. Rep. Jan. 1 to June 30, 1975*, ORNL/TM-5006 (August 1975).

ORNL DWG. 76-533

Fig. 10.2. Voltages in excess of 600 V result in increased current flow probably due to increased solution conductivity caused by insufficient system cooling capacity.

ORNL DWG 76-534R1

Fig. 10.3. Current flow as a function of the temperature of the inlet cooling stream.

ORNL PHOTO 889R1-75

Fig. 10.4. Front view of prototype blood sample preparation system with the top cover in place.

Fig. 10.5. View of the blood preparation rotor and sample collection ring showing the rotary seal for application of vacuum, air, and dynamic introduction of fluids.

gation. No significant improvement in resolution of the isoenzymes is apparent for those samples that have undergone the high-speed spin; thus, removal of stroma during processing of the sample on the automated system is adequate.

Analytical Applications

Several advanced analytical systems employing chromatographic separations are being used to analyze specific molecular constituents of physiologic fluids. The principal value of these is their capability for providing specific and sensitive analyses for individual molecular species in a complex matrix such as serum or urine. Rapid analysis, while desirable, is secondary to specificity when attempting to correlate changes in the clinical status of certain patients with alterations in one or more potential biochemical markers of a clinical dysfunction. Both sensitivity and specificity are im-

portant in the high-resolution chromatographic analysis of protein-bound carbohydrates in serum, whereas specificity is of primary importance in the affinity chromatographic separation of specific proteins by centrifugal elution chromatography.

Analysis of protein-bound carbohydrates in serum. Average concentrations of 48, 444, and 436 mg/liter for protein-bound fucose, mannose, and galactose, respectively, have been obtained in chromatographic analyses of sera from clinically normal women.¹ Corresponding values for the coefficient of variation (CV) were 25.7, 17.6, and 19.5%. Chromatographic analysis for protein-bound sialic acid in sera from 19 healthy female subjects yielded a mean concentration of 680 mg/liter with a CV of 23.3%.

In an attempt to evaluate the efficacy of protein-bound carbohydrates as potential biochemical markers of breast cancer, a series of serum samples from clinically defined patients with breast cancer was

LACTATE DEHYDROGENASE

MALIC DEHYDROGENASE

Fig. 10.6. Electrophoretic comparison of hemolysate samples from the automated blood preparation system showing an absence of streaking in samples that had not undergone an additional high-speed (18,000-rpm) centrifugation.

assayed. Patients in each of three disease categories—stable, responsive, and progressive—were selected, and at least two samples of sera, obtained over periods of time ranging from two to five months, were analyzed for protein-bound mannose, galactose, fucose, and sialic acid.

Patients included in this study had clinically demonstrable and biopsy-proved metastatic breast cancer. Therapeutic regimes include surgery in some cases, followed by radiotherapy and chemotherapy. Serum samples from patients undergoing chemotherapy were obtained 10 to 20 days after administration of a dose of the appropriate drug. The clinical classification of patients as responsive was generally based on a 50% decrease in observable tumor mass present for at least

28 days. Progressive disease was defined as the appearance of any new lesion or a greater than 25% increase in any existing lesion that persisted for more than six days. A stable clinical status was designated in those situations where criteria did not exist for either responsive or progressive disease status.

Figure 10.7 illustrates a comparison of the changes in protein-bound fucose for breast-cancer patients whose disease status had been classified into the three clinical categories. Figure 10.8 compares, for many of the same patients (same symbols in each category represent the same patient), protein-bound sialic acid for each of the three clinical categories. In every case, the changes in protein-bound fucose correctly mirrored the clinical assessment of the patient's malignancy; however, this was not true for sialic acid. Changes in protein-bound fucose averaged less than 6.7% ($\sigma = 4.9\%$) for eight patients whose disease was classified as clinically stable. All 12 patients classified as having clinically responsive disease projected decreases in fucose averaging 34.5% ($\sigma = 16.1$). All patients (ten) with progressive malignancies displayed increases averaging 38.3% ($\sigma = 21.5\%$).

Decreases in sialic acid were noted for each of the five patients whose clinical status was classified as stable; a rather dramatic decrease was noted for one patient (see Fig. 10.8). Six of eight patients in the responsive category showed declines in sialic acid, while only three of eight patients with progressive malignancy showed increases. Note that most of the sialic acid data are within $\pm 2\sigma$ of the mean for the normal data, whereas 67% of the initial fucose measurements for responsive disease and 60% of the final measurements for progressive disease exceeded $\pm 2\sigma$ from the mean.

Both fucose and sialic acid are terminal molecules in the carbohydrate chains of glycoproteins. Based on this fact, we might expect an increase in the number of residues of fucose to be accompanied by a corresponding decrease in sialic acid. Unfortunately, our initial results do not seem to show such an interrelationship between these two compounds. On the other hand, we are encouraged by the good correlations of increasing protein-bound fucose with progressive breast cancer and decreasing fucose with responsive malignancy. Further studies using analytical methods of high specificity, especially methods for determining protein-bound fucose and sialic acid, are needed to establish similar relationships for other types of malignancies.

Centrifugal elution chromatography of serum immunoglobulins. Previous work had established the feasibility of separating specific proteins by affinity chromatography on the centrifugal elution chromato-

Fig. 10.7 Variations in protein-bound fucose for breast-cancer patients with stable, responsive, and progressive malignancies.

graph.³⁻⁸ These initial studies failed to demonstrate such important capabilities as quantitation and separation of multiple proteins from a single sample on the

8. S. E. Shumate II, C. D. Scott, and W. F. Johnson, "A Prototype System for Centrifugal Elution Chromatography with Eluate Monitoring," *Proceedings of the 28th Annual Conference on Engineering in Medicine and Biology*, vol. 17, p. 345 (1975).

system. Operational problems caused by compaction of the gel affinity columns prevented the completion of experiments to establish these important points. However, preparation of an immunosorbent using the more rigid alumina particles enabled successful conclusion of these feasibility experiments.

The newly designed rotor with removable columns was assembled using four columns packed with anti-(human)-IgG immunosorbent. A 40-μl volume of

Fig. 10.8. Variations in protein-bound sialic acid for breast-cancer patients with stable, responsive, and progressive malignancies.

human serum, appropriately diluted, was dynamically injected into the splitting vanes of the rotor insert. The nonabsorbed proteins were eluted as a large peak at the front of the chromatogram (Fig. 10.9). The second peak, consisting of nonspecifically adsorbed proteins, was eluted with 1.0 *M* NaCl in a phosphate buffer of pH 7.0. Finally the immunosorbed protein of interest, IgG, was eluted with 3.0 *M* NaSCN. The effect of serum

sample size was studied using 10 to 100 μ l of serum. A 10- μ l sample yielded an easily detectable peak for IgG within 16 min, reflecting the capability for both rapid analysis and high sensitivity.

One of the important features of this instrumental concept is its potential for performing rapid determinations of multiple proteins from a single sample of serum. To illustrate this potential, the simultaneous

Fig. 10.9. Separation of IgG from human serum by affinity chromatography on the centrifugal elution chromatograph.

determination of immunoglobulins G and M was demonstrated. Two columns were packed with anti-(human)-IgG, and two other columns were packed with anti-(human)-IgM. After these columns had been placed in the rotor of the centrifugal elution chromatograph and eluent flow had been established, serum volumes of 10, 20, and 40 μ l were dynamically injected, and the immunoglobulins were eluted under identical conditions. Figure 10.10 shows the immunoglobulin peak heights as a function of serum sample size for the simultaneous determinations of IgG and IgM; in each case the response was linear over the range of sample size studied.

This prototype centrifugal system has been used to demonstrate the feasibility of a new analytical concept for multichannel affinity chromatography with eluate monitoring. The concept could provide a very desirable alternative to other methods of serum protein determination. The ease with which columns may be added, removed, or interchanged enhances the utility of the system for performing rapid, simultaneous determinations of many serum proteins from a single sample. The eluted protein is free from any contamination that could cause detector interference. Also the economical advantages of recyclable antibodies, high sample

Fig. 10.10. Linear peak height as demonstrated for the simultaneous elution of two human immunoglobulins, using a centrifugal elution chromatograph.

throughput, automated multiple analyses with a single photometer, and on-board data processing are impressive.

10.2 DEVELOPMENT OF THE CENTRIFUGAL FAST ANALYZER

One of the major objectives of this program is the development of a multipurpose analyzer system capable of making many measurements on diverse biological or chemical reactions in a short period of time with high precision and accuracy. The miniature Centrifugal Fast Analyzer (CFA), a second-generation outgrowth of the original GeMSAEC CFA,⁹ represents a major technological advance in the field of centrifugal fast analyzers with its compact size, microliter volume requirements, and sophisticated data processing capabilities.^{10,11}

ORNL's development of a new concept in centrifugal analyzers, the portable CFA, along with new advances in instrumentation being implemented in commercial systems promises to keep this analytical concept at the forefront of technological developments in the field of fast analyzers.

The major impact of centrifugal analyzers has been in the area of clinical chemistry, as evidenced by the burgeoning number of oral presentations and publications in this field since its introduction¹ in 1969 (see Table 10.1). However, the diverse capabilities of these systems are being realized, with several publications appearing on analytical and environmental analyses.¹²⁻¹⁵

Engineering Development

As a part of a program to appraise the performance and broaden the utility of analytical systems that have a miniature CFA as their basic component, six prototype

Table 10.1. Chronological summary of information disseminated on the Centrifugal Fast Analyzer: presentations given at national and international clinical chemistry meetings and in publications

Year	Presentations given		Number of publications
	Locality	Number	
1969	Geneva, Switzerland	1	8
1970	Buffalo, New York	4	3
1971	Seattle, Washington	5	8
1972	Cincinnati, Ohio	8	15
	Copenhagen, Denmark	8	
1973	New York, New York	11	16
1974	Las Vegas, Nevada	18	29
1975	Toronto, Canada	25	26

systems have been fabricated and are being routinely used or evaluated in selected analytical laboratories. These include laboratories of the ORNL Health Division; the NASA Johnson Space Center, Houston, Texas; the National Institutes of Health (NIH), Bethesda, Maryland; the National Center for Toxicological Research, Jefferson, Arkansas; and the Department of Human Genetics, University of Michigan, Ann Arbor. An additional system has been fabricated and is awaiting assignment to another laboratory for evaluation.

The concept of a multipurpose optical system has been discussed in the literature.¹⁶ Such a system has been designed, fabricated, and retrofitted on the miniature CFA located at the Clinical Center, NIH. The optical system features a stationary two-lens assembly that focuses the light from the center of the cuvet onto the photomultiplier (PM) tube, increasing the fluorescence signal intensity by about a factor of 10 and enabling operation at lower PM voltages. The filter bar is rotated between the stationary two-lens assembly (Fig. 10.11), which simplifies optical alignment, since only one lens assembly is used for all wavelengths. The fiber optical bundle that directs excitation radiation into the cuvet at a 90° angle to the PM tube passes through the center of the overhead light support (see Fig. 10.11). Sensitivity of the retrofitted system for the fluorometric determination of 4-methylumbelliferone was approximately $1 \times 10^{-7} M$.

A prototype of the portable CFA is being developed that incorporates the following components: an analytical module; data acquisition, analysis, and output

9. N. G. Anderson, "Basic Principles of Fast Analyzers," *Am. J. Clin. Pathol.* 53, 778 (1970).

10. C. A. Burtis, J. C. Mailen, W. F. Johnson, C. D. Scott, T. O. Tiffany, and N. G. Anderson, "Development of a Miniature Fast Analyzer," *Clin. Chem.* 18, 753 (1972).

11. 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).

12. J. C. Mailen and T. O. Tiffany, "The Reaction of Iodine with Concentrated Nitric Acid," *J. Inorg. Nucl. Chem.* 37, 127 (1975).

13. W. D. Bostick, C. A. Burtis, and C. D. Scott, "Simultaneous Determination of Silica and Phosphate in Water from a Single Experiment Using a Miniature Centrifugal Fast Analyzer," *Anal. Lett.* 9, 65 (1976).

14. C. A. Burtis et al., *Biochemical Technology Program Prog. Rep. July 1 to Dec. 31, 1975*, ORNL/TM-5167 (January 1976), pp. 20-36.

15. G. Goldstein, J. E. Strain, and J. L. Bowling, *Environmental Applications of Centrifugal Fast Analyzers. Final Progress Report*, ORNL/NSF/EATC-15 (December 1975).

16. C. A. Burtis, W. D. Bostick, and W. F. Johnson, "Development of a Multipurpose Optical System for Use with a Centrifugal Analyzer," *Clin. Chem.* 21, 1225 (1975).

ORNL PHOTO 1595-76A

Fig. 10.11. Multipurpose optical head designed for retrofitting to the miniature Centrifugal Fast Analyzer.

module; and analyzer control in one 14 X 14 X 8 in. (35.6 X 35.6 X 20 cm) package (Fig. 10.12). This prototype utilizes a clutch-brake mechanism that enables the motor and flywheel to be brought to speed with the rotor at rest. Engaging the clutch then rapidly accelerates the rotor to 4000 rpm, transferring and mixing samples and reagents in a properly designed rotor. Studies in a parallel-channel⁶ rotor have indicated that liquid transfer is completed during the first revolution of the rotor, that is, within about 65 msec of the first movement of the rotor (Fig. 10.13).

The microprocessor module in the prototype portable CFA and its software have been thoroughly checked and were found to be operational. This data system, which is based on the Intel 8080 chip with a 4- μ sec average execution time for instructions, incorporates 12K byte capacity for program storage (PROM devices) and 8K byte capacity for data storage (RAM devices). It utilizes a newly developed computer clock whose accuracy and resolution are greater than 0.1% and 100

μ sec respectively. The latter is particularly important in the acquisition of fast kinetic data, because a period of only 880 μ sec elapses between successive cuvetts at 4000 rpm.

The microprocessor not only acquires information, analyzes it, and prints the results, but also exercises some control of the analytical module. Currently, the microprocessor controls the clutch-brake assembly and the motor. In the future it will also control the filter selection, PM voltage, preamplifier gain, and perhaps even the temperature of the analyzer.

Studies of rotors preloaded with reagents for the assay of certain enzymes are continuing in conjunction with two commercial reagent manufacturers. Two concepts for preloaded rotors are being evaluated: reagents lyophilized in place within a rotor, and reagents prepared in tablet form.

Results obtained for the enzymatic assay of glucose, serum glutamic oxaloacetic transaminase, and alkaline phosphatase indicated that reagents can be successfully

lyophilized in situ by the reagent manufacturer and subsequently reconstituted and used for analysis. The preparation of reagents for assay of lactate dehydrogenase (lactate medium) by this method was unsuccessful owing to reagent instability when all components were lyophilized simultaneously; however, this problem may be minimized by lyophilizing the individual components of this reagent in separate chambers of the rotor.

Reagents in tablet form have been evaluated for the enzymatic assay of glucose in a ten-week study. In general, comparison of the tablet formulation with

conventional reagent kits for this assay has demonstrated that equivalent, accurate, and precise results were obtained with the tablets. Sealing the tablets in cuvetts and storing them for up to ten weeks had no adverse effect on the reagents. Similar stability studies of tablets for the other three enzymes are under way.

Analytical Applications

Numerous analytical applications of CFA technology are being investigated. These include the development of new kinetic assays for enzymes of clinical interest

Fig. 10.12. Operating prototype of the portable Centrifugal Fast Analyzer with integral microprocessor and thermal printer.

Fig. 10.13. Transfer of a homogeneous dye solution, using a parallel-channel rotor on the portable Centrifugal Fast Analyzer. Liquid transfer was completed within one revolution of the rotor.

and the development of enzymatic or colorimetric assays for environmental pollutants. In addition, an interesting study of evaporative losses from CFA sample cups has resulted in a minimization of this important source of error.

Clinical assay of enzymes. A kinetic assay for the biliary tract enzyme, γ -glutamyl transpeptidase (GGTP), was developed for the miniature CFA.⁴ The substrate employed was L-glutamyl-*p*-nitroaniline; the assay is based on the liberation of the chromophore *p*-nitroaniline and measurement of its absorbance at 400 nm. As a prelude to the study of GGTP as a potential biochemical marker of metastases in cancer, several apparently normal subjects were analyzed to establish a normal range for the measurement. Table 10.2 lists the GGTP activities for men and women classified according to age and sex. Women under 50

years of age generally had lower activities than men; however, women older than 50 had about the same activities as men. The mean activity for all subjects was 17.1 units(IU)/liter, with a 2σ upper limit of 32.7 IU/liter.

Sera from 139 cancer patients with liver involvement were assayed for GGTP activity. Ninety-two of these patients had activities greater than 100 IU/liter, with 25 exceeding 500 IU/liter and 9 exceeding 1000 IU/liter. Further experiments correlating GGTP activities with the clinical status of patients are necessary to confirm the potential of this enzymatic measurement as a biochemical marker.

Environmental analysis. The measurement of various environmental pollutants by means of the CFA is an area of considerable interest for the Chemical Technology Division. Methodology is being developed in

Table 10.2. Serum γ -glutamyl transpeptidase activities for apparently normal human subjects

Group description	Number of subjects	GGTP activity (IU/liter at 30°C)		
		Mean	Median	Range
All	237	17.1	14.6	6.6-38.4
Males	177	17.9	16.0	8.2-38.4
20-29 years	6	14.2	10.8	8.2-28.1
30-39 years	30	18.2	14.0	8.6-36.8
40-49 years	58	17.7	15.6	8.5-32.2
50-59 years	60	17.1	15.1	8.4-38.4
>60 years	14	19.8	17.4	12.9-29.6
Females	49	13.3	11.5	8.2-38.3
20-29 years	10	11.4	9.8	6.9-27.6
30-39 years	10	11.9	11.5	6.6-23.2
40-49 years	10	10.9	9.2	6.8-19.7
50-59 years	13	17.4	13.3	8.8-38.3
>60 years	3	17.0	15.7	15.6-19.5

collaboration with other ORNL divisions (including Environmental Sciences and Analytical Chemistry). Personnel from the Environmental Sciences Division are interested in determining adenosine triphosphate (ATP) concentrations in environmental samples as a measure of microbiological activity and biomass. Toward this end, a rapid, sensitive method has been adapted for use with the CFA to measure ATP in a series of environmental samples.¹⁷ Another interesting method with environmental implications, which is being studied in conjunction with personnel from the Analytical Chemistry Division, is a kinetic assay for low levels of sulfate (see Fig. 10.14). This assay, which is based on the catalytic effect of sulfate ion on the depolymerization of zirconyl species in acidic solution, does exhibit problems in connection with the aging of solutions of zirconium polymer; however, it shows promise for the measurement of low concentrations of sulfate. Development of such an assay is important, since no method is available for providing accurate low-level sulfate analyses.

Emphasis has been focused on the analyses of inorganic nutrients, including phosphate, silica, ammonia, and nitrate. Procedures have been developed or adapted toward the ultimate goal of simultaneously determining these nutrients in a single rotor under identical conditions, including the monitoring of wave-

17. B. S. Ausmus, M. Witkamp, C. Shriver, and W. D. Bostick, "Evaluation of Extraction and Analysis of ATP and Its Interpretation as an Estimate of Microbial Activity," submitted for publication in the *Journal of Environmental Quality*.

Fig. 10.14. Determination of sulfate based on its catalytic depolymerization of zirconyl polymer and a subsequent colorimetric measurement of zirconium.

length. Silica and phosphate are determined by a differential kinetic procedure that monitors the formation of their 12-heteropolymolybdate complexes.⁵ Ammonia and nitrate are determined by means of enzymatic reactions involving the oxidation of NAD(P)H (nicotinamide-adenine dinucleotide or nicotinamide-adenine dinucleotide phosphate). The former utilizes the enzyme L-glutamate dehydrogenase (GLDH):¹⁸

$\text{NH}_3 + \alpha\text{-ketoglutarate}$

This reaction was found to be stoichiometric and highly selective for ammonia (Table 10.3). The reaction for the assay of nitrate involves the enzyme nitrate reductase (NR):¹⁹

18. W. D. Bostick, R. C. Lovelace, and C. A. Butts, "Enzymatic Determination of Ammonia with a Miniature Centrifugal Fast Analyzer," *Water Research* (in press).

19. W. D. Bostick, "The Use of *Neisseria crassa* Nitrate Reductase for the Analysis of Small Quantities of Nitrate Ion," submitted for publication in *Analytical Chemistry*.

Table 10.3. Enzymatic determination of ammoniac-nitrogen

NH ₃ -N taken (ppm)	NH ₃ -N found ^a (ppm)	Error (%)
2.0	1.983 ± 0.015 ^b	-0.85
4.0	4.017 ± 0.045	+0.43
6.0	5.967 ± 0.050	-0.55
8.0	7.967 ± 0.029	-0.41
10.0	10.96 ± 0.029	+0.60

^aFrom the formula:

$$C, \text{ ppm} = (\text{SF} \Delta A)_{340}.$$

where SF is the theoretical substrate factor.

^bMean ± standard deviation of three replicates.

The source, *Neurospora crassa*, used for the isolation of this enzyme was found to have an NADPH-oxidase activity associated with its nitrate reductase activity. This resulted in excessive consumption of NADPH and a variable blank that complicated the assay.²⁰ The enzyme, which is isolated from *Chlorella*, will be studied to determine whether it is free of this oxidase activity, enabling the assay to be performed by following the disappearance of NADPH. Thus, assays of three of the four inorganic nutrients are operational. These assays, monitored at 340 nm, have been demonstrated to be suitable for inclusion in a "nutrient" rotor on the CFA.

Evaporation and its effect on analytical error. We have made some new instrumental developments that offer real and potential advantages in clinical analyses. Typically, sensitivity and small-volume requirements have been major features of this instrumentation. These requirements have added a new dimension to various factors that previously have contributed relatively little to the total analytical error. One such factor, which can have a major effect on results from the CFA because of its microliter volume requirements, is evaporative loss from either the sample or the reagent after it has been placed in the sample cup.

Results of evaporation studies in sample cups of different geometries led to the development of a mathematical model that enabled estimation of the quantity of a particular liquid lost by evaporation over a specific period of time from a cup of known geometry. The theoretical basis for the model was diffusion through a stagnant gas film.²¹ The model yielded the following expression for the rate of fractional evaporative loss, R , for short times:²²

$$R = \frac{dF}{dt} = \frac{p \cdot M_{\text{H}_2\text{O}} \cdot (D_{\text{H}_2\text{O-air}})}{(h - h_0) \cdot h_0 \cdot \rho_{\text{H}_2\text{O}} \cdot R \cdot T} \cdot \ln \frac{p_{\text{air}_2}}{p_{\text{air}_1}} \quad (3)$$

where

 p = atmospheric pressure, atm. $M_{\text{H}_2\text{O}}$ = molarity of water, g/mole. $D_{\text{H}_2\text{O-air}}$ = diffusivity of water in air, cm²/sec. h_0 = initial depth of liquid, cm. h = height of the sample cup, cm. $\rho_{\text{H}_2\text{O}}$ = density of water, g/cm³. R = gas constant = 82.05 atm·cm³/mole·K. T = temperature, K. $p_{\text{air}_1} = p - p_{\text{H}_2\text{O}}$ ($p_{\text{H}_2\text{O}}$ = vapor pressure of water). $p_{\text{air}_2} = p - (\text{RH})(p_{\text{H}_2\text{O}}/100)$ (RH, relative humidity, %).

In addition to predicting the evaporative rate for a given cup, Eq. (3) also suggests the optimum depth for filling the cup with liquid to reduce the effects of evaporation. The rate of fractional evaporative loss, which is a function of the liquid depth, is a minimum when the denominator of Eq. (3) is a maximum. This occurs when

$$\frac{d[(h - h_0) \cdot h_0]}{dh_0} = 0 = h - 2h_0 \quad (4)$$

for example, when $h_0 = h/2$. Thus, to minimize the fractional evaporative loss from a sample cup, the cup initially should be half full. This somewhat surprising relationship has been confirmed experimentally for a number of cups of various geometries. During the course of this study, it was also determined that evaporative losses can be minimized by use of a particular cup design having a relatively large height-to-diameter ratio. This conclusion resulted in the selection of a new sample cup¹⁴ for use with the automated rotor-loading system of the CFA.

In general, evaporative loss can be minimized by controlling the laboratory environment, selecting a sample cup of favorable design, filling the cup only half full of sample, using effective covers, and following good laboratory practice. In this way, the analytical error, even with microliter volumes of sample, can be held to 1 to 2% or less.

21. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, p. 522, Wiley, New York, 1960.

22. C. A. Bortis, J. M. Begovich, and J. S. Watson, "Factors Influencing Evaporation from Sample Cups and Assessment of Their Effect on Analytical Error," *Clin. Chem.* 21, 1907 (1975).

20. J. E. Sirochek, C. A. Bortis, and C. D. Scott, *Biochemical Technology Program: Prog. Rep. Jan. 1-June 30, 1976*, ORNL/TM-5446 (in preparation).

11. Environmental Studies

In addition to continuing our efforts relative to the isolation and identification of soluble organic constituents and pollutants and the determination of chlorination effects on cooling waters, we have organized a national conference on the Environmental Impact of Water Chlorination. Also, a program has been initiated to develop automated continuous monitors for dissolved pollutants.

11.1 CONTINUOUS MONITORING OF POLLUTANTS

The objective of the continuous monitoring program is the development of automated analytical systems for isolation and identification of specific pollutants and the development of monitors that can detect properties of specific pollutants on a continual basis for application in environmental monitoring. The initial emphasis is being placed on two types of monitors: (1) a continuous chemical oxygen demand (CCOD) monitor and (2) a surface fluorometer.

A CCOD monitor that measures fluorescent Ce(III) resulting from the reduction of Ce(IV) by any oxidizable compound in the stream being monitored has been assembled and is undergoing evaluation. The monitor is based on an earlier version, which gave results comparable to those obtained by the standard COD tests in the low-ppm range. Perchloratoceric acid [0.005 M Ce(ClO₄)₄ in 6 M HClO₄] is continuously mixed with the polluted water stream, the mixture is passed through a boiling water bath with a 10-min residence time, and the resulting Ce(III) is measured fluorometrically. Using phenol as a stand-in pollutant, the optimum sample-to-reagent flow ratio was determined to be about 4 to 1. Under these conditions, the CCOD monitor could detect

less than 10 ppb of phenol and gave a linear response up to 5 ppm.

A bifurcated fiber optic (BFO) fluorometer (Fig. 11.1) for surface fluorometric measurements was constructed to determine dissolved fluorescing pollutants. The use of BFOs allows the measurement of fluorescence at a zero angle (i.e., excitation and emission paths are the same). This minimizes the depth of fluid required for measurement. In addition, by using filters of the same wavelength or removing the filters altogether, the fluorometer can be used as a reflected-light turbidimeter.

The BFO fluorometer was evaluated as a dissolved uranium monitor. Shown in Fig. 11.2 are plots of detector response vs uranyl concentration in sulfuric and nitric acids. The decrease in response in nitric acid results from the absorbance of the excitation light by nitrate. The BFO tested had fibers divided into quadrants, rather than randomly mixed fibers which would have minimized the quenching. The BFO is now being evaluated for the determination of trace polynuclear aromatic hydrocarbons in coal liquefaction and gasification liquors and has demonstrated a capability of detecting phenanthrene at levels as low as 5 µg/liter in water.

11.2 IDENTIFICATION OF POLLUTANTS

Assessment of possible epidemiologic relationships of human health to organic constituents in potable waters and assessment of environmental problems associated with organics in surface waters require both qualitative and quantitative information about the identity and concentrations of the organics in the waters of concern. A major objective of this identification program is the development of methodology to permit the analysis of such waters. Because of its sensitivity and capability for analyzing many low-molecular-weight refractory organics in aqueous samples, high-resolution liquid chromatography is used as the basic separations method for

1. W. W. Pitt, Jr., S. Katz, and E. H. Thacker, "A Rapid, Sensitive Method for the Determination of the Chemical Oxygen Demand of Polluted Waters," pp. 1-5 in *Water '72*, American Institute of Chemical Engineers Symposium Series, vol. 69, No. 129, 1973.

Fig. 11.1. Schematic of a bifurcated fiber optic fluorometer.

examination of environmentally significant waters.² A routine multicomponent analytical scheme using several testing procedures is utilized for the determination of the chemical structure of the separated constituents.

Concentration studies. Concentration is a fundamentally important prerequisite for analysis of organics present at ppb concentrations in water with the present sensitivity of analytical detection. We are developing a new concentration procedure that potentially will overcome many of the disadvantages of previously used techniques. This process involves: (1) adjustment of the pH of the water sample to 8.5, (2) passing the sample through an anion exchange cartridge [0.62-cm-ID $\times$ 4-in. (10.2-cm) stainless steel column filled with AG 1X8 resin, $\geq 40 \mu$], (3) adjustment of the pH of the eluate to 4.0, and (4) passing the sample through a cation exchange cartridge [0.62-cm-ID $\times$ 4-in. (10.2-cm) stainless steel column filled with AG 50-WX12 resin, $\geq 20 \mu$]. The resin cartridges are then placed on either an anion or a cation exchange high-resolution system, and the organic constituents are chromatographically separated as in a routine chromatographic run. Concentration factors up to 30,000 have been achieved by this method. The recovery of urine constituents used to test the efficacy of the process has been satisfactory from distilled water, Walker Prong water (a well-

characterized pristine water within the ERDA reservation), Watts Bar Lake water (collected from the cooling water inlet of the Kingston Steam Plant), and a metropolitan chlorinated tap water. The practical flow limit to maintain high concentration efficiency for cartridges of this size is about 500 ml/hr. A modification of the process, using a small amount of borate to form anionic complexes with the carbohydrate-like material, also permits sugars to be concentrated with this technique.

Organophosphorus compounds. Eutrophication of reservoirs and lakes is often attributed to increased phosphate concentrations, because phosphorus is considered to be the major limiting factor in waters with respect to formation of biomass. Therefore, the identification and quantitation of organophosphorus compounds in natural and polluted waters is of considerable interest relative to maintaining surface water supplies of high quality for use as sources of potable water. In a cooperative program with the University of Tennessee Environmental Engineering Department, high-resolution liquid chromatography has been used to separate the organophosphorus

2. W. W. Pitt, Jr., R. L. Jolley, and S. Katz, *Automated Analysis of Individual Refractory Organics in Polluted Water*, EPA-440/2-74-076 (August 1974).

3. R. L. Jolley, W. W. Pitt, Jr., C. D. Scott, G. Jones, Jr., and J. E. Thompson, "Analysis of Soluble Organic Constituents in Natural and Process Waters by High-Pressure Liquid Chromatography," pp. 247-53 in *Trace Substances in Environmental Health IX, 1974, a Symposium*, ed. D. D. Hemphill, University of Missouri, Columbia (May 1974).

4. R. L. Jolley, 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," *Proceedings of the Symposium on Identification and Analysis of Organic Pollutants in Water*, Mexico City, November 30-December 5, 1975, ed. L. H. Keith (in press).

5. W. W. Pitt, Jr., R. L. Jolley, and S. Katz, "Separation and Analysis of Refractory Pollutants in Water by High-Resolution Liquid Chromatography," *Proceedings of the Symposium on Identification and Analysis of Organic Pollutants in Water*, Mexico City, November 30-December 5, 1975, ed. L. H. Keith (in press).

6. R. L. Jolley, G. Jones, Jr., W. W. Pitt, Jr., and J. E. Thompson, "Chlorination of Organics in Cooling Waters and Process Effluents," *Proceedings of the Conference on the Environmental Impact of Water Chlorination*, Oak Ridge, Tenn., October 22-24, 1975, ed. R. L. Jolley (in press).

7. R. L. Jolley, S. Katz, J. E. Mrochek, W. W. Pitt, Jr., and W. T. Ramsey, "Analyzing Organics in Dilute Aqueous Solutions," *Chem. Technol.* 1975, 312-13.

8. W. W. Pitt, Jr., R. L. Jolley, and C. D. Scott, "Determination of Trace Organics in Municipal Sewage Effluents and Natural Waters by High-Resolution Ion-Exchange Chromatography," *Environ. Sci. Technol.* 9, 1066-73 (1975).

Fig. 11.2. Fluorescence of uranium measured by bifurcated optic fluorometer.

constituents from an algae culture. Over 60 organophosphorous compounds were separated in a 120-hr chromatographic run from the unconcentrated water medium in which a culture of *Chlamydomonas reinhardtii* (an algal species associated with eutrophic waters) had been grown with ^{32}P -tagged orthophosphate in the growth medium. This effort is continuing with an ultimate goal of characterization and identification of the separated constituents.

Estuarine waters. Because estuarine and marine sites are being used and are under consideration for electric power generating plants, both conventional and nuclear, the characterization of brackish estuarine water and seawater is of considerable environmental interest. In a preliminary investiga-

tion, a 40-liter water sample from the Cooper River estuary, Charleston, South Carolina, was collected and several concentration methods were evaluated. Neither vacuum distillation nor use of cation exchange resin to remove sodium salts permitted the concentration of the saline water (chloride, 10.26 g/liter) without the formation of a copious salt precipitate and consequent poor recovery of occluded trace organics. Chromatography of a 5-liter aliquot concentrated by the latter technique resulted in the separation of 14 uv-absorbing and/or cerate-oxidizable constituents.

Potable waters. Concern with human health problems has created an interest in the organic constituents of low volatility that may be found in

potable waters. Such compounds in other waters, for example, sewage effluents and natural waters, have been successfully examined by high-resolution chromatography. Therefore, a sample of chlorinated potable water from a large metropolitan water treatment plant was collected for examination by liquid chromatography. Thirty carbohydrate peaks were separated from a 500-fold concentrate of the drinking water by using the carbohydrate analyzer.⁹ Analysis on the UV-Analyzer indicated 21 uv-absorbing peaks and 23 cerate-oxidizable peaks.¹⁰ Using the multicomponent identification procedure, four constituents were positively identified at the following concentrations (based on the original water sample): inositol, 0.5 ppb; α -methylinositol, 11 ppb; mannitol, 0.7 ppb; and succinic acid, 8 ppb. A major problem in the application of our present methodology to the analysis of trace organics (i.e., ppb or less) has been the formation of salts during the concentration procedure. The new concentration procedure discussed above may facilitate the increased application of high-resolution chromatography for the analysis of trace organics in potable and surface waters.

11.3 CHLORINATION STUDIES

Cooling waters. Chlorine is the principal biocide for antifoulant treatment of cooling systems for electric power generating plants. It has been previously shown that chlorination of cooling waters results in the formation of chloro-organic compounds.¹¹ In a continuation of this study, it has been determined that chlorination of Mississippi River water collected from the Allen Steam Plant (operated by the Tennessee Valley Authority and located at Memphis, Tennessee) under conditions similar to those occurring during antifoulant treatment resulted in a chlorination yield of 1 to 3% (as Cl) of chlorinated organic compounds. In this experi-

ment the water sample was chlorinated at a 3.4-mg liter chlorine dose to a 1.2-mg liter chlorine residual (orthotolidine) for a 15-min reaction period, using ³⁵Cl-tagged chlorine gas. Over 50 chlorine-containing organic constituents were chromatographically separated from the 1470-fold concentrate of the reaction mixture¹² (Fig. 11.3).

National chlorination conference. Approximately 300 scientists attended the Conference on the Environmental Impact of Water Chlorination, which was held at Oak Ridge National Laboratory on October 22-24, 1975. Twenty technical papers were presented at this conference, which was jointly sponsored by the Energy Research and Development Administration, the U.S. Environmental Protection Agency, and the Oak Ridge National Laboratory. The conference was conducted and coordinated by the Water Pollution Studies Group, and the Proceedings were edited by personnel in that same group. The conference document is scheduled for printing in July 1976.¹³

9. S. Katz, W. W. Pitt, Jr., J. E. Mroczek, and S. R. Dunsmore, "Sensitive Fluorescence Monitoring of Carbohydrates Eluted by a Borate Mobile Phase from an Anion-Exchange Column," *J. Chromatogr.* **101**, 193-97 (1974).

10. S. Katz, W. W. Pitt, Jr., and G. Jones, Jr., "Sensitive Fluorescence Monitoring of Aromatic Acids after Anion-Exchange Chromatography of Body Fluids," *Chin. Chem. Lett.* **5**, 20 (1974).

11. R. I. Jolley, C. W. Gehrs, and W. W. Pitt, Jr., "Chlorination of Cooling Water: A Source of Chlorine-Containing Organic Compounds with Possible Environmental Significance," *Proceedings of the Fourth National Symposium on Radiobiology*, Corvallis, Ore., May 12-18, 1975 (in press).

12. R. I. Jolley, "Determination of Chlorine-Containing Organics in Chlorinated Sewage Effluents by Coupled ³⁵Cl Tracer High-Resolution Chromatography," *Environ. Lett.* **7**, 321-30 (1974).

13. R. I. Jolley, ed., *Proceedings of the conference on the Environmental Impact of Water Chlorination*, Oak Ridge, Tenn., October 22-24, 1975, CONF-751016 (in press).

12. Biochemical Engineering

Our efforts in biochemical engineering continue to be concentrated in three areas: (1) the kinetics of enzyme-catalyzed processes, (2) bioreactor development, and (3) bioprocess development.

12.1 KINETICS OF ENZYME-CATALYZED PROCESSES

Previous reports^{1, 2} described the use of hydrogenase and ferredoxin enzymes to catalyze the reduction of water with sodium dithionite or pyruvate to produce hydrogen. Experiments aimed at increasing the rate of hydrogen production were continued. Enzyme activities in cell extracts prepared by different methods were compared, and the effect of additional ferredoxin in the cell extracts on the hydrogen production rate was measured. We have continued to explore possible techniques for immobilizing enzymes because, for maximum efficiency of an enzyme-catalyzed process, it is desirable that the enzyme system be reusable.

One of the most effective parameters for changing the rate of enzyme-catalyzed hydrogen production is the concentration of ferredoxin and hydrogenase. To obtain higher enzyme concentrations than were present in cell extracts, the cell extract was distilled at reduced pressure after dialysis. The effect of increasing the enzyme concentration in the reaction mixture on the hydrogen production rate is shown in Fig. 12.1. Measurements were made on small volumes of solution to facilitate easier measurement of pressure changes in a Warburg apparatus. Each reaction was run in 0.05 M potassium phosphate buffer, pH 6.6, at 40°C. The sodium dithionite concentration was about 3 mg/ml for

curves 1, 2, and 3 in Fig. 12.1. To obtain curve 4, 6.0 ml of cell extract was dialyzed against 4 liters of 0.005 M potassium phosphate, pH 6.6, saturated with argon. The dialyze was evaporated at reduced pressure to 0.5 ml and transferred to a Warburg flask with 0.5 ml of water. One milliliter of buffer containing 14 mg of sodium dithionite was added, and the hydrogen produced was measured. The maximum initial rate obtained on curve 4 in Fig. 12.1 corresponds to a hydrogen production rate of about 6 liters (STP) of hydrogen per hour per liter of solution.

In a series of experiments, varying amounts of purified ferredoxin and cell extract were added to reaction mixtures containing 35 mg of sodium dithionite in 10 ml of 0.05 M phosphate buffer, pH 6.6. The amount of hydrogen produced in 10 min at 40°C was measured. The results are summarized in Table 12.1. A comparison of runs 2 and 3 shows the large increase in the hydrogen production rate on the addition of ferredoxin. These results suggest that the cell extract as obtained directly from the cells may be lacking in ferredoxin in terms of the amount required for maximum hydrogen production rate in a cell-free system.

Several possible methods for immobilizing the hydrogenase-ferredoxin enzyme system have been investigated. Methods we have studied include entrapment in polyacrylamide gels and hollow fibers, adsorption on alumina and RPC-5,⁴ and covalent binding through "linker" molecules to Bio-Gel P-150, Chromosorb, alumina, and kieselguhr. In each case the activity of the immobilized enzymes was considerably less than that of the free enzymes. The activity of the immobilized enzymes generally decreased with successive contacts with substrate solution, but activity remained for several days. Figure 12.2 shows typical behavior of the enzymes immobilized on alumina. The alumina-immobilized enzyme was placed in a closed vessel

1. Chem. Technol. Div. Annu. Prog. Rep., Mar. 31, 1975, ORNL-5050, pp. 57-58.

2. C. D. Scott et al., *Experimental Engineering Sect. Semi-annu. Prog. Rep.*, Sept. 1, 1974, to Feb. 28, 1975, ORNL/TM-4961, pp. 211-17.

3. C. D. Scott et al., *Experimental Engineering Sect. Semi-annu. Prog. Rep.*, Mar. 1, 1975, to Aug. 31, 1975, ORNL/TM-5291, pp. 244-53.

4. B. Z. Egan, "Separation of Oligonucleotides by Reversed-Phase Chromatography," *Biochim. Biophys. Acta* 299, 245-52 (1973).

Fig. 12.1. Increasing hydrogen production rates by increasing enzyme concentrations.

Table 12.1. Effect of added ferredoxin on hydrogen production rate

Run	Volume of cell extract (ml)	Amount of ferredoxin added (mg)	Hydrogen produced (ml/10 min)	Relative rate of hydrogen production
1	0	1.0	0	0
2	0.50	0	0.46	1.0
3	0.50	1.0	1.68	3.6
4	0.50	2.0	1.76	3.9
5	1.50	1.0	1.83	4.1

Fig. 12.2. Rates of hydrogen production using alumina-supported enzymes and sodium dithionite substrate.

containing sodium dithionite solution, and the rate of hydrogen formation was measured. The solution was replaced with a fresh dithionite solution after 24 hr (curve 2) and again after 72 hr (curve 3).

The use of the immobilized enzymes in a tapered fluidized bed was demonstrated, as shown schematically in Fig. 12.3.

12.2 BIOREACTOR DEVELOPMENT

The operational characteristics of three continuous chemical reactors as bioreactors were compared using the same bioprocess. The biological degradation of scrub liquors similar to those that arise in coal conversion processes was studied for symbiotic bacterial populations contained in a continuous stirred-tank

Fig. 12.3. Hydrogen production using immobilized enzymes in a tapered fluidized bed.

bioreactor (CSTBR), a packed-bed bioreactor (PBBR) with three phases (air, liquid, and packing coated with bacteria), and a tapered fluidized-bed bioreactor (TFBBR) with three phases. The three bioreactors were of comparable geometric volume so that an approximate comparison could be made of overall degradation rates, regardless of the differences in the individual stagewise mechanisms and mass transfer rates operative in each.

The CSTBR converted the most carbon compounds at the highest concentration, in both synthetic and raw waste liquors, due largely to its long retention times. The maximum CSTBR degradation rate, $Q_L(C_i - C)/V_R$, for 0.99 conversion of phenol concentrations up to 1400 mg/liter was 2.67 g of phenol per day per liter of reactor volume. Conversion of phenol compounds in the three-phase PBBR was comparable to that in the CSTBR, but with the advantage that retention times were reduced to as short as 2 hr for a 500-mg/liter feed and with degradation rates of about two times those of the CSTBR. The three-phase TFBBR achieved the highest degradation rates and lowest attendant retention times of the three bioreactors. In studies

with a 3-liter total geometric reactor volume, a degradation rate of 8.3 g per day per liter of reactor for 0.99 conversion of 750-mg/liter phenol feed was observed; in later experiments with the same tapered column expanded to a 10-liter volume, a degradation rate of 11.0 g day⁻¹ liter⁻¹ was observed for 0.99 conversion of a 100-mg/liter phenol feed. Removal of total organic carbon by all bioreactors was consistently 80 to 99% for operating conditions in which processing of feeds produced 0.99 conversion of phenol and phenol effluent concentrations of 0.5 to 1.0 mg/liter. The efficiency of the TFBBR was such that typical phenol concentrations in its effluent were 0.01 to 0.05 mg/liter. Further experimental results are given in Sect. 12.3.

12.3 BIOPROCESS DEVELOPMENT

A bioprocess is an entire collection of steps (at least one of which involves a biological entity) where a known feed material is modified or transformed by a chemical or physical process into the desired product. The biological entity may be either a living organism or an active fraction derived from a living organism. Since each of the steps constituting a bioprocess is subject to variations, the development of the bioprocess must determine the effects of changes on the entire process to arrive at the optimum configuration.

The existence of a bioprocess implies a change of incoming material to desirable products. Compared with typical chemical processes, bioprocesses are particularly applicable to systems where (1) reacting species are at low concentrations, (2) specific reactions are required, or (3) desired products can only be obtained by biochemical reaction.

As in any process development, the questions that must be addressed are: What is the appropriate type and size of equipment needed? What is the optimum sequence of unit operations to achieve the desired products? Among other things, the following must be considered: (1) the viability of the organisms used, (2) the reaction rates attainable, and (3) the economics of the overall process compared with various competitive processes. Potential areas where bioprocessing may have an attractive future include: (1) removal of organic contaminants from aqueous streams, (2) removal of sulfur from finely ground coal before further processing, (3) removal of trace metallic or organometallic constituents from an aquatic environment, and (4) recovery and/or production of products of value from worthless or low-value feed streams.

Biological process steps are being investigated and developed for use in energy production, resource recovery, and the abatement of environmental pollutants. The approach is oriented in the direction of bench-scale engineering studies that will constitute the first step toward proving process feasibility. Currently, the three specific process areas being investigated are: (1) the use of continuous-flow bioreactors for the abatement of organic pollutants in the effluent streams of energy production facilities, especially coal conversion processes; (2) the use of anaerobic bioreactors for the removal of nitrate from nuclear fuel reprocessing aqueous wastes; and (3) the use of bioreactor systems for the concentration or removal of dissolved metals (including useful resource materials and radioactive waste materials from process waste streams).

Organic Pollution Abatement

Efforts are continuing toward the development of processes to remove biohazardous chemicals from coal conversion aqueous waste streams. The major contaminants to be removed are phenol, thiocyanates, and ammonia. Two different bacterial populations are being used in these studies. A mixed symbiotic population of aerobic bacteria was obtained from Bethlehem Steel Company's activated sludge unit, which is used to treat liquors from coking processes. This population was studied in a CSTBR and a three-phase PBBR for the treatment of a scrub liquor from the coal hydrocarbonization process at ORNL. Phenobac (a commercially available dry-bacteria mixture) was used as the bacterial starting source for studying phenol conversion in a TFBBR.

The Bethlehem population was transplanted and established in our CSTBR and PBBR processes, using a scrub liquor from the coal hydrocarbonization process at ORNL as the feed. Conversion rates comparable to the Bethlehem process (which operates as a CSTBR) were obtained in the test CSTBR.

In Table 12.2, the operation of the ORNL scrub liquor CSTBR is compared with the actual operating conditions at the Bethlehem Plant for treatment of 110,000 gpd (416,394 liters/day) of liquid with a 1500-ppm phenol content. The phenol degradation rate of the ORNL CSTBR compares quite favorably with that of the Bethlehem facility for comparable retention time. Subsequently, a three-phase (solid support for active surface, liquid feed, and air to supply oxygen to the aerobic bacteria) PBBR process using the symbiotic population was tested.

Table 12.2. Phenol conversion in CSTBRs

Operating parameters	Bethlehem CSTBR	ORNL CSTBR	
Weak ammoniacal liquor flow (or equivalent liquor)	110,000 gpd (416,394 liters/day)	120 ml/hr	200 ml/hr
Dilution water	300,000 gpd (1,135,620 liters/day)		
Phenolic flow to bioreactor	410,000 gpd (1,552,014 liters/day)	120 ml/hr	200 ml/hr
Aerator volume	265,000 gal (1,003,131 liters)	2.5 liters	2.5 liters
Clarifier volume	100,000 gal (378,540 liters)	1.0 liter	1.0 liter
Total bio-oxidizer volume	365,000 gal (1,381,671 liters)	3.5 liters	3.5 liters
Sludge recycle	330,000 gpd (1,249,192 liters/day)		
Total flow to aerator and clarifier	740,000 gpd (2,801,196 liters/day)	120 ml/hr	200 ml/hr
Aerator retention time	8.5 hr	21 hr	12.5 hr
Clarifier retention time	3.2 hr	8.3 hr	5.0 hr
Overall bio-oxidation retention time	21.2 hr	29.3 hr	17.5 hr
Degradation rate based on 1500 ppm phenol (365 ppm after Bethlehem dilution)	0.62 g of phenol per day per liter (aerator)	1.75 g of phenol per day per liter (aerator)	2.9 g of phenol per day per liter (aerator)
	0.44 g of phenol per day per liter (bio-oxidizer)	1.25 g of phenol per day per liter (bio-oxidizer)	2.08 g of phenol per day per liter (bio-oxidizer)
Effluent phenol level	0.05 to 0.5 ppm	0.5 to 1.0 ppm	1 to 5 ppm
Effluent thiocyanate level	1 to 20 ppm	1 to 5 ppm	10 to 50 ppm

Seeding of the 1-in.-ID by 3-ft-long (2.5-cm-ID by 0.9-m-long) reactor randomly packed with $\frac{1}{4}$ -in. (0.6-cm) Berl saddles (bed porosity of 0.625) required about one week. Biomass growth on the packing began in the bottom section and then expanded to cover the entire column length. As more surface area became covered by bacteria, the column performance improved proportionately; however, after two months of operation, the biomass (although at its maximum conversion ability) reached sufficient density to significantly affect liquid and air flow rates.

A primary goal of the initial studies with the CSTBR and PBBR was to establish optimum operating conditions that would provide maximum degradation rates compatible with an effluent acceptably low in phenols. Present "best" values are given in Table 12.3. Although both degradation rates may increase as the process improves, it seems likely that their relative rates will remain about the same (i.e., the rate in the PBBR is approximately twice that in the CSTBR). Caution should be exercised in the extrapolation of these results to predict specific conversion for other reactor sizes,

since the conversion is a complex function of reactor dimensions, bacterial rate mechanisms, and three-phase mass transfer characteristics that is not understood. The PBBR conversion rate could safely be extrapolated to reactors of the same length but with different cross-sectional areas.

As previously mentioned, phenol conversion was also studied using Phenobac in a three-phase TFBBR which contained -50 +70 mesh coal as the solid support for adherence of the bacteria. In these experiments, a synthetic feed was used rather than the liquor from the ORNL hydrocarbonization process. In early experiments, when gas was allowed to contact the liquid-biomass-solid system directly, the biomass was separated from the fluidizing solid and washed out of the reactor. Attempts to use air- or oxygen-presaturated feed proved unsatisfactory. A new liquid-solid disengagement unit, recently designed, now permits direct gas sparging without biomass washout.

The three-phase TFBBR has been in operation since January 7, 1976. Initially, the emphasis was on increasing the conversion rate until phenol was detected

Table 12.3. Comparison of degradation rates of phenols in a CSTBR and three-phase FBRR

Type of bioreactor	Reactor volume (liters)	Flow rate (ml/hr)	Phenol concentration in effluent (mg/liter)	Degradation rate ^a
Continuous stirred-tank bioreactor (CSTBR)	3.5	200	0.5 to 1.0	2.0
Three-phase packed-bed bioreactor (PBRR)	0.560	100	1 to 5	5.0

^aGrams of phenol per day per liter of reactor volume.

in the discharge waste. The flow rate was increased from 200 to 800 ml/min at phenol concentrations of about 50 ppm, with little phenol in the discharge.

During the first part of the test period, the bacteria were allowed to grow multilayers on the coal support particle, reducing the number of active bacteria since the total area was decreased. Later, a semicontinuous solid cleaning procedure was used. In this procedure, about 10 liters of coal-bacteria slurry containing about 300 ml of coal (30% of total coal) is removed from the top fluidized bed daily, at 2-hr intervals. Equal amounts of clean or new coal are recharged at the same time at the bottom of the fluidized bed. The bacteria can be removed from the solid coal support ultrasonically or with 3 M NaOH.

When the TFBBR was operated in this manner with a feed containing 100 ppm of phenol at a flow rate of 300 ml/min, no phenol breakthrough or bacterial buildup on the solids was observed. The conversion rate obtained, 5 g of phenol per day per liter (total 10-liter system), was probably not the maximum attainable, because the liquid discharge contained 20 ppm of dissolved oxygen.

Denitrification Tests

Tests of the TFBBR as a bioreactor for denitrification of aqueous waste streams continued.⁵ Two TFBBRs charged with a *Pseudomonas* denitrifying bacteria on anthracite coal particles were operated in series for several months, using a typical low-level nitrate waste as feed (Fig. 12.4). With a 0.04 M nitrate feed at an

Fig. 12.4. Two tapered fluidized-bed bioreactors connected in series.

average flow rate of 14 liters/hr, the average nitrogen conversion rate was 103 g of NO_3^- per day per liter (maximum, 260 g day⁻¹ liter⁻¹) for the first reactor and 66 g of NO_3^- per day per liter for the two reactors in series. The outlet nitrate concentration was consistently less than 0.001 M. In one series of tests, the discharge solution was retained and recycled through the two reactors to give a four-reactor system. Typical results are shown in Table 12.4.

5. C. D. Scott et al., *Experimental Engineering Sect. Semi-annu. Prog. Rep. Mar. 1, 1974, to Aug. 31, 1974*, ORNL/TM-4777, pp. 114-23.

Table 12.4. Nitrate reduction in a four-reactor system

Conditions: Flow rate, 12.0 liters/hr
Reactor volume, 2.5 liters

Nitrate concentration		Reactor	Conversion rate (g NO ₃ ⁻ day ⁻¹ liter ⁻¹)
Molar	μg/liter		
0.054	3510	In	First
	Out		
0.031	2000	In	Second
	Out		
0.016	1040	In	Third
	Out		
0.007	455	In	Fourth
	Out		
<0.001	<60		

Concentration and Isolation of Dissolved Heavy Metals

Certain biological organisms tend to accumulate and significantly concentrate dissolved heavy metals. Within the ecosystem, as these materials progress up a particular food chain, a series of such concentrations can occur, ultimately resulting in levels that are toxic to various plants and animals or to man.

In this regard, the microbial concentration of many radionuclides has been measured. These include ²³⁹Pu, ⁹⁰Sr, ⁸⁵Sr, ¹³⁴Cs, ¹³¹I, and ⁶⁰Co. Generally, the most simple organisms can achieve the highest concentration factors, some microorganisms by as much as 10,000 times. We have found it appropriate to consider utilization of these same microbial "concentrators" in a bioprocess to help alleviate the problem of dissolved heavy-metal contamination.

Although the relationship between microorganisms and dissolved metals is an area of considerable interest, little has been done with regard to the development of technology for utilizing such biological systems for the isolation of dissolved metals. Fluidized-bed systems can be utilized with microorganisms by using fluidized particulates to which microorganisms adhere.⁶ Many microorganisms tend to adhere tenaciously to various types of particulates, thus allowing the microorganisms to be properly handled and moved. The advent of this type of development now allows serious consideration of microorganisms for the isolation of dissolved trace metals.

6. C. D. Scott, C. W. Hancher, and S. E. Shumate II, "A Tapered Fluidized Bed as a Bioreactor," *Proceedings of the Third International Conference on Enzyme Engineering* (1975).

We are approaching the problem in dissolved-metal isolation and concentration in two ways: (1) applied microbiological research, and (2) bioprocess development. The microbiological research is specifically supportive to the process development and is primarily oriented toward establishing equilibrium dissolved-metal accumulation as a function of species and operating parameters. In this regard we have begun to study the uptake of uranium by bacterial and algal populations in small batch experiments.

One set of experiments utilized Phenobac, a mixed culture of *Pseudomonas* bacteria sold commercially for hydrocarbon digestion. The bacteria were grown in a culture medium containing no uranium and then harvested. Equal volumes of harvested cells were subsequently added to flasks containing culture medium and uranium concentrations of 10, 20, and 30 ppm. After 4 hr, the cells were separated from the liquid phase by centrifugation and dried. The cells were then digested using 50% HNO₃. Uranium concentration in the liquid phase of each flask remained constant (within the scatter of the data) throughout the experiments. The results (Table 12.5) are reported in terms of a uranium distribution coefficient, K_u , where

$$K_u = \frac{[U]_{\text{cells}} \cdot \mu\text{g/g dry cells}}{[U]_{\text{liquid}} \cdot \mu\text{g/ml}}$$

Table 12.5. Uranium uptake by Phenobac

[U] _{cells} (μg/g dry cells)	[U] _{liquid} (μg/ml)	K_u (ml/g dry cells)
481	10	48.1
869	20	43.5
2327	30	77.6

We plan to study several types of bacteria and algae for utility in isolation of specific dissolved materials at low concentrations. Most tests will be made in small batch reactors to determine equilibrium conditions. Uranium and strontium are being used as model compounds in determining the optimum conditions for the isolation of dissolved metals.

With regard to bioprocess development, three different types of bioreactors have been constructed and are

being used in metal isolation studies. A CSTBR is being used to study uranium and strontium isolation and concentration by bacterial systems from activated sludges. A TFBBR is being used with another bacterial system, a denitrifying soil bacteria growing on the surface of coal particles. Studies of metal isolation and concentration by algal systems are being made in a three-phase TFBBR equipped with a variable-intensity light source.

13. Coal Technology Program

13.1 COAL HYDROCARBONIZATION AND RESIDUE CARBONIZATION

Fluidized-bed pyrolysis is an important part of coal conversion technology, both in the form of primary coal conversion processes (e.g., in the coal hydrocarbonization process) and as supplemental processes (e.g., in the carbonization of residues). This section describes progress in two projects dealing with pyrolysis in fluidized beds and includes experimental development in support of each project.

Hydrocarbonization is an important type of coal liquefaction process that combines low temperatures, high pressures, and fluidized-bed operation using hydrogen-rich gas for fluidization. The hydrocarbonization process can produce desulfurized char, liquid fuels, and substitute natural gas. The relative yields of these products can be controlled. The char is suitable for use without stack-gas treatment in fluidized-bed or traveling-grate boilers. The liquid fuels include naphtha, light gas oils, and heavy gas oils. Conditions for hydrocarbonization include temperatures up to 1200° F (650° C) and pressures up to 80 atm (1200 psi or 8100 kPa), but optimum conditions may be significantly milder.

The objectives of the ORNL coal hydrocarbonization project are: (1) to estimate the optimum conditions for the operation of fluidized-bed hydrocarbonization reactors; (2) to operate a bench-scale fluidized-bed reactor capable of continuously processing 10 lb of coal per hour (1.3 g/sec) at conditions up to and including 1200° F (650° C) and 80 atm (8100 kPa); and (3) to establish hydrocarbonization conditions favoring reliable operability, low char yield, and economical operation.

Carbonization of solids-laden residues in a fluidized-bed reactor will be a supplemental process for many coal liquefaction plants. Solids may be removed from primary coal liquids by vacuum distillation and solvent extraction. The residue (bottoms or underflows) from these operations will

contain appreciable quantities of valuable product liquid and, in the case of extraction, part of the solvent. Economic processing of coal depends on recovering these liquids. Even if economics were not a factor, disposal of residues would be a problem if the liquid were not removed. Carbonization of these residues will recover most of the volatile material.

The objectives of the residue carbonization project are: (1) to modify and utilize an existing atmospheric-pressure hydrocarbonization reactor for residue carbonization, and (2) to establish optimum temperature and feed rates for recovering 90% of volatile material contained in H-Coal vacuum distillation residuum and Solvent-refined Coal (SRC) and Consol Synthetic Fuel solvent extraction underflows.

Experimental development. Two- and three-dimensional Lucite mockups of a recirculating fluidized-bed reactor were operated over a range of conditions to obtain data for modeling and design of the high-temperature experiments. In cooperation with the MIT School of Chemical Engineering Practice, preliminary mathematical models were developed and applied to the data with limited success. A simple empirical correlation was also developed (Fig. 13.1) and used to select gas flow rates for a successful high-temperature experiment.

A rotary coal feeder and coal flow monitor were developed and installed in the bench-scale hydrocarbonizer. Coal was pneumatically transported into the fluidized-bed reactor. A ball valve was modified so that the ball became a cup that could be rotated, slowly feeding coal from a pressurized hopper into the transport line. Coal flow may be monitored by measuring the changes in the temperature difference between the fluid upstream and downstream of a heated segment of the transport line.

Fluidized-bed carbonization and hydrocarbonization experiments were conducted in a batch reactor system operated at atmospheric pressure, using Wyoming subbituminous coal (-50 + 140 mesh) and a heating rate of approximately 20° F/min

- ZERO OR UNSATISFACTORY CIRCULATION
- SATISFACTORY CIRCULATION
- OPERATING POINT PREDICTED BY CORRELATION

Fig. 13.1. Recirculation of AHC-9 char through $\frac{1}{2}$ -in. draft tube in a 4-in.-diam bed.

($\sim 0.2^\circ\text{C/sec}$). Review and evaluation of previous hydrocarbonization data had indicated that the maximum liquid yield would be obtained at 1020°F (550°C); data from these experiments were consistent with this predicted value. A single test of the recirculating fluidized-bed reactor was completed; and although the results were inconclusive, the data suggest that higher liquid yields may be obtained with this mode of operation, probably because of decreased residence time for evolved vapors.

Bench-scale Hydrocarbonization Experiment. A hydrocarbonization reactor system was fabricated and installed in Building 2528 (Fig. 13.2). The reactor is designed to process coal at a nominal feed rate of 10 lb/hr (1.3 g/sec) at temperatures up to 1250°F .

I. J. M. Holmes, H. D. Cochran, Jr., M. S. Edwards, D. S. Joy, and P. M. Lantz, *Hydrocarbonization Research Phase I Report: Review and Evaluation of Hydrocarbonization Data*, ORNL TM-4835 (August 1975).

Fig. 13.2. Bench-scale Hydrocarbonization Experiment during installation.

(680°C) and pressures up to 20 atm (2000 kPa). Minimal facilities are provided for coal pretreatment, gas handling, and product recovery so that emphasis can be focused on the reactor.

At the end of this report period, the system was ready for routine operation. Design is under way to modify the present system for operating at hydrogen pressures up to 80 atm (8100 kPa). Extensive safety reviews have been completed; these have been concerned primarily with hazards associated with handling hydrogen and polynuclear aromatic hydrocarbons. Three months of shakedown tests (during final installation) using nitrogen as the fluidizing gas and one month of shakedown tests with hydrogen as the fluidizing gas have been completed; routine operation is expected to begin in April 1976. In the initial set of experiments, a low-sulfur Wyoming subbituminous coal will be hydrocarbonized at varying temperatures and pressures in a uniformly fluidized bed. A recirculating fluidized bed will also be tested.

Residue carbonization. Three tasks are included in this new project, which was initiated in November 1975: (1) review and evaluation of low-temperature carbonizer operation at the Consolidation Coal Company's pilot plant at Cresap, West Virginia; (2) modification of the atmospheric-pressure hydrocarbonization system to permit continuous feeding of coal conversion residue; and (3) determination of carbonization temperatures and feed rates that will maximize liquid yields from three different residues. The first two of these tasks were completed during the current report period, and experimentation with the highly agglomerating H-Coal residue has begun.

13.2 SEPARATIONS TECHNOLOGY

Following the Phase I review² of coal liquefaction processes, scouting tests to separate solids from the liquid streams were initiated in the following areas: agglomeration, settling, centrifugation, filtration, and solvent fractionation. Materials from the SRC and Char Oil Energy Development (COED) processes were used exclusively, as directed by ERDA. In addition, characterization analyses were begun to define physical and chemical properties of major coal liquefaction processes. A major effort was expended in characterizing process solids by particle size

distributions because of their relevance to solid-liquid separations.

Some degree of agglomeration was produced by aromatic solvents (e.g., toluene). These solvents produced filtration rate increases due to the reduced viscosities and the effect of agglomeration on filter-bed packing characteristics. The filtrates from these fractionated mixtures were relatively free of sulfur and ash.³ Solvent agglomeration-fractionation (SAF), followed by settling at elevated temperatures and pressures, also shows promise as a solids separation scheme for SRC and similar processes. A 5 to 20% solvent content appears to be adequate to produce agglomeration and to increase settling or filtration rates. Settling is most rapid in the temperature range 300 to 350°C (573 to 623°K), but excellent results have also been obtained at 150°C (423°K) and 20% toluene concentration. In most cases, the filtrate from SAF meets the Environmental Protection Agency (EPA) guidelines for ash and sulfur and could be used directly as a boiler fuel. A preliminary economic evaluation of SAF, followed by settling and filtration of the bottoms material, shows a \$3.50 bbl (\$22.02 m³) cost advantage for the SRC process over conventional rotary drum filtration (3:1 solvent:coal ratio). For processes that filter product only, the filtration costs would be reduced from about \$1.00 bbl (\$6.29 m³) to about \$0.20 bbl (\$1.26 m³).

Filtrations of raw, unfiltered oil (UFO) from the SRC-Wilsonville process were examined by precoat filtration techniques.⁴ Results of these examinations indicated that ground coal could be used as a precoat up to a temperature of about 450°F (505°K).⁵ Figure 13.3 shows the allowable mesh sizes and filtration rate increases obtained. Table 13.1 shows that the filtrates meet EPA standards with regard to ash and sulfur contents (0.15 and 0.96% respectively). This represents a considerable process improvement and will be explored further at bench scale. Coal and diatomaceous earth were also found to be beneficial when added to the prefiltration stream as a body feed

2. 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).

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

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

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

Fig. 13.3. Effect of coal precoat particle size on filtration of SRC-UFO.

Table 13.1. Ash and sulfur analyses of SRC-UFO filtrates from coal precoat filtration

Precoat coal (mesh size)	Filtrate analyses	
	Ash (wt %)	Sulfur (wt %)
100 x 120	0.12	0.69
120 x 150	<0.05	0.61
150 x 170	<0.05	0.65
170 x 200	<0.05	0.66

(see Fig. 13.4). Filter cake compressibility of SRC solids was found to be moderate (i.e., 0.5), but early indications are that the cakes may become incompressible above 50 psi (3.45×10^5 Pa). Other filtration equation parameters that were determined⁶ will allow predictions at various operating conditions and facilitate preliminary scale-up studies.

Additive agglomeration studies using solid additives have been continued as an ongoing, low-priority effort since April 1975. Excellent results were obtained with the laboratory-scale apparatus using liquid additives designed for the petroleum industry. Twenty-four proprietary additives from the Tretolite

Division, Petrolite Corporation, were tested. One produced excellent clarification of upper fractions from a settling test, while three others yielded good clarification. The results appear to be valid over a range of temperatures. Other inexpensive, commercially available chemical additives that need not be recovered have also shown promise as settling accelerators.⁷

Initial construction of the 1-liter bench-scale apparatus was completed. Pneumatic pressure tests revealed a few inadequacies, which were subsequently corrected. The integrity of the apparatus was tested at 300-psig (21.7×10^5 Pa) air pressure (110% design pressure) for 1 hr (3600 sec). Preliminary tests using filtered oil verified the operability of other system components such as heaters, controllers, and recorders. Initial results for SRC-UFO indicated that settling characteristics of this material in the bench-

6. S. Katz and B. R. Rodgers, "A Laboratory Evaluation of Precoat Filtration Parameters for the Solvent Refined Coal Process," to be published in *Industrial and Engineering Chemistry, Process Design and Development*.

7. J. P. Nichols (Program Director), *Coal Technol. Program Q. Prog. Rep. Dec. 31, 1975*, ORNL-5120 (March 1976).

8. J. P. Nichols (Program Director), *Coal Technol. Program Q. Prog. Rep. Mar. 31, 1976*, ORNL-5159 (May 1976).

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Fig. 13.4. Precoat filtrations of SRC unfiltered oil with body feed.

scale apparatus were similar to those obtained with the laboratory-scale apparatus. However, settling times have been longer for the additive SRC-UFO mixtures, and a number of modifications to the settler are in progress.⁹

Characterization analyses of SRC and COED process materials have been reported elsewhere^{4-7,9} and include the following: sample aging tests, particle size distributions determined by the use of the electron microscope, gel permeation chromatography, viscosity-temperature measurements, petro-

graphic analyses, ultimate analyses, proximate analyses, spectrographic analyses, and neutron activation analyses.

13.3 COAL CONVERSION PROCESS DEVELOPMENT

In situ gasification of coal, presently under active development by the Energy Research and Development Administration, entails injection of oxygen or air with or without steam into a coal seam which has been fractured previously by explosives, high-pressure liquid injection, or some other means. The presence of injected oxygen permits ignition of the coal and subsequent

9. J. P. Nichols (Program Director), *Coal Technol. Program Q. Prog. Rep. Sept. 30, 1975*, ORNL-5093 (December 1975).

maintenance of a combustion front which moves through the coal bed, producing an intermediate-Btu product gas which is piped to the surface. Pyrolysis of coal ahead of the combustion front is an important part of the process, but pyrolysis studies have traditionally dealt only with small coal particles which were heated quite rapidly. By contrast, in situ gasification involves the slow heating of large coal blocks resulting from permeability enhancement operations or, possibly, roof collapse. Conversion of these large masses is necessary for improving overall utilization of the available resource.

The specific objective of the ORNL program supportive of underground coal gasification development has been to generate data on the pyrolysis of large coal blocks under conditions which can be expected to occur underground. The effects of heating rate, maximum temperature, and cover gas

composition on reaction rates and products of coal pyrolysis are being determined to aid in the design of field experiments and in process scale-up and optimization.

Two-dimensional pyrolysis studies. Simulation of in situ pyrolysis has consisted in experiments utilizing large, instrumented blocks of subbituminous coal. Maximum reactor temperatures of 500 to 1000°C (773 to 1273°K) have been achieved over periods of 4 to 27 hr (1.44×10^5 to 9.72×10^5 sec). The apparatus for Fig. 13.5 is a schematic representation of the block pyrolysis apparatus showing provision for liquid product collection and gas analysis. Heat is supplied by a programmable furnace system which provides three-mode control of the heating rate between 0.1 and 10°C/min (3×10^{-5} and 3×10^{-3} °K/sec). (Heating rates are referenced to the surface of the coal block being pyrolyzed.) Details of block

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preparation, instrumentation, and analysis have been presented elsewhere.¹⁰

Figure 13.6 shows a typical series of thermal wave forms observed during a high-temperature pyrolysis experiment; temperature is plotted as a function of dimensionless distance from the center of the coal block (r/R_0). These wave forms suggest two interesting conclusions. First, uneven burning effects are not seen: all probes appear to describe a single thermal profile. Second, axial probes at the top of the block measure temperatures that fall upon the radial profile, whereas the bottom of the block does not appear to be heating. We conclude that pyrolysis of the block proceeds radially inward and axially downward, but not axially upward. Convective effects are probably responsible for this behavior.

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

Fig. 13.6. Typical thermal wave forms observed during two-dimensional coal pyrolysis experiments.

The rates of heating at various points within the block are indicated in Fig. 13.7. These curves clearly show an initial period in which the entire block is heated rather uniformly to 373° K, followed by a final period in which heat transfer is rate-limited by vaporization of water. Temperature overshoot at the sample interior indicates that exothermic reactions dominate high-temperature pyrolysis. These results have been discussed extensively with Lawrence Livermore Laboratory researchers, whose modeling efforts include the development of a computer code that describes the kinetics of two-dimensional coal pyrolysis.¹¹ Measured temperature profiles for ORNL test blocks will be used to "drive" the model, which has been divided into annular segments. Calculated gas production rates and compositions will be compared with measured results.

Char pyrophoricity. Char produced in an early experiment exhibited marked pyrophoricity, a phenomenon not reported by other researchers. Since material of this type was not obtained in several subsequent tests which were made under similar conditions, the pyrophoricity observed previously was thought to have been an anomalous result. Recent experiments, however, have consistently produced highly pyrophoric chars, and preliminary data suggest that the pyrophoricity may be a function of the maximum pyrolysis temperature (lower temperatures appear to produce more pyrophoric materials).

A brief survey of the literature describing the pyrophoricity of various substances (coal, lignites, or heavy-metal powders) failed to uncover a reference to pyrophoric chars but did provide many detailed theories concerned with the mechanism of self-ignition and ways to prevent this behavior. A bibliography containing more than 300 literature references to pyrophoricity and related problems has been compiled.

Techniques for disengagement of coal tar aerosol. Rapid cooling of condensable organic vapors produced by pyrolysis of coal leads to the formation of aerosols that are extremely difficult to separate from the product gas stream. The problems encountered in recovering these aerosols led us to conduct some short-term scouting tests of traditional disengagement techniques. The objectives of these tests were to improve the results obtained from the pyrolysis and to provide recommendations for others in the ORNL Coal Technology Program who might

11. Jack Campbell, Lawrence Livermore Laboratory, personal communication, November 1975.

Fig. 13.7. Variation of heating rate within a large coal block during pyrolysis.

Table 13.2. Qualitative evaluation of some traditional disengagement techniques for trapping coal-derived aerosols

Device ^a	Evaluation and comments
Spray towers	Ineffective
Bubble columns	Ineffective
Packed towers	Very effective
Cartridge-type string filters	Very effective
Electrostatic precipitator	Partially effective
Glass-wool demisters	Partially effective
Internal cooling coils and glass wool	Effective

^aThese were one-stage devices using water as the working fluid. Tests using an organic solvent with a low vapor pressure (e.g., methyl naphthalene) are planned.

have experienced similar difficulties relative to aerosol disengagement. Qualitative evaluations of systems tested to date are shown in Table 13.2.

13.4 ENGINEERING EVALUATION OF THE SYNTHOIL PROCESS

Oak Ridge National Laboratory is currently engaged in the engineering and economic evaluation of the Synthoil process, a fixed-bed catalytic hydrogenation process for the production of desulfurized fuel oil from coal. The work is being conducted for the Division of Fossil Demonstration Plants, ERDA-Fossil Energy. The objectives of the evaluation include the following:

1. to provide estimates of the costs of producing synthetic fuels from coal on a commercial scale, for comparison with other processes or sources of energy;
2. to assess the state of development of the process in terms of the experimental data available, the adequacy of the data for design purposes, possible areas of difficulty in process or equipment scale-up, and the status of the process as a candidate for commercial demonstration;
3. to provide recommendations for additional process or equipment research and development where needed.

The evaluation will be based on a complete conceptual process design for a 100,000-bbl-per-stream-day ($0.18 \text{ m}^3/\text{sec}$ or $15,900 \text{ m}^3/\text{day}$) "grass-roots" Synthoil facility. The design will include flow diagrams, mass and energy balances, equipment sizing, and cost estimates. Work on the evaluation began on April 8, 1975, and is scheduled to be completed by September 1, 1976.

The first phase of the engineering evaluation, which is now complete, was devoted to the gathering of information and data for the various processes involved and to the preparation of preliminary bases for design for the various process units. A preliminary assessment of the adequacy of the data base for process design purposes was also made. An overall block flow diagram for the Synthoil facility was prepared, and the ancillary processes required were specified. This work was summarized in an interim report.¹²

The material balance and operating conditions of the Synthoil unit were based on experimental bench-scale work done by the U.S. Bureau of Mines Pittsburgh Energy Research Center. Examination of

the experimental data thus far available indicates that a conceptual plant design suitable for evaluation purposes can be completed, but that numerous assumptions regarding operating conditions, yields, and product characteristics will have to be made. The economic evaluation based on the conceptual design will, therefore, be subject to revision when further process data are obtained. However, the conceptual design and evaluation will be useful in that they will serve to focus attention on those parts of the Synthoil process that are the most important determinants of the overall cost and will indicate the additional experimental data needed for design of a commercial facility.

The information base available for the ancillary processes is adequate for full-scale design, with the exception of the solids-liquid separation process. Additional bench-scale experimentation is needed before any conclusions can be reached regarding the sizes, types, and costs of the equipment required. Present indications are that this section of the Synthoil plant will be quite expensive. This factor accentuates the importance of obtaining more experimental data on the separation of the solid-liquid materials involved. Related studies in progress on similar streams from other coal-conversion processes should also yield results that will prove useful in this area.

The current status of the evaluation may be summarized as follows: Flow diagrams and heat and material balances have been completed for all process units of the Synthoil facility with the exception of the sulfur, ammonia, and oxygen plants. These are all proprietary units for which simplified flow diagrams will be presented. The overall utilities requirements have been determined; a utilities system balance has been reached for steam, water, electricity, and fuel gas; and utilities systems flow diagrams have been completed. All major equipment items in the various process units have been sized, and materials of construction have been tentatively selected. Preparation of a preliminary cost estimate is under way, and an initial version of a computer code for cost estimation by the factor method is now operational. Costs for the proprietary process units will be obtained from vendors.

12. Royes Salmon et al., *Engineering Evaluations of Coal Conversion Processes, Part I. Hydrocarbonization and Synthoil. Information Base, Process Selection, and Preliminary Evaluation of Alternatives*, ORNL TM-5034 (in preparation).

13.5 ENGINEERING EVALUATION OF A HYDROCARBONIZATION PROCESS

A hydrocarbonization process is being evaluated for ERDA-Fossil Energy; completion of the evaluation is scheduled for September 1, 1976. The process will have a basic yield of char, oil, and gas products with a total heating value comparable to 100,000 bbl (15,900 m³) of 6.4×10^7 -Btu bbl fuel oil (4.25×10^{10} J m³) per day, and the total coal feed to the plant will be about 40,700 tons (3.69×10^7 kg) of bituminous coal per day.

The hydrocarbonization process involves a two-stage carbonization in beds fluidized with recycle gas from the carbonization. In order to obtain adequate desulfurization of the char during carbonization, the coal feed must be beneficiated. The coal is separated into a low-sulfur, low-ash fraction and a high-sulfur, high-ash fraction. In the process selected for evaluation, the latter fraction will be fed to a fluid-bed combustor that will supply heat to the hydrocarbonization reactor by heating the recycle gas stream. The low-sulfur, low-ash fraction is carbonized to form a mixture of desulfurized char, coal liquids, and a gas stream. The coal liquids and gases are

processed further to yield clean, marketable fuel oil and pipeline gas products respectively.

The process chosen for evaluation is based on the U.S. Steel Clean Coke process; a schematic diagram of the basic hydrocarbonization step is shown in Fig. 13.8. The low-sulfur, low-ash fraction (68% of coal feed) is fed to the first-stage hydrocarbonizer operating at 840° F (449° C), where most of the coal liquids are produced. Semichar produced in stage I is fed to the second stage, where the char is desulfurized at 1380° F (749° C) by a recycle gas stream. The char product from the second stage is cooled and slurried with water for shipment in a pipeline. The off-gases from the reactors are quenched to condense the oils and tars that are hydrotreated and filtered to produce a low-sulfur fuel oil. The make gas stream from the quench systems is treated to remove the acid gases (H₂S and CO₂). A large portion of this gas is recycled to the reactors. The remaining gas is purified and sent to a cryogenic separation unit to produce a high-purity hydrogen stream and a pipeline gas stream. A similar gas treatment is performed on the make gas from the hydrotreater. However, since the purpose of this section is to supply the hydrogen requirements for the hydrotreater, a reformer is used to form

Fig. 13.8. Hydrocarbonization process.

hydrogen from the light hydrocarbon gases. The hydrogen is then purified and recycled to the hydrotreater.

A list of the feed and product streams is shown in Table 13.3. The potential heat for each stream is also listed, showing the process to have a thermal efficiency of 70.15%. Specific details on the other processing units of importance are discussed below.

(1) Coal preparation, beneficiation, and drying.

To provide the hydrocarbonization process with both high- and low-grade coal feedstocks, the engineering design for a coal processing plant has been developed with a daily capacity of 48,135 tons (4.37×10^7 kg) of run-of-mine coal with high ash and sulfur contents. The operations of the coal plant include receiving, preparation, line storage, conveying, beneficiation, and drying operations. The general plant, which for study purposes was assumed to be located in or near southern Illinois, will process an hvCb (high-volatile C bituminous) Illinois No. 6 coal. The coal supply will be procured from several local mines because of the unusually large coal requirement.

The coal beneficiation plant will have a nominal capacity of 1750 tons/hr (TPH) (1.59×10^6 kg/hr).

Three complete parallel washing lines, with a nominal capacity of 875 TPH (793,786 kg/hr) each are proposed. The washing throughput will be handled with two lines operating 24 hr/day, on a seven-day-per-week basis. Because erosion and corrosion are severe in coal washing plants, the third line will be down for scheduled maintenance while the other two lines are in operation and, therefore, would be available in the event of equipment failure.

The objective for the beneficiation plant is to provide a high-grade coal (low-ash, low-sulfur) feedstock to the hydrocarbonization unit and a low-grade coal (high-ash, high-sulfur) feedstock to the fluid-bed combustor unit in a ratio of at least 3:1 with a minimum refuse stream. A simplified flowsheet of the beneficiation process is shown in Fig. 13.9. The process¹³ ultimately developed will separate the raw coal (2 in. $\times$ 0) into coarse (2 in. $\times$ 28 mesh) and fine (28 mesh $\times$ 0) fractions. The coarse fraction will be processed in a two-stage cycloid operation utilizing a heavy medium (magnetite). The float fraction from

13. McNally-Pittsburg Manufacturing Company, under sub-contract to Union Carbide Corporation Nuclear Division, provided the basic process design and equipment selection.

Table 13.3. Feed and product streams from the hydrocarbonization process

Component	Flow (tons/day) [kg/day]	Higher heating value (Btu/lb) [J/kg]	Potential heat (Btu/day) [J/day]
Raw coal (maf) ^a	33,686.8 [30,560 $\times 10^3$]	14,438 [33,582 $\times 10^6$]	9.727×10^{11} [1.026 $\times 10^{15}$]
Products			
Char (maf) ^a	15,827.6 [14,359 $\times 10^3$]	14,821 [34,474 $\times 10^6$]	4.692×10^{11} [4.950 $\times 10^{14}$]
Pipeline gas	1,307.7 [1,186 $\times 10^3$]	24,062 [55,968 $\times 10^6$]	6.293×10^{10} [6.639 $\times 10^{13}$]
Oil + naphtha	3,974.3 [3,605 $\times 10^3$]	18,200 [42,333 $\times 10^6$]	1.447×10^{11} [1.527 $\times 10^{14}$]
Sulfur	519.3 [4.711 $\times 10^5$]	3,983 [9,264 $\times 10^6$]	4.14×10^8 [4.370 $\times 10^{11}$]
NH ₃	251.24 [2.279 $\times 10^5$]	9,668 [22,488 $\times 10^6$]	4.868×10^9 [5.136 $\times 10^{12}$]
Phenols	52.15 [4.731 $\times 10^4$]	2,383 [5,543 $\times 10^6$]	2.49×10^8 [2.627 $\times 10^{11}$]
Total products			6.824×10^{11} [7.200 $\times 10^{14}$]
Thermal efficiency	70.15%		

^amaf = moisture- and ash-free basis.

Fig. 13.9. Simplified flowsheet for the beneficiation of raw coal.

the first stage (sp gr. 1.40), after crushing to $\frac{1}{4}$ in. $\times$ 0, dewatering, and drying, is the major portion of the high-grade coal stream. The sink fraction from the first stage is the second-stage feed slurry (sp gr. 1.85). The float fraction from the second stage after crushing, dewatering, and drying becomes the greater portion of the low-grade coal stream.

The fine coal (28 mesh $\times$ 0) is processed in a classifying cyclone to effect separation of the coal fines at ± 100 mesh. The 28 $\times$ 100 mesh material, which is lowest in ash and sulfur contents, is combined with the high-grade coal. The 100 mesh $\times$ 0 material reports to the low-grade coal.

The ratio of high-grade to low-grade coal is 4:1; however, 4064 TPD (3.69×10^6 kg. day) of raw coal bypasses the beneficiation process and is combined with the low-grade stream to provide the amount of fuel needed by the fluid-bed combustor. The underflow from the second-stage separation utilizing a heavy medium contains very high ash and sulfur contents and is discarded.

Table 13.4 summarizes the data for the raw coal feed and products from the beneficiation plant. According to these data, the refuse stream amounts to 6.30 wt % of the total capacity; however, the actual coal value losses in the refuse stream are 1.99 wt %, indicating a 98.01% recovery of the total coal value.

(2) **Hydrotreating section.** Oil hydrotreating serves three useful purposes: (1) stabilization of the oil to prevent polymerization, (2) hydrocracking to form lower-molecular-weight hydrocarbon liquids and gases, and (3) removal of the heteroatoms (S, N, and O) in the form of H_2S , NH_3 , and H_2O . Each of these steps consumes hydrogen, which is supplied to the reactor as a high-priority gas at elevated temperatures and pressures. The reactions take place in the presence of a catalyst.

An ebulating bed reactor was chosen for the hydrocarbonization process because it can handle a feed stream containing a small amount of solids. If a fixed-bed reactor were used, the feed stream would have to be filtered before hydrotreating. It is anticipated that initial hydrotreating of the heavy tars followed by filtration of the lighter product would be a more efficient operation.

The hydrotreated oil product, which contains approximately 0.2% sulfur, will have a gravity of 10 to 12° API (American Petroleum Institute gravity). The unhydrotreated tar had a gravity of -15° API and contained over 2% sulfur.

(3) **Fluidized-bed combustion system.** A fluidized-bed combustion (FBC) system was chosen to generate most of the process heating and steam for the hydrocarbonization plant. Based on preliminary

Table 13.4. Summary of data for the beneficiation plant process

	MF coal ^a (tons/day) [kg/day]	Ash (wt %)	Sulfur (wt %)	Stream (wt %)
Feed				
Raw coal	40,664.88 ^b [36,890 x 10 ⁶]	17.16	3.01	100
Product				
High-grade coal	27,473.77 [24,924 x 10 ⁶]	8.56	2.20	67.56
Low-grade coal	6,564.70 [5,956 x 10 ⁶]	31.47	3.75	16.14
Combined coal to fluid-bed combustor	10,629.70 ^b [9,643 x 10 ⁶]	26.0	3.47	26.14
Reuse stream	2,561.40 [2,324 x 10 ⁶]	71.35	9.76	6.30

^aMF = moisture-free.^bIncludes the quantity of MF raw coal (4064.52 TPD) that bypasses beneficiation.

cost studies, this system offers the lowest cost approach and a more straightforward matching to the plant heating requirements relative to a low-Btu gasifier or a conventional coal-fired system with stack-gas scrubbing.

A total of 2325 MW(t) (2.325×10^9 J sec) of heating is developed by burning the high-ash, high-sulfur coal stream from the coal beneficiation system. The FBC system consists of six modules, each having seven vertically stacked fluidized beds arranged in a 15- by 36-ft (4.57- by 10.97-m) area. A typical module is shown in Fig. 13.10. The six modules with associated coal and limestone handling equipment, air and gas equipment, and interconnecting ducting occupy an area of 240 by 420 ft (73.15 by 128.02 m). The tops of the coal bunkers are 164 ft (50.00 m) above ground elevation, and the bottoms of the FBC modules are 25 ft (7.62 m) below ground level.

Because of the specialized nature and development status of FBC technology, the conceptual design and cost estimate of the FBC system are being developed through a subcontract with the Fluidized Bed Company (a consortium formed by the Foster Wheeler Corporation and Pope, Evans, and Robbins, the leading designers, constructors, and operators of coal-fired fluidized beds in the United States).

(4) **Fuel oil-solids separation.** The fuel oil-solids separation plant (unit 19) has been designed to use precoat rotary drum filtration. Filtration at about 350° F (177° C) is required in order to remove micron-sized solids from the liquid product. At this

temperature, the use of coal as a precoat is feasible [above 450° F (232° C), coal would not be suitable]. Therefore, a sized fraction of coal is sent from beneficiation (unit 11) to unit 19 and used as a filter aid. This coal returns, along with collected solids, to the hydrocarbonization reactors in unit 12.

13.6 ENGINEERING EVALUATIONS OF NUCLEAR PROCESS HEAT FOR COAL CONVERSION

A critical evaluation was made of the concept of using graphite-moderated gas-cooled high-temperature reactors (HTGRs) as a source of high-temperature process heat in coal conversion. Interim reports^{14,15} were prepared, and a final report to ERDA-Fossil Energy¹⁶ was drafted. The final report, which is now undergoing review, includes the following topics: (1) a discussion of the rationale for developing nuclear process heat for coal conversion; (2) a comparison (overview) of the electrolytic and thermochemical routes for producing hydrogen from water; (3) the application of external hydrogen from

14. J. E. Jones, Jr., and W. R. Gambill, *Interim Report on Assessment of VHTRs in Process Applications* (Draft) (August 1975).

15. I. Spiewak, J. E. Jones, Jr., and W. R. Gambill, *Assessment of Very High-Temperature Reactors in Process Applications* (Draft), ORNL TM-5242 (February 1976).

16. W. R. Gambill, C. C. Littlefield, R. H. Cooper, Jr., and J. E. Jones, Jr., *A Critical Evaluation of the Application of Gas-Cooled Reactors to Coal Conversion* (Draft), ORNL TM-5341 (March 1976).

Fig. 13.10. Fluidized-bed combustion module.

a thermochemical water-splitting unit to fuels synthesis (synocrude, substitute natural gas, methanol, and gasoline); (4) the evaluation of a coal liquefaction process using either a nuclear or a fossil heat source for reforming; (5) a conceptual design of a coal-steam direct gasification process heated by a gas-cooled reactor; and (6) a review of candidate materials for process heat exchangers (for convective reformers, steam gasifiers, and a thermochemical hydrogen process). The major developmental problems include high-temperature materials, safety-related questions (especially those regarding the need for an intermediate heat exchanger), and the design of a viable process heat exchanger. The use of nuclear process heat in coal conversion does not appear particularly attractive at present coal prices, but this situation could change if the price of coal rises sufficiently.

A comprehensive ORNL report to ERDA (which includes the coal-conversion evaluations) also treats

a wide range of other potential HTGR applications, including petroleum refining, steel production, processing of oil shale and tar sands, and peaking power generation, as partially depicted in Fig. 13.11.¹⁷ The concepts and technology were evaluated for producing process stream temperatures of 1200, 1400, 1600, 1800, and 2000 F (649, 760, 871, 982, and 1093 C respectively).

Fossil Energy funding for further gas-cooled reactor Coal Conversion evaluations was terminated in February 1976, and any additional work will be conducted under the Nuclear Research and Applications program.

¹⁷ J. E. Jones, Jr., J. Spewak, and W. R. Gambill, "Assessment of Very High-Temperature Reactors in Process Applications," paper to be presented at the Eleventh International Energy Conversion Engineering Conference, September 1976.

Fig. 13.11. Potential nuclear process heat application.

14. Actinide Oxides, Nitrides, and Carbides

14.1 THERMODYNAMICS OF THE Pu-C-O SYSTEM

A critical assessment has been made of the equilibrium phase diagrams and other thermodynamic data for the Pu-C-O system. In addition, the literature describing the reaction of PuO_2 and carbon to form plutonium carbides and oxycarbides has been examined. A paper describing the results of these studies is being prepared for submission to the *Journal of Nuclear Materials*. The abstract follows:

"Thermodynamics of the Conversion of Plutonium Dioxide to Plutonium Monocarbide," by T. M. Besmann and T. B. Lindemer. *Abstract:* The present study contains an equilibrium thermodynamic analysis of the Pu-C-O system and a discussion from an equilibrium thermodynamic point of view of the direct carbothermic reduction and two-step carbothermic-hydrogen reduction of PuO_2 to PuC_{1-x} . Included are considerations of the partial pressures of the various species in the Pu-C-O and Pu-C-H systems, the process parameters required for conversion of the oxide to the carbide, and the loss of plutonium due to evaporation.

14.2 TRANSITION METAL-U-N PHASE EQUILIBRIA

Studies are being conducted to determine the thermodynamic conditions for interactions of the iron, nickel,

and chromium components of stainless steel with the U-N system. The majority of the interaction compounds have the composition UM_2 , where $\text{M} = \text{Fe}, \text{Ni},$ or Cr , and have closely related crystallographic structures called Laves phases. These investigations have led to the prediction and identification of many previously unknown UM_2 compositions resulting from extensive mutual substitution of iron, nickel, and chromium as the "M" component. A paper describing one set of results has been accepted for publication in the *Journal of the Less-Common Metals*. The abstract follows:

"Laves Phases of Uranium and 3d Transition Metals," by E. C. Beahm, C. A. Culpepper,¹ and O. B. Cavin.² *Abstract:* Laves phases of uranium and 3d transition metals have been investigated theoretically and experimentally. 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 hybridization. Simple equations are presented to calculate interatomic distances and composition limits of these Laves phases. Lattice constants for Laves phases in the U-Cr-Fe, U-Cr-Co, and U-Cr-Fe-Ni systems are also presented and discussed.

1. Solid State Division.

2. Metals and Ceramics Division.

15. Studies in Chemical Engineering Science

15.1 THREE-PHASE FLUIDIZED-BED REACTING SYSTEMS

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. The liquid forms the continuous phase, while the gas and solids are discontinuous. A check of the literature plus preliminary mass transfer experiments¹ with an air-CO₂-water-solids system has indicated that the hydrodynamics of these systems are not understood well enough to permit meaningful interpretation of mass transfer data. Thus a study of the hydrodynamic characteristics of these systems has been initiated. Details of the experimental apparatus, procedure, and data analysis will be reported elsewhere.

Experimental results in a 7.62-cm-ID column with distinct bed heights of 4.6-mm glass beads have shown the influence of fluid (liquid and gas) flow rates and liquid viscosity on the holdup of each phase and the onset of fluidization. Figure 15.1 illustrates the effect of fluid flow rates on the phase holdups for one liquid viscosity (3.8 cP). As the liquid velocity increased, the bed expanded, accompanied by a significant decrease in the solid volume fraction and a corresponding increase in the liquid volume fraction. The gas holdup was only slightly affected. An increase in the gas velocity caused the gas holdup to increase with a corresponding decrease in the liquid holdup. The gas velocity had a negligible effect on the solid volume fraction. Experiments with aqueous glycerol solutions to evaluate the effects of higher liquid viscosities showed that the solid holdup decreased and the liquid holdup increased with

increasing viscosity. The gas holdup was unaffected by liquid viscosity. At a given gas velocity, increased viscosity also caused a decrease in the minimum liquid fluidization velocity. For the more viscous aqueous glycerol solutions (>3.8 cP) with gas velocities in excess of 4 cm/sec, the minimum liquid fluidization velocity showed very little dependence on gas velocity.

Experimental studies are continuing to investigate the effects of packing characteristics and column diameter on the hydrodynamic variables. An electroconductivity technique is being evaluated to determine its effectiveness in measuring the phase holdups as a function of height in a three-phase fluidized bed. This technique is expected to permit the study of three-phase fluidized beds under conditions that are expected to be of more practical interest, that is, in reactors with high gas velocities where the bed heights become indistinct. The same electroconductivity system may be used to measure axial dispersion in the liquid phase over the same range of conditions.

15.2 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.¹ Low concentrations of oxygen will inevitably be present in either a helium coolant or a secondary containment atmosphere; if necessary, still higher concentrations of oxygen could be added. Atomic tritium, permeating a metal barrier, should react with

1. C. D. Scott et al., *Experimental Engineering Sect. Semiannual Prog. Rep. (Excluding Reactor Programs)*, Mar. 1, 1975, to Aug. 31, 1975, ORNL TM-5291, pp. 333-51 (in press).

2. C. D. Scott et al., *Experimental Engineering Sect. Semiannual Prog. Rep. (Excluding Reactor Programs)*, Sept. 1, 1975, to Feb. 29, 1976, ORNL TM-5533, sect. 6.1 (in preparation).

3. J. S. Watson, *A Summary of Tritium Handling Problems in Fusion Reactors*, ORNL TM-4022 (November 1972).

Fig. 15.1. Effect of fluid velocities on phase holdups.

oxygen sorbed on the metal surface to form the oxide. An experimental study is in progress to determine the oxidation efficiency of deuterium permeating different metal walls at conditions that can be expected within fusion power reactor systems.

The equipment for the hydrogen isotope permeation-oxidation experiment⁴ consists of a

permeation tube surrounded by a tubular vacuum chamber and furnace, a variable leak valve for introducing oxygen, and a 20-liter sec noble-ion pump. Two nude ion gages measure the system pressure, and the gas composition within the vacuum chamber is monitored by a mass spectrometer. Since the operating pressure of the UFI model 100 C gas analyzer is limited, the vacuum chamber contains a 2-mil-diam orifice to permit higher oxygen partial pressures at the permeation tube surface. With an oxygen pumping speed of 11 liters/sec (the noble-ion

4. C. D. Scott et al., *Experimental Engineering Sect. Savannah Prog. Rep. (Excluding Reactor Programs)*, Mar. 1, 1975, to Aug. 31, 1975, ORNL TM-5291, pp. 352-54 (in press).

pump does not remove oxygen at the rated speed), the pressure ratio across the flow resistance is 5×10^3 . For example, the oxygen partial pressure could be 2×10^{-3} torr at the gas analyzer and 0.1 torr at the permeation surface. Two permeation metal surfaces, palladium and nickel, were tested. The palladium permeation tube was 0.150 in. OD by 1.0 in. long (0.381 cm OD by 2.54 cm long) with a 15-mil wall thickness, and the nickel tube was 0.210 in. OD by 4.0 in. long (0.533 cm OD by 10.16 cm long) with a 15-mil wall. A deuterium pressure of 1.0 psig (108 kPa absolute) was maintained on the inside wall of the permeation tube.

Permeation-oxidation results were obtained with deuterium and a palladium metal surface at 25 and 60°C. At 25°C and oxygen partial pressures at the permeation surface from 0.001 to 0.1 torr, the conversion of deuterium to heavy water was 80 to 85%. The conversion efficiency did not appear to be dependent on the oxygen partial pressure; however, the spectrometer emission current could not be maintained at the optimum setting with oxygen partial pressures greater than 0.01 torr. With an oxygen partial pressure of 0.01 to 0.02 torr at 60°C, the conversion of deuterium to heavy water was 95%. This operating condition could only be maintained for 2 hr because of instability of the emission current. Although the deuterium and palladium permeation-oxidation results obtained thus far are not conclusive, the data indicate an increasing oxidation efficiency with increasing temperature.

Permeation-oxidation data were also obtained with deuterium and a nickel permeation tube at temperatures from 100 to 230°C. The oxygen partial pressures at the nickel surface varied from about 0.004 to 0.1 torr; however, the conversion of deuterium to water was not affected by increased oxygen pressures. As the temperature of the nickel was increased from 100 to 150°C, the deuterium oxidation efficiency increased from 50 to 75%. Between 160 and 230°C the efficiency fluctuated between 80 and 85%, with no apparent temperature dependence. At 240°C the spectrometer emission current became unstable, and the series of runs with the nickel permeation tube had to be terminated.

Young has evaluated the pumping of hydrogen by a palladium diaphragm at 500 to 600°C. He reported that the hydrogen pumping rate dropped to a negligible value when the palladium was cooled to room temperature. The following conditions were

found to be required for hydrogen pumping: (1) a hydrogen-permeable membrane must be present, (2) one side must be exposed to an oxidizing atmosphere, and (3) the membrane must catalyze the reaction between hydrogen and oxygen to form water. Young also reported that hydrogen was pumped by a nickel surface, but the observed pumping speeds were much less than for palladium. The results suggest the need for higher temperatures in the permeation-oxidation studies. In order to maintain a stable emission current with the increased temperature, the quantity of deuterium permeating into the vacuum chamber will have to be limited. This can be achieved by decreasing the deuterium pressure on the inner wall. Permeation-oxidation studies will be continued with nickel and stainless steel surfaces at temperatures up to 500°C.

15.3 CONTINUOUS CHROMATOGRAPHY

Large-scale preparative separations are needed in the energy production field and in various biochemical applications. The development of a continuous chromatographic system would be valuable for such separations, since the maximum diameter possible in the scale-up of conventional chromatographic columns is limited to about 1 in. Although the concept under study was first presented in 1949, only limited success had been achieved. A rotating annulus with stationary feed and elution streams and stationary elute collection ports is being evaluated in our laboratory.

Annular chromatograph. A prototype of the proposed chromatograph was fabricated from Plexiglas (see Fig. 15.2) and has appropriate seals to allow pressurized chromatography and spacers in the annulus to allow gradient elution. In the gradient-elution mode of operation, the sorbent bed surface is just above the spacer bottom, and the eluent level is below the spacer top. Therefore, the spacers prevent intermixing of the different eluent volumes above the sorbent bed. The chromatograph must be operated so that the surface of the sorbent is essentially dry at the feed point, but wet at all other points.

Photometric band scanner. A device to measure band positions and bandwidths on the annular chromatograph has been developed (see Fig. 15.3). This device focuses a beam of light onto the surface of

5. J. R. Young, "Palladium-Diaphragm Hydrogen Pump," *Rev. Sci. Instrum.* **34**, 374 (1963).

6. J. P. Martin, *Discuss. Faraday Soc.* **7**, 332 (1949).

7. C. D. Scott et al., *Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs)*, Sept. 1, 1975, to Feb. 29, 1976, ORNL TM-5533, sect. 6.6 (in preparation).

ORNL DWG 74-12630R2

GAS OVERPRESSURE

Fig. 15.2. First prototype of pressurized annular continuous chromatograph.

ORNL DWG 75-15123R1

Fig. 15.3. Schematic of band detecting device.

the resin. The reflected light is measured with a photovoltaic silicon detector coupled with an amplifier and recorder. Solute on the resin surface reduces the amount of light reflected and lowers the signal. The device is attached at a given height on the outside wall. As the solutes are swept past, the recorder makes a record of the distribution curve for each solute. This record can be analyzed to give the angular position of maximum concentration at the given height and the corresponding bandwidth.

Theoretical. The annular chromatograph can be described approximately by a theoretical-plate model. Using this approach, the angular concentration distribution was shown to be a Poisson distribution, and the angular position of maximum concentration was derived as a simple function of annular rotation rate, bed height, eluent superficial velocity, bed void volume, and solute distribution coefficient. All of these terms except the solute distribution coefficient can be determined independently. By measuring the solute elution angle and by calculating the distribution coefficient for one set of operating conditions, the solute elution angle can be predicted for other operating conditions.

To predict separation of two or more solutes, one must know the solute bandwidths as well as the solute elution angles. The total solute bandwidth at exit was derived as a function of bandwidth at the feed point, the angular position of maximum solute concentration at the exit (solute elution angle), and the number of theoretical plates. In this case the number of theoretical plates is the unknown factor and is constant, regardless of operating conditions. Therefore, the distribution coefficient and number of theoretical plates that have been calculated from experimental observations for one set of operating conditions can be used to predict solute behavior and separation of solutes for other operating conditions.

Experimental results. A molecular-sieve bed was used in the prototype annular chromatograph to investigate the separation of Blue Dextran and cobalt chloride. An ion exchange bed was used in the prototype annular chromatograph to investigate the separation of a complex nickel ion and two complex cobalt ions.

Blue Dextran-cobalt chloride. Blue Dextran 2000 solute was first eluted with water from a bed of Sephadex G-25 beads. Since the Blue Dextran molecules are too large to penetrate the beads, no distribution coefficient is involved; this simplifies the expression for the elution angle, which is proportional to the bed height for constant rotation rate and superficial velocity (see Fig. 15.4). The void volume

Fig. 15.4. Angular position vs bed height of a Blue Dextran band for different rotation rates.

was calculated from the least-squares slopes of elution angle vs bed height and was found to vary from 0.22 to 0.29.

Next, the annular chromatograph was used to continuously separate Blue Dextran and cobalt chloride (see Fig. 15.5). The void volume was evaluated from the Blue Dextran data as described above, and this value was used to calculate a distribution coefficient for the cobalt chloride. Also, the bandwidth data taken during the runs were used to calculate the number of theoretical plates. However, the number of theoretical plates varied considerably from run to run, indicating inaccuracies in the experimental method.

Nickel-cobalt. The annular chromatograph was also used to separate nickel (actually a nickel amine complex ion), Co-1 (cobalt tetramine carbonate complex ion), and Co-2 (cobalt pentamine carbonate complex ion) (see Fig. 15.6). These three components plus a fourth component, cobalt hexamine complex ion, are found in a commercial process liquor generated by ammonia-ammonium carbonate leaching of ore to recover nickel metal.²

2. R. F. J. Hurst, "Separation of Cobalt from Nickel in Ammonia-Ammonium Carbonate Solutions Using Pressurized Ion Exchange," *Hydrometallurgy* 1, 319-38 (1976).

Fig. 15.5. Separation of Blue Dextran and cobalt chloride on Gephadex resin, using continuous chromatograph. The Blue Dextran band is to the left; the cobalt chloride band is to the right.

Fig. 15.6. Separation of nickel and cobalt complex ions on Dowex resin, using continuous chromatograph. The band for the nickel complex ion is to the left; the bands for the two cobalt complex ions are to the right. The band scanning device is also shown.

Distribution coefficients calculated by least-squares analysis were in excellent agreement with those calculated from data taken on a batch chromatograph. Once again, the bandwidth data showed considerable scatter; however, progress is being made in improving such data.

A linear correlation between nickel bandwidth and the ratio of feed rate to superficial velocity (f/u) was determined experimentally. Operation of the prototype at f/u greater than 9.0 caused fluidization around the feed point and resulted in very broad bands.

15.4 HYDRAULIC CYCLONE STUDIES

Hydraulic cyclones (or hydroclones) have found many applications in the physical removal of solids from liquids or in the concentration of solids. The advantage of the use of hydroclones over other

solid-liquid separation techniques are simplicity, economy, and possible operation at temperatures up to 850° F (454° C). They are potentially useful for removing solids from coal liquids, either alone or in conjunction with filtration equipment. A typical coal-oil stream at a process temperature range of 300 to 500° F (149 to 260° C) and with a viscosity of about 5 cP has particles ranging in size from 0.25 to 3 μ . The performance of hydroclones with relatively viscous liquids and micron-size particles, such as those produced in coal hydroliquefaction processes, has not been adequately studied. Experiments have been initiated to determine particle size classification

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

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

Fig. 15.7. Schematic of the system to study hydrocyclone performance.

range as a function of feed-to-overflow ratio, pressure drop, density of particles, and density and viscosity of the liquid medium. A schematic of the system to study hydrocyclone performance is shown in Fig. 15.7. In initial experiments, we will use a feed slurry of 5 to 10 wt % aluminum oxide in water-glycerin solutions with viscosities of 1 to about 20 cP. The objective of the first tests will be to evaluate the operation of a 10-mm-diam Dorr-Oliver cyclone design. A photograph of the apparatus is shown in Fig. 15.8. Particle size distributions in feed, overflow, and underflow streams will be determined by using a Coulter counter and an optical microscope. Different hydrocyclone designs and multistage systems will be studied later.

15.5 MECHANICALLY AGITATED LIQUID-LIQUID CONTACTORS

Nondispersing mechanically agitated contactors (Lewis cells) have potential utility for performing liquid-liquid extraction operations in cases where dispersal of one phase in the other must be avoided. These contactors also provide well-defined conditions for fundamental studies of mass transfer with known interfacial area and controlled levels of turbulence. This type of contactor prevents contami-

nation of one phase with the other while permitting the mass transfer rate to be increased by adding energy to the system via agitators. Turbine agitators in both phases circulate the liquids and introduce turbulence at the interface, but dispersed droplets are not formed in either phase. An electrochemical technique for measuring electrolyte film resistance has been developed and tested. This technique permits direct and rapid measurement of mass transfer rates across electrolyte films as a function of such parameters as the rate of energy input (via agitation), turbine diameter, individual phase height, and cell dimensions.

Some of the results obtained by using the new technique are shown in Fig. 15.9. Mass transfer rates for a particular contactor operating with mercury as the heavy phase and water as the light phase were measured with agitation in each phase and with agitation in both phases. Over the range of conditions studied, the effects of agitation in each phase are additive, at least in a qualitative sense (i.e., when both phases are agitated, the mass transfer rate is always greater than when only one phase is agitated). Note also that mass transfer rates are enhanced more effectively by agitation in the light phase when the lower agitator speeds are used, whereas agitation of the heavy phase becomes more effective at the higher speeds.

ORNL PHOTO 0625-76

Fig. 15.8. Photograph of the apparatus to study hydrocyclones.

Fig. 15.9. Effect of agitator speed on mass transfer coefficient in the 30- by 30-cm contactor with a 19-cm-diam agitator

15.6 ADIABATIC COMBUSTION OF GRAPHITE

Oxidation studies of graphite rods in a cylindrical reactor were initiated during this report period. The reactor operates with oxygen feed and off-gas recycle to maintain high gas velocities and heat removal rates. All of the combustion heat is removed by the gas stream. Graphite temperatures are measured at several locations along the burner rod, and the exit gas stream is analyzed continuously for O_2 , CO , and CO_2 . The equipment, which has been described previously,¹¹ is shown schematically in Fig. 15.10.

Evaluations of the system for controlling the exit gas temperature have been completed. During these experiments, we observed stable oscillations of $\pm 75^\circ C$, which were probably due to the heat capacity of the burner. In experimental studies we are

investigating the effects of gas flow rates and oxygen concentrations in an effort to identify the controlling variables. If the gas-solid reactions are assumed to be instantaneous, the relation

$$BR \cdot A_s = k_g \cdot \bar{p} \quad (1)$$

can be used to adjust the burning rate per unit area (BR) for varying oxygen concentrations. Here A_s is the mole fraction of oxygen, k_g is the gas-phase mass transfer coefficient (cm/sec), and $\bar{p}$ is the average molar gas density ($g\text{-moles}/cm^3$). Data in the laminar region ($Re < 4000$) are shown in the left side of Fig. 15.11 and are best represented by the equation

$$(k_g \cdot \bar{p})_{LM} = (8.8 \pm 3.3) \times 10^{-4} (A_s \cdot V_s)_{LM}^{0.75} \quad (2)$$

where the subscript LM refers to the log mean. The dashed lines indicate the 95% confidence level. The turbulent regime data shown on the right side of Fig. 15.11 are best represented by

$$(k_g \cdot \bar{p})_{LM} = (2.01 \pm 0.22) \times 10^{-4} (A_s \cdot V_s)_{LM}^{0.75} \quad (3)$$

The correlation coefficients for the laminar and turbulent data are 0.99 and 0.95 respectively. The constants in these equations have units of $g\text{-moles}/cm^3 \cdot sec$.

Fig. 15.10. Schematic diagram of equipment used in graphite combustion experiment.

11 C. D. Scott et al., *Experimental Engineering Sect. Semiannu. Prog. Rep. (Exhaustive Reactor Programs)*, Mar. 1, 1975 to Aug. 31, 1975 (ORNL TM-520), pp. 64-74 (in press).

12 C. D. Scott et al., *Experimental Engineering Sect. Semiannu. Prog. Rep. (Exhaustive Reactor Programs)*, Sept. 1, 1975 to Feb. 29, 1976 (ORNL TM-553), sect. 6.4 (in preparation).

A steady state computer model is being developed to predict gas compositions and temperatures during a burn. Its success is demonstrated by the results for selected experiments shown in Table 15.1. A continuous model, which is in an earlier stage of

development, has predicted the quantities of graphite remaining unburned for most experiments within 10%.

Further experiments and development of both the steady-state and continuous models are planned.

Fig. 15.11 Effect of Reynolds number $\times$ Schmidt number on oxygen transfer.

Table 15.1. Comparison of model STAB6 with experimental results

	Run 12		Run 17		Run 43	
	Model	Experiment	Model	Experiment	Model	Experiment
Feed oxygen, g-moles/min	1.29	1.30	0.56	0.53	1.40	1.16
Recycle rate, g-moles/min	3.91	3.91	5.81	5.84	7.60	7.84
Exit oxygen, mole %	9.6	10.0	23.0	24.0	11.4	12.5
Oxygen burnup, g-moles/min	1.16	1.15	0.45	0.40	1.24	1.02
Average burn rate, g-moles/min-cm	1.85×10^{-3}	1.72×10^{-3}	1.08×10^{-3}	9.02×10^{-4}	1.86×10^{-3}	1.58×10^{-3}
Oxygen utilization	0.90	0.88	0.78	0.76	0.89	0.88
Error in rate, %		7.56		5.88		17.7

15.7 PACKED COLUMNS FOR CRYOGENIC SORPTION SYSTEMS

Several high-efficiency metal packings are under consideration for use in cryogenic gas-liquid sorption systems for treatment of off-gas streams in nuclear fuel processing plants. To evaluate these packings, an experimental study of flooding rates and mass transfer characteristics in air-carbon dioxide-water systems has been initiated. Packings under study in three columns of 6.35-, 15.2-, and 27.9-cm ID are shown in Fig. 15.12 and include Goodloe packing, Pall rings, protruded distillation packing, and Heli-pak. The flooding data obtained in the 6.35- and 15.2-cm-ID columns using Goodloe packing are compared with previous results using a 7.62-cm-ID column in Fig. 15.13. The coordinate axes of Fig. 15.13 correspond to the generalized flooding correlation for packed beds, where

G = superficial gas mass flux, $\text{g cm}^{-2} \text{sec}^{-1}$
 Ψ = ratio of water density to liquid density, dimensionless.

μ_L = liquid viscosity, cP.

g = gravitational constant, 980 cm sec^{-2} .

ρ_g = gas density, g cm^{-3} .

ρ_L = liquid density, g cm^{-3} .

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

The packing factor, F , has been omitted from the ordinate, since its sole purpose is to force experimental flooding data for different packing shapes to fit the generalized correlation.

13. Manufactured by the Packed Column Co., a Division of the Metco Corp., Edison, N.J.

14. Manufactured by Norton Co., Akron, Ohio.

15. Manufactured by Scientific Development Co., State College, Pa.

16. Manufactured by Pallbrinco, Inc., Bensenville, Ill.

17. Wu Chou et al., ORNL-MIT-223 (1976).

18. L. I. Chao et al., ORNL-MIT-234 (1976).

19. Chem. Technol. Div. Ann. Prog. Rep. Mar. 31, 1975, ORNL-5050.

20. J. S. Eckert, Chem. Eng. Prog. 66(3), 39 (1970).

ORNL PHOTO 1679-76A

Fig. 15.12. Packing materials for cryogenic sorption.

Fig. 15.13. Comparison of flooding data obtained in Goodfue-packed columns.

Although the correlation for Goodfue packing supplied by the manufacturer accurately predicts flooding rates at high L/G ratios, it deviates significantly at lower L/G ratios. Since the experimental data are more conservative than the Goodfue correlation in the low L/G region, their use is recommended in designing systems with this type of packing. For design purposes a safety factor of approximately 30% should be allowed for scatter in the data.

Flooding data on the remaining packings will be compared with the generalized flooding correlation as results become available. The mass transfer data will be analyzed, using the appropriate dispersion model, in terms of overall volumetric mass transfer coefficients.

15.8 PREPARATION OF SMALL-PARTICLE SORBENTS

Small-particle sorbents can significantly increase mass transfer rates in several energy-related pro-

cesses. Although small particles are desired for high mass transfer rates, they require higher pressures to pump liquids or gases through the sorbent beds. The pressure drop across a packed bed of a given size particle can be minimized by using uniformly sized spheres as the bed material. Sol-gel processes which produce uniformly sized metal oxide spheres in the range of several hundred microns have been demonstrated at ORNL, and studies have now been made to extend the capabilities of these processes down to particle sizes less than 10μ .

A turbulent two-fluid nozzle with a right-angle entry has been used to produce erbium oxide spheres less than 10μ in diameter. Although the particle size distribution was not as uniform as desired, the few grams of material produced were placed into a column and used to successfully separate components for a coal conversion liquid. New commercial sorbents that have recently come onto the market make further development of this process less necessary.

15.9 PERFUSION-IMPACTION PARTICULATE SEPARATOR

An innovation to the classical inertial impactor is being investigated. As usual, a jet stream impinges on a flat collector plate where a fraction of the aerosols impacts. The innovation in the new device is that the collector plate is porous, and a liquid continuously perfusing through the plate sweeps the surface clean of particulates. The inventor claims that very small particles can be removed and that very low liquid flow rates are required.

Theoretical. The innovation does not change the differential equations involved that describe inertial impaction. Thus, previous analyses of inertial impaction also apply to the present system. However, no rigorous analytical solution has ever been found, even for standard impactors. Solutions in the

literature assume a simple flow field. Once the flow field was established, the particle motion equations were solved either analytically or numerically. The correlations developed in the literature should prove to be extremely useful.

For the present, work on an algorithm was developed to obtain a more accurate solution for the flow field. The flow field solution is then used to predict particle behavior.

Experimental. A prototype of the proposed perfusion-impactor was fabricated. A Royco 220 particulate analyzer has been obtained for evaluating the efficiency of particulate removal. Thus far, this analyzer and an older model have given unsatisfactory calibration results. A more stringent calibration is being performed on the Royco 220 analyzer to permit more accurate and reliable evaluation of the perfusion-impactor.

16. Controlled Thermonuclear Program

16.1 CRYOSORPTION VACUUM PUMPING FOR FUSION REACTORS

Significant advances in vacuum technology are required for the development of full-scale fusion power reactors. Advanced vacuum equipment is needed for the plasma recovery system, the neutral beam injection recovery system, and perhaps the blanket tritium recovery system. Each of these subsystems has separate vacuum systems with different requirements, but cryosorption pumps are the prime candidates in every case. The controlled thermonuclear reactor (CTR) plasma recovery system must be capable of pumping mixtures of helium and hydrogen isotopes at speeds on the order of 30 kiloliters sec⁻¹ and pressures as high as 10^{-4} torr. Cryosorption pumps should be capable of fulfilling these requirements; however, no experimental data on cryosorption pumps have been collected under these conditions.

This program, designed to evaluate the behavior of cryosorption pumps for CTR applications,

centers around the Escalibur CVR 1106 cryosorption pump, which is prototypical of the type of pump normally proposed for this system. The pump, shown schematically in Fig. 16.1, contains a 50-in.² (322.6-cm²) cryosorption panel cooled by intimate contact with liquid helium. The panel is cross-milled with $\frac{1}{16}$ -in. (0.16-cm) grooves filled with approximately 30 g of type 5A molecular sieve. The helium that boils off is routed through tubes to cool the chevron immediately in front of the cryopanel and is then used to cool the radiation shield surrounding the liquid-helium reservoir. This system is completely surrounded by a liquid-nitrogen-cooled chevron and radiation shield. The vacuum pump test stand constructed to evaluate this pump has been described elsewhere.

I. C. D. Scott et al., *Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs)*, Mar. 1, 1975, to Aug. 31, 1975, (ORNL TM-529) (in press)

Fig. 16.1 Schematic of Escalibur CVR 1106 cryosorption pump.

Figure 16.2 shows the pumping speed of deuterium. Speeds slightly in excess of 1000 liters/sec (3.1 liters/sec cm^3) were obtained at pressures less than 10^{-6} torr. The increase in pumping speed from 10^{-6} to 3×10^{-3} torr is due to increased conductance in the pump. The source of the increase could be the transition of molecular flow to viscous flow or the condensation of deuterium on the first chevron, or a combination of the two effects. The second effect occurs because the helium boil-off rate increases above 10^{-6} torr. This supplies additional cooling to the first chevron and lowers its temperature to near 4.2°K.

We operated this pump at its highest speed (1800 liters/sec) for 2 hr. During this time, there was no noticeable change in pumping speed, even though the quantities of deuterium pumped were equivalent to ten times the adsorption capacity of the pump. This indicates that the principal mechanism is cryocondensation (for deuterium), not cryosorption. We

expect to find similar results for tritium, because its vapor pressure is even lower than that of deuterium.

Figure 16.3 shows the pumping speeds of hydrogen. In the pressure range from 4×10^{-6} to 4×10^{-5} torr, the speed is affected by the vapor pressure of solid hydrogen, which is 1.0×10^{-5} torr at 4.2°K. The initial pumping speeds in this region are significantly higher than steady-state speeds, indicating that several layers of hydrogen must accumulate on the cryosurface before condensation becomes the principal pumping mechanism. Our results have shown that the pumping speed actually varies periodically with time when operating at pressures near 10^{-5} torr. The transition from low speeds to high speeds occurs rapidly and is accompanied by a large increase in system pressure and rapid boil-off of liquid helium. During this transition, material that was previously frozen on the cryosurface appears to become adsorbed in the sorbent.

The steady-state pumping speed for deuterium observed in this study is acceptable for CTR application; however, the dynamic behavior of the pump now emerges as a possible area of concern. Apparent unstable phenomena must be understood

2 C. D. Scott et al., *Experimental Engineering Sci.: Seminars Prog. Rep. (Excluding Reactor Progress)*, Sept. 1, 1975, to Feb. 29, 1976, ORNL TM-5533 (in preparation)

Fig. 16.2. Deuterium pumping speeds.

Fig. 16.3 Hydrogen pumping speeds

and evaluated with regard to the consequences they may have for CTR applications.

16.2 EVALUATION OF METHODS FOR RECOVERING TRITIUM FROM CTR BLANKETS

Proposed methods for recovering tritium from CTR blankets were reviewed in order to determine their relative feasibility, to suggest process modifications that would enhance feasibility or reduce costs, and to outline the development work that would be needed for demonstration of feasibility and development of the process. This review concentrated on methods for recovering tritium from liquid lithium, since that was the blanket material favored in Experimental (Fusion) Power Reactor conceptual designs; in addition, the one proposed process for molten-salt blankets⁴ was evaluated. Little attention was given to solid breeding materials except to tabulate the experimental data needed to prove their suitability.

The two most promising processes for recovering tritium from lithium blankets were found to be extraction into a molten salt and permeation through

naidium "windows." The extraction process, which was first suggested by Maroni et al., consists of two steps: extraction of tritium into a molten salt (probably LiCl-KCl) and subsequent removal from the salt with an electrolytic cell. Both the extraction step and suitable salt-metal contacting devices are believed to be feasible. The electrolytic cell for removing tritium from the molten salt, however, does not look promising. The relatively high solubility of lithium metal (and potassium metal) in the molten salt is expected to interfere with operations of the electrolytic cell. Alternative methods suggested for removing tritium from the molten salt⁵ would oxidize the tritium to TCl by gas sparging. One of these is expected to make the extraction process feasible, but corrosion and entrainment problems must be investigated.

We have long considered a permeable "metal window" a feasible recovery process; however, large windows would be required. A simple cost estimate was prepared to show the costs of the metal window structure and the tritium inventory as a function of tritium concentration within the blanket. This allows us to estimate an optimum tritium concentration for the blanket. For low-temperature blanket systems (maximum temperature ~500°C) using stainless steel structures, tritium permeation rates to the steam system do not impose limits on the tritium concentra-

3. J. S. Watson, S. D. Clinton, P. W. Fisher, and J. B. Tailor, "Evaluation of Several Liquid and Solid Tritium Breeding Blankets," *Proceedings of the International Conference on Radiation Effects and Tritium Technology for Fusion Reactors*, Gatlinburg, Tennessee, Oct. 1-3, 1975, CONF-750909, vols. 1-4.

4. F. F. Johnson, "Fuel Handling," *A Fusion Power Plant*, MA11-1050, Princeton Plasma Physics Laboratory (1974), pp. 362-410.

5. V. A. Maroni, T. D. Wolson, and G. F. Staehli, "Some Preliminary Considerations of a Molten-Salt Extraction Process to Remove Tritium from Liquid Fusion Reactor Blankets," *Nucl. Technol.* 25, 83 (1975).

6. Warren Grimes, ORNL, personal communication, 1975.

tion in the blanket. The optimum concentrations corresponded to relatively high tritium inventories and only marginally acceptable costs. Surface impurities on niobium samples have introduced considerable scatter in permeation measurements; therefore a range of permeabilities had to be considered. Only the more favorable permeability data makes this process practical. The permeability of niobium at the temperature and pressures of interest needs to be determined more reliably. Furthermore, the capability of liquid lithium for transporting impurities to "fog" a niobium metal window should be studied.

Recent data from ORNL show that the rates at which tritium is sorbed into hydride-forming metals are likely to be slow, and sorbers would be impractically large for the tritium concentrations of interest in CTRs. Distillation and gas sparging processes are completely impractical.

Molten-salt blankets have been proposed by the Princeton Plasma Physics Laboratory, and a flowsheet for tritium recovery is included in their reference design.⁴ In this flowsheet the salt is maintained in an oxidizing state with an overpressure of 0.01 torr T₂ and 1.2 torr TF. A side stream of salt is routed to a vacuum spray tower where the TF (and T₂) is removed. The TF is then condensed in cold traps. Although the recovery of T₂ from the vacuum exhaust is not mentioned, this would be necessary. The difficulty in this flowsheet lies in the provision for the spray tower, which we estimate would have to be more than 400 ft (122 m) high. However, the flowsheet can probably be modified to a practical system by operating the salt in a reducing condition (perhaps by circulating the salt over beryllium metal) and allowing the tritium pressure to rise to much higher values. The spray tower can be made without increasing the tritium inventory in the salt to significant values, tritium has a very low solubility in the salt. However, the higher tritium pressure in the salt will increase the tritium permeation rate into the helium coolant, and provisions will have to be made for trapping this tritium before it reaches the steam generator. Oxidation of the tritium either on the permeated surface or in a separate catalyst bed is expected to constitute an adequate trapping method.

16.3 TRITIUM SORPTION STUDIES

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

Fig. 16.4. Contacting apparatus for tritium sorption studies.

recovering 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 potassium has been studied in a batch contactor by using metal sorbent samples of yttrium, zirconium, uranium, and titanium. Yttrium has shown significant tritium removal rates from molten potassium.

A schematic diagram of the equipment to contact tritiated liquid metals with selected metal sorbents is shown on Fig. 16.4. Basically, the equipment consists of a reservoir of tritiated liquid metal, two sampling valves, two identical contacting chambers, a vacuum source, and an argon supply (less than 0.0005% total impurities). The tritiated liquid metal is drawn into the two contacting chambers at a temperature of 150 to 400°C. One chamber contains the metal sorbent, while the second chamber serves as a control. To terminate the experiments, the two liquid metal samples are removed from the contact chambers and analyzed for tritium.⁸ To reduce the problems of oxygen contamination, the entire process is enclosed in a

7. C. D. Scott et al., *Experimental Engineering Section Semiannual Prog. Rep. (Excluding Reactor Programs)*, Mar. 1, 1975, to Aug. 31, 1975, ORNL TM-5291 (in press).

8. R. C. Forrester III and J. S. Watson, "A Procedure for Determination of Tritium in Potassium," *Anal. Lett.* **8**, 63-70 (1975).

glove box with a once-through dry argon atmosphere. The glove box also serves as a secondary tritium containment, operating at a slight negative pressure and exhausting to a hot off-gas system.

The initial data have been obtained with tritiated potassium, but preparations are under way to examine the effectiveness of metal sorbents in tritiated lithium. Since early tests indicated that the removal of tritium by metal sorbents was slow and controlled by solid diffusion, a differential-bed approach to the evaluation of sorbent materials was abandoned in favor of a batch contactor.⁹ Twenty-four metal sorbent samples were contacted with tritiated potassium at temperatures from 150 to 400°C and time periods extending up to several days before any significant mass transfer of tritium was observed. Although yttrium, uranium, and tritium samples were tested, most of the early metal sorbent experiments were made with zirconium. The zirconium samples were given different surface treatments to reduce or eliminate film resistance from impurities on the metal surface.

A sample of yttrium (obtained from Research Chemicals, a division of Nuclear Corporation of America) was the only sorbent material to remove

significant quantities of tritium from the molten potassium. The sample, whose dimensions were $0.06 \times 0.5 \times 1.5$ in. ($0.15 \times 1.3 \times 3.8$ cm) (geometric surface area, 11.2 cm^2), weighed 3.42 g. It appeared to have a layered structure, was friable, and had a grayish color.

The results of the yttrium-tritium sorption experiments in molten potassium are given in Table 16.1. The yttrium sorber was not removed from the contacting chamber until after run 12; the two subsequent runs (13 and 14) were made with a second yttrium sample of the same dimensions and weight. A temperature of 400°C was maintained in runs 7 through 11, while the remaining runs were carried out at 300°C. The yttrium-tritiated potassium contact times, t , are given in column 2, and the tritium concentrations remaining in the potassium, C , are shown in column 3. Column 4 tabulated the tritium concentrations in the potassium control samples, C_0 . From the twelve control analyses, the average tritium concentration in the potassium feed reservoir was determined to be 621 ± 27 ppb. The potassium volumes, V , which were recovered from the sorber contacting chamber, are shown in column 5. Column 6 tabulates the product of yttrium area per unit volume of potassium (A/V) and the contact time (t). The last column lists the ratio of tritium concentration in the yttrium to tritium concentration remaining in the potassium, C_y/C , at

9. C. D. Scott et al., *Experimental Engineering Sect. Semiannual Prog. Rep. (Excluding Reactor Programs)*, Sept. 1, 1973, to Feb. 28, 1974, ORNL TM-4602 (December 1974).

Table 16.1. Results of the tritiated potassium-yttrium sorption experiments

Run No.	Contact time, t (hr)	Tritium concentration in potassium		Potassium volume, V (cc)	$(At/v)^a$ (hr/cm)	$(C_y/C)^b$ (ppb/ppb)
		Sorber, C (ppb)	Control, C_0 (ppb)			
1	51	483	639	18.9	30.2	1.2
2	99	80	579	19.5	56.8	37.1
3	145	30	646	14.6	111	163
4	24	347	590	17.2	15.6	17.2
5	4	620	643	21.0	2.1	9.6
6	48	241	612	12.4	43.3	29.2
7	24	40	618	13.9	19.3	220
8	16	54	611	12.9	13.9	206
9	6	266	637	18.2	3.7	47.3
10	30	22	673	10.0	33.6	631
11	12	319	592	17.5	7.7	47.1
12	72	490	609	18.8	42.9	31.8
13	72	68		18.3	44.1	30.6
14	24	257		19.8	13.6	13.8

^a A = geometric surface area of yttrium, 11 cm^2 .

^b C_y = tritium concentration in yttrium, ppb.

the end of each run. The ratio of the contact area to the unit volume of potassium was $0.72 \pm 0.18 \text{ cm}^{-1}$.

Except for runs 1 and 12, the tritium concentration in the potassium decreased with contact time as a first-order reaction (see Fig. 16.5). The mass transfer resistance in run 1 could be explained by an activation of the yttrium surface; however, a similar yttrium sample in run 13 did not require any extended time for activation. From the accumulated bulk tritium concentration in the yttrium (i.e., 15.6 ppm), the driving force was estimated to be sufficient to reduce the tritium concentration in run 12 (72 hr at 300°C) by more than the 21% observed, but there was considerable uncertainty in the estimate.

If we neglect runs 1 and 12, the times required to reduce the concentration of tritium in the potassium by a factor of 2 with the first yttrium sorber were 32 hr at 300°C and 6 hr at 400°C . Only

two runs were completed with the second yttrium sorber because of a limited supply of tritiated potassium. The data points corresponding to these runs predict a tritium half-life of 22 hr at 300°C . Although the geometric areas of the two yttrium samples were the same (11.2 cm^2), the effective sorption rate for the second yttrium sample appears to be about 50% greater than that for the first sample.

With a surface film driving force that can be approximated by the tritium concentration in the potassium, a tritium sorption mass transfer coefficient can be calculated for the first yttrium sample. The mass transfer coefficient increased from $8.3 \times 10^{-6} \text{ cm/sec}$ at 300°C to $4.2 \times 10^{-6} \text{ cm/sec}$ at 400°C . The activation energy of the reaction was estimated to be 12 kcal/g-mole. The slow mass transfer rate observed in this study indicates that a large metal sorber system would be required for recovering tritium at the concentrations proposed

Fig. 16.5. Tritium concentration in potassium vs contact time.

for fusion reactor blankets; however, the results are sufficiently encouraging to merit further sorption studies with tritiated lithium. Since most metal oxides can be reduced by lithium, the performance of some tritium sorbent materials may be improved if lithium is used.

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

Solid Li-Al alloy has been suggested as a potential tritium breeding material for fusion reactors, and sintered aluminum product (SAP) has been suggested as a blanket or structural material.¹⁰ Each of these materials would produce minimum neutron activation and, perhaps, low tritium inventories. However, the validity of the second advantage is contingent upon the ability of the material to rapidly release tritium to a flush gas such as helium. The objective of this program is to investigate the tritium removal rates from two alloys, Li-Al (approximately 0.05 wt % lithium) and lithium-doped SAP, which have been irradiated in the High Flux Isotope Reactor. (Approximately 60% of the ⁶Li in the SAP samples and 9% of the ⁶Li in the Li-Al samples were converted to tritium as a result of this irradiation.

A schematic diagram of the experimental system to study tritium recovery rates from irradiated Li-Al and SAP samples is shown in Fig. 16.6. An

irradiated sample is heated to 300 to 400°C as argon flushes the released tritium to a tritium monitor. The gas then flows through a water bubbler to remove tritiated water from the gas. Next, the tritiated gas from the first bubbler is oxidized in a CuO bed (600°C), cooled, and passed through another bubbler. Finally, the stream flows through a molecular sieve trap and then to the ORNL "hot" off-gas stack. This small tritium release rate to the off-gas is also monitored. On conclusion of the run, the sample is removed and dissolved in a manner described previously¹¹ so that the residual tritium can be measured. Initial experiments with SAP samples indicate that reasonably rapid removal rates are possible, but the rates do not follow simple relationships corresponding to diffusion through bulk metal and or through surface films.

16.5 SORPTION PUMPING IN DEEP BEDS

Sorption pumps are finding increasing application both for high-vacuum pumps and for vacuum-roughing pumps. Newly developing needs in the CTR program are expected to accelerate this

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. C. D. Scott et al., *Experimental Engineering Sect. Semiannual Prog. Rep. (Excluding Reactor Programs)*, Mar. 1, 1975, to Aug. 31, 1975, ORNL TM-5291 (in press).

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Fig. 16.6. Schematic of the system used to study tritium release for solid blanket materials.

trend. Very thin beds of sorbent are required for cryosorption of helium onto molecular sieves at 4.2° K, but deep beds are likely to be preferred for roughing pumps, for sorption purification, for transfer pumping, and possibly for cryosorption pumping of hydrogen isotopes at temperatures well above 10° K. In each of these applications, increasing the bed depth will significantly aid pumping rates and pump sorption capacity only up to a point. The purpose of this study is to develop methods for predicting sorption pump performance and for selecting the proper bed depth.

Although the applications of greatest interest are concerned with the use of molecular sieves and

active metals such as uranium to pump tritium-deuterium or to pump air, the present study uses a much simpler system, carbon dioxide or methane with molecular sieves. This is a fundamental study to develop techniques for understanding sorption pumping; the various applications will then be studied separately. An experimental system has been constructed (see Fig. 16.7), and measurements of carbon dioxide pumping rates have begun. A mathematical model has been developed to describe sorption pumping processes controlled by diffusion in the solid sorbent. Current efforts include comparison of the experimental data with the experimental model.

ORNL DWG 76-1330

Fig. 16.7. Apparatus used to study sorption pumping in deep beds.

17. Iodine Studies

17.1 IODINE SORPTION ON CHARCOAL—IGNITION AND DESORPTION

Large quantities of specially impregnated charcoal are used in nuclear reactor installations for the cleanup of radioactive iodine during normal reactor operation. For some reactors, the charcoal adsorbers may also be required to retain much larger quantities of radioactive iodine if certain postulated accidents occur. We have completed a laboratory-scale experimental program in which we determined the effects of such loading on the retention of iodine and whether the resulting decay heat would ultimately lead to the ignition of the charcoal.

Our experimental method was to load radioactive ^{131}I on a well-insulated charcoal bed 1 in. (2.5 cm) in diameter and 2 in. (5.1 cm) deep. Air flowed at 17 cm/sec (33 fpm) and 70°C to provide adequate cooling for 2 hr or more, while sequentially operated collection traps measured radioactive iodine desorbed from the end of the test bed. During most experiments, the air velocity was then reduced to one-tenth of normal velocity or less; this allowed the charcoal bed temperature to rise slowly, culminating in ignition of the charcoal in some experiments.

Details of previous experiments with dry air have been reported. These and several experiments with moist air were summarized in a previous annual report. The final three experiments in this program are summarized in Table 17.1 and confirm the following observations (applicable to all 13 experiments).

The rate of oxidation heat release at temperatures near 200°C (see Table 17.1) is probably a better

indicator of the ignitability of a type of charcoal than its ignition temperature. At temperatures near 200°C and with low air flow, the heat from oxidation may be greater than the heat from radioactive decay and, further, may be sufficient to raise the charcoal bed temperature to the ignition point unless additional cooling is supplied (usually by increased air flow velocity). [The rate of oxidation heat release in our apparatus is approximately 15 cal/min (g charcoal) at the ignition temperature; as the ignition temperature is approached, increased air flow may be unable to halt the escalation to ignition.] Atmospheric contaminants adsorbed by charcoal apparently oxidize at lower temperatures than does charcoal and can cause early ignition of the charcoal if present in sufficient quantity. As demonstrated previously, the heating and ignition of charcoal beds by combined radiation decay heating and oxidation heating can be calculated with reasonable accuracy.

The ignition temperature was reached without significant loss of radioactive iodine from the test bed. At low air flow rates [<2 fpm (0.6 m/min) at 25°C reference], the bed temperatures stabilized below 500°C and the radioactive iodine slowly moved toward the outlet end of the bed, as observed by a movable collimated radiation detector. We calculated linear sorption coefficients from the observed rate of movement. For our test condition of low air flow rate, considerable time will be available for combating a charcoal fire before significant desorption occurs.

During experiments with moist air, the principal release of radioactive iodine from the end of the test bed occurred as a chemical form that was unusually highly penetrating with respect to impregnated charcoal and silver-containing adsorbents. The chemical form has not been identified, but its low solubility in water and high solubility in carbon tetrachloride suggest an organic material or mixture of organic forms. This material was released at the very low fractional release rate of 7 to 14×10^{-7} hr; however, this rate was not affected by temperature,

1. R. A. Lorenz, W. J. Martin, and H. Nagao, "The Behavior of Highly Radioactive Iodine on Charcoal," pp. 70-74, in *Proceedings of the Thirteenth AEC Air Cleaning Conference Held in San Francisco, California, 12-15 August 1973*, (ORNL-3800) (March 1975).

2. *Chem. Technol. Div. Annu. Prog. Rep.*, Mar. 31, 1974 (ORNL-5056), pp. 82-83.

Table 17.1. Summary of recent experiments with highly radioactive ^{130}I adsorbed on charcoal

	Type of charcoal used in experiment ^a		
	GX-176 ^a Run 11	G-615 ^a Run 12	MSA-85851 ^a Run 13
Amount of ^{130}I , Ci ^b	570.290	480.225	50.29
Experiment duration including iodine loading, hr	13.83	15.68	52.67
Lowest air velocity, fpm at 25 °C	1.6	2.5	26.2
Maximum temperature at lowest velocity, °C	502	241	71
Water vapor partial pressure, torr	110	115	140
Oxidation heat release rate $^{\circ}\text{C} \cdot \text{min}^{-1} (\text{g charcoal})^{-1}$			
At 200 °C	0.6	1.3	Not measured
At 300 °C	13	28 ^d	Not measured
Desorption coefficient $^{\circ}\text{C} (\text{g charcoal})^{-1} (\text{atm I}_2)^{-1}$			
At 80 °C	4.0×10^5	2.8×10^5	10×10^5
At 180 °C	4.3×10^3	3.0×10^3	Not measured
Fraction desorbed, ppm			
Elemental iodine	~6.4	~6.0	~20
Particulate iodine	5.5	0.98	0.024
Penetrating iodine	~1.3	~5	~20
Highly penetrating iodine	108	202	147 ± 10
Total	120	209	157

^aGX-176 is a coconut-base charcoal impregnated with 1% KI, 1% triethylenediamine (TEDA), and a proprietary flame retardant. G-615 is a coconut-base charcoal impregnated with 2% KI, 2% TEDA, and a proprietary flame retardant. This batch of charcoal had been used nine months at the Savannah River Laboratory. MSA-85851 is a coconut-base charcoal impregnated with approximately 4% (KI + I₂).

^bOne curie of ^{130}I produces a maximum beta radiation intensity of about 5×10^5 rads/hr in the first 1/4-in. bed segment and an essentially uniform gamma radiation intensity of 1.3×10^4 rads/hr. The half-life of ^{130}I is 12.3 hr.

^cThe heat release rate and adsorption coefficient show a log rate (coefficient) vs $1/T - 1/K$ correlation.

^dExtrapolated beyond the range of experimental data for comparison.

air flow rate, or radiation intensity in the range 30 to 500 Ci. After run 13 had been in progress for several hours, the release rate decreased as the ^{130}I activity decayed. The only release of methyl iodide like material occurred while radioactive iodine was being loaded onto the test bed (except for a test which used charcoal that had been in service for four years).²

17.2 OXIDATION AND DEGRADATION OF SHORT-CHAIN ALIPHATIC COMPOUNDS IN NITRIC ACID SOLUTIONS

Work on the reaction of organic iodides with hyperazeotropic nitric acid, reported last year,¹ has been completed. The purpose of this work was to determine the ultimate fate of organic materials in nitric acid systems. Knowledge thus obtained is expected to be useful in the development of methods for removing traces of organic materials which in the past have caused difficulty in the separation and

isolation of various fission products,⁴ particularly iodine.^{4,5}

Typically, about 40% of the total carbon is converted to CO₂, another 40% to aliphatic acids, and the remainder to a mixture of hydroxy-aliphatic acids, their lactones and nitrite esters, nitro-aliphatic

3. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1975, ORNL-5050, pp. 84-85.

4. K. B. Brown et al., *Symposium on Solvent Extraction Chemistry*, Gatlinburg, Tenn., Oct. 23-26, 1962. See *Nucl. Sci. Eng.* 16, 381-455 (1963); 17, 234-308, 557-650 (1964).

5. D. H. E. Atkins and A. F. J. Eggleton, *Iodine Compounds Formed on Release of Carrier-Free Iodine-131*, AI RE-M-1211 (May 1963).

6. A. K. Postma and R. W. Zawadoski, *Review of Organic Iodide Formation Under Accident Conditions in Water-Cooled Reactors*, WASH-1233 (1972).

7. W. A. Rodger and S. L. Reese, *React. Fuel-Process. Technol.* 12(2), 173 (1969).

8. M. Sacki, K. Numakura, and F. Tachikawa, *Int. J. Appl. Radiat. Isot.* 25, 407-14 (1974).

acids, and dibasic acids. Traces of shorter-chain nitrates and of carbon monoxide were also detected. Beginning with *n*-butyl iodide, we have been able to identify compounds accounting for 95 to 96% of the total amount of carbon added. A hypothetical mechanism has been developed to explain the results (paper in preparation).

The oxidation of acetic acid by ozone in nitric acid and in distilled water is under investigation. The reaction follows a zero-order path with respect to the acetic acid concentration in both pure water and aqueous nitric acid. In the absence of catalysts, the rate of oxidation in nitric acid solutions is consistently less than in water. The presence of silver nitrate catalyst speeds up the oxidation rate in nitric acid but has little effect on the rate in water. The kinetic order remains zero in both cases.

Some difficulty has been experienced in obtaining quantitatively consistent results because of the presence of small amounts of unidentified organic materials in reagent-grade nitric acid and even in triply distilled water. We are working toward eliminating this problem.

17.3 REMOVAL OF IODINE FROM GAS STREAMS BY ELECTROLYTIC SCRUBBING

This work was undertaken to develop an electrolytic method for efficient trapping of radioiodine species from an off-gas stream during processing of spent reactor fuels. Since short cooling times may be desirable for the processing of some of these fuels (e.g., liquid-metal fast breeder reactor fuels), very high retention factors (10^3 to 10^4) are required. Previously available processes for trapping iodine include the use of silver zeolite solid sorbents^{9,11} or hyperazeotropic nitric acid.^{12,16} The first method is expensive; the second requires handling of very concentrated acids.

This promising electrolytic scrubbing method uses Co^{2+} to very effectively oxidize both organic and inorganic iodides to soluble species that are easily trapped in dilute nitric acid. Formed by oxidation of Co^{2+} at the anode, the Co^{3+} acts as a very strong oxidation carrier, which is necessary to oxidize the organic iodides; other oxidants, including Ce^{4+} , MnO_2 , Fe^{3+} , Ag^+ , and $\text{Cr}_2\text{O}_7^{2-}$, were much less effective. The experimental cell consisted of a glass cylinder containing an inner concentric cylinder to separate the anode from the auxiliary cathode. In a typical test, an air stream flowing at 1350 ml/min containing 100 ppm of CH_3I or 20 to 40 ppm of I_2 was

contacted in the cell with 30 ml of 8 M HNO_3 , 0.1 M Co^{2+} (current of 4 A), resulting in decontamination factors (DFs) of 100 for CH_3I and 600 for I_2 . Increasing the anode cell potential increased the DFs for both I_2 and CH_3I . Molecular iodine was trapped about four times as effectively as CH_3I at 4 A and about 30 times as effectively at 1 A, suggesting different trapping mechanisms, increasing the HNO_3 concentration from 4 to 12 M at either 1 or 4 A resulted in higher DFs for both CH_3I and I_2 . Use of less than 8 M nitric acid as the catholyte resulted in formation of H_2 instead of nitrogen oxides, the latter being the more desirable cathode product. Increasing the Co^{2+} concentration from 0.01 to 0.1 M resulted in an increase in the CH_3I DF by a factor of about 3, at 1 or 4 A, and an increase in the I_2 DF by factors of about 1.4 and about 3 at 1 and 4 A respectively.

Nitrogen oxides in the gas feed streams also are oxidized (to HNO_3) and trapped. With a feed air stream containing 2% NO_2 , 90% was oxidized and trapped. However, the presence of NO decreases the iodine oxidation and trapping. For example, over the range of 0 to 1% NO in the feed stream, the DF for CH_3I decreased by a factor of 10 and the DF for I_2 by a factor of 4. The rate of decrease of iodine DF was much less over the range of 1 to 2% NO , while with 3% NO the iodine trapping ability was entirely lost because of the inability to maintain any Co^{3+} . In a cascade of electrolytic cells, the first two stages would destroy the NO , allowing the remaining stages to effectively trap the iodine.

9 R. D. Achley and Zell Combs, *Applicability of Inorganic Sorbents for Trapping Radioiodine from MFBR Fuel Reprocessing Off-Gas*, ORNL TM-4227 (May 1973).

10 R. D. Achley and R. J. Davis, *Effect of Extended Exposure to Simulated MFBR Fuel Reprocessing Off-Gas on Radioiodine Trapping Performance of Sorbents (Final Report)*, ORNL TM-4529 (August 1974).

11 D. T. Pence, F. A. Duce, and W. J. Maech, *Metal Zeolites: Iodine Absorption Studies*, IN-1455 (1971).

12 *Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1971*, ORNL-4602, p. 61.

13 G. I. Cathers, D. J. Crouse, O. O. Yarbrow, and W. F. Shockley, p. 11 in *MFBR Fuel Cycle Studies Progress Report for March 1972*, No. 37, ORNL TM-3807 (1972).

14 J. C. Mailen, W. F. Clark, and C. T. Thompson, p. 31 in *Aqueous Fuel Reprocessing Quarterly Report for Period Ending Dec. 31, 1973*, ORNL TM-4488 (1974).

15 J. C. Mailen and T. O. Tiffany, "The Reaction of Iodine with Concentrated Nitric Acid," *J. Inorg. Nucl. Chem.* 37, 127 (1975).

16 J. C. Mailen, "Equilibrium in the Oxidation of Iodine by Hyperazeotropic Nitric Acid," *J. Inorg. Nucl. Chem.* 37, 1019 (1975).

For large-scale application, titanium, zirconium, glass, or ceramics would be required as structural materials for the anodic half-cell because of oxidative corrosion. The preferred anode material is commercially available platinum-plated titanium mesh.

Evaporation could be used as a simple concentration step following the electrolytic process. This would leave a solid product mixture of cobaltic periodate and cobalt nitrates, easily amenable for storage.

This method offers an attractive alternative to the existing methods for efficiently trapping inorganic and organic iodides from gas streams to yield a concentrated aqueous product.

17.4 REMOVAL OF IODINE FROM REACTOR FUEL SOLUTIONS AS INSOLUBLE PdI₂

Oak Ridge National Laboratory is engaged in the development of methods for use in the reprocessing of fuel from various types of nuclear reactors. A common need in any nuclear fuel reprocessing system is good retention of radioiodine. The existing and commonly proposed techniques for handling radioiodine involve volatilizing the iodine from the fuel solution and then removing the iodine from the off-gas stream, either by various aqueous scrubbing solutions or by solid sorbents. As an alternative to volatilization of the iodine, we have found that the iodine can be precipitated from synthetic fission product solutions as insoluble PdI₂ by the addition of hydroxylamine nitrate (HAN).

The palladium-to-iodine weight ratio in typical light-water reactor (LWR) fuel is about 4.8, giving about a factor of 10 excess of palladium over that required to form PdI₂. Most of the palladium in the fuel initially dissolves, since palladium metal is soluble in nitric acid; however, the quantity of iodine remaining in the solution from the dissolver depends on the dissolution technique. A standard dissolution with special efforts to remove the iodine may leave 10% or less of the initial iodine in the final solution. Fumeless dissolution^{17,18} where the NO₂ is converted to nitric acid and recycled to the dissolver will yield a dissolver solution containing most of the iodine in the original fuel. Precipitation of palladium iodide is not normally observed in nitric acid, because the presence of nitrous acid causes rapid oxidation of iodide to I₂.

The addition of HAN destroys the nitrous acid²¹ and, in addition, reduces molecular iodine to iodide.²²

In addition to tests using simulated fuel solutions, we have completed two tests with radioactive fuel solutions. These solutions (obtained from D. O. Campbell of ORNL) resulted from the dissolution of 250 g of Robinson reactor fuel in 600 ml of 7 M HNO₃. Burnup was about 30,000 MWd metric ton, and the fuel had cooled about 23 months. The final solution contained about 1.4 M uranium in 3 M HNO₃. Since the solution was continuously sparged during dissolution, the original iodine content had been lost; therefore, we added iodine plus tracer. The two tests were identical except for the chemical form of the added iodine: in one case the form was iodide in water, and in the other it was elemental iodine in 3 M HNO₃ plus nitrous acid. The combined iodine and fuel solution was stored in a sealed tube overnight to allow the iodine to equilibrate. A centrifugation and sampling the next day determined the quantity of precipitate in the absence of HAN. Excess HAN was then added to destroy nitrous acid and reduce the iodine, and the solution was periodically centrifuged and sampled to determine iodine in solution. The results are illustrated in Fig. 17.1 and compared with the best test, using a simulated fuel solution. Case A is the best simulated fuel solution test. Case B is the radioactive fuel test where iodide was added, and case C used elemental iodine. Behavior of the two fuel solutions is similar, with a maximum iodine removal of 98.5%. The simulated solution gave a better iodine removal. Two possible explanations for the lesser removals from fuel solutions are the difficulty of obtaining clean samples in the hot cell and the possible presence of organic iodides in the fuel solution.

The iodine removals of 98 to 99% that we have demonstrated with radioactive fuel solutions are adequate to meet present iodine retention requirements for long-cooled fuel.

17. C. W. Kee, ORNL, private communication, September 1975.

18. D. O. Campbell, ORNL, private communication, November 1975.

19. G. I. Miles, *The Fumeless Dissolving of Uranium*, AERE-CR-1804, Atomic Energy Research Establishment, Harwell (1955).

20. R. H. Rainey and R. C. Lovelace, ORNL, private communication, January 1976.

21. M. N. Hughes and G. Stedman, *J. Chem. Soc.* 1963, 2824.

22. I. Wolf and H. Holzapfel, *Angew. Chem.* 62, 88 (1950).

Fig. 17.1. Dissolved iodine levels in simulated and irradiated fuel solutions before and after addition of hydroxylamine nitrate.

18. Reactor Safety Research

18.1 FISSION PRODUCT RELEASE FROM LWR FUEL

The primary objectives of this program are to provide a more detailed understanding of fission product behavior under postulated spent fuel transportation and successfully terminated loss-of-coolant accident conditions, and to determine the chemical and physical forms of the released species. This information is needed for accurate evaluation of the consequences of radioactivity release and assurance of conformance with reactor licensing guidelines concerning radiological dose.

The program is divided into four series of experiments: (1) studies of the behavior of specific fission product species (I_2 , CH_3I , Cs_2O , CsI) in the apparatus, as shown in Fig. 18.1 (Control Test Series); (2) determinations of the release and behavior of simulated fission products implanted in unirradiated fuel rod specimens (Implant Test Series); (3) investigations of the release of real fission products from fuel rod specimens irradiated to low burnups (~ 1000 MWd metric ton) (Low-Burnup Series); and (4) studies of the release of fission products from 12-in. (30.5-cm) segments of commercial pressurized-water reactor (PWR) fuel rods that had been irradiated in the H. B. Robinson Plant to 30,000 MWd metric ton (High-Burnup Test Series). During this reporting period, the experimental work for the first series was completed, and a report¹ covering this work was published. Ten experiments in the second series (Implant Test Series) were also performed, and much of this work was reported.^{2,3} A parallel study of cesium-uranium interactions utilizing a Knudsen cell-mass spectrometer was also conducted, concluded, and reported.⁴

The specimens investigated in the Control Test Series were I_2 , CH_3I , Cs_2O , and CsI , primarily in a steam-argon atmosphere over a temperature range 500 to 950°C. Figure 18.1 shows the most effective arrangement of apparatus, which was developed as the result of this series and is being used in the

Implant Test Series. The arrangement consists of a thermal gradient tube for deposition of compounds condensable above 125°C, a low-pressure cascade impactor and high-efficiency filters for collection of particulate materials, silver-plated screens for the collection of reactive forms of iodine such as HI and I_2 , impregnated charcoal and silver-exchange zeolite for trapping organic iodides, and cold charcoal (which can be used for the collection of noble gases).

Iodine remained stable at 800°C in steam and argon, but CH_3I decomposed; decomposition rate constants were calculated. Cesium monoxide reacted rapidly with steam to form $CsOH$ (probably the monohydrate), which, in turn, reacted with the quartz furnace tube. Cesium iodide in steam at 700°C decomposed partially by reaction with quartz. Although most of the CsI and the unreacted $CsOH$ were collected in the thermal gradient tube, a small fraction of both these compounds was deposited in the form of particles in the cascade impactor and on the filters.

The Implant Test Series involves studies of the release of fission-product-type species from the surfaces of unirradiated UO_2 pellets housed in Zircaloy-4 cladding [12-in. (30.5-cm) segments]. In these tests, fission product inventories resulting from irradiation were simulated by implanting selected

1. 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).

2. 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).

3. 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 (June 1976).

4. J. L. Collins, M. F. Osborne, A. P. Malinowski, R. A. Lorenz, and S. R. Manning, *Knudsen Cell Mass Spectrometer Studies of Cesium-Uranium Interactions*, ORNL NUREG TM-24 (June 1976).

Fig. 18.1. Flow diagram of apparatus used in fission product release program.

stable nuclides (along with appropriate radiotracer nuclides) in predetermined chemical forms as TeO_2 , CsI , and $\text{CsOH} \cdot \text{H}_2\text{O}$ on the surfaces of the fuel pellets. Cladding failure was simulated either by perforating the cladding beforehand or by pressurizing the rod internally to induce rupture.

Table 18.1 presents the experimental operating conditions, the percentages of nuclides released from the fuel rods, and estimates of the percentage of iodine released after certain time periods (1 min, 1 hr, 20 hr) of the experiments. In the tests where the rods were preperforated (1.6-m-diam holes) and the temperature was 500 or 700°C, the rates of release of iodine from the rods were observed to decrease slowly with time. Release of iodine in a flowing steam-argon mixture at 500°C over the 20-hr test period was 0.6% of the original iodine. However, the release rate was approximately ten times higher when dry air was used, whereas the cesium fractional

release was approximately one-tenth that of the iodine release from both types of atmosphere. At 700°C the iodine and cesium release rates were approximately ten times higher than at 500°C for both the steam and air atmospheres. The tellurium release rate was approximately 0.3% per hour at both temperatures in steam and was much lower in dry air. A notable result in the tests utilizing dry air atmosphere was expansion of the cladding (near the perforations) caused by oxidation of the UO_2 pellets.

Experiments in which the cladding was ruptured by applying argon pressure to the test fuel rod were also performed in steam over the temperature range 700 to 1100°C. Significant amounts of vapor and aerosol were released with the argon pressurizing gas upon rupture. Iodine escape from the test rods over a 1-hr period was approximately 15% at 700°C, 20% at 900°C, and 60% at 1100°C. Cesium release was usually a factor of 2 lower than for iodine, and

Table 18.1. Release from gap of simulated fuel rods

	Experiments and perforated rods					Experiments with pressure-ruptured rods				
	Dry air ^a (°C)		Steam ^b (°C)			Steam ^b (°C)				
	500	700	500	700	1100	700	700	700	900	1100
Test number	9 ^c	7	6	10	4	1	2	5	3	8
Duration, hr	20	5	20	5	1	1	1.5	2	2	1
Simulant type ^d	Mixture	Mixture	Mixture	Mixture	Mixture	High conc. CsI	Low conc. CsI	Mixture	Mixture	Mixture
Release from gap, % of original										
Iodine	6.5	11.2	0.61	1.60	31.7	19.6	16.5	15.5	25.5	62.6
Cesium	0.83	1.11	<0.39	0.20	18.6	12.7	7.3	4.1	4.8	37.1
Tellurium	0.0016	0.01	0.56	0.12	0.12			6.5	1.55	3.3
Estimated iodine release, % of original iodine										
1 min	0.0065	0.13	0.00055	0.015		5.8	0.9	14	10	7.5 (900°C)
1 hr	0.39	5.3	0.033	0.72	31.7	19.6	15.6	14.7	18	62.6
20 hr	6.5	~17	0.61	~2.5			~20	~30		

^a380 cm³ min (STP) dry air.^b320 cm³ min (STP) steam and 60 cm³ min (STP) argon, except about three times greater for test 8.^cInitially four holes drilled; expanded to about nine times original open area.^dMixture = 8 mg of cesium as CsOH·H₂O and CsI, 0.8 mg of iodine as CsI, and 3 mg of tellurium as TeO₂.

tellurium was about a factor of 3 lower than for cesium. The rods were induction heated for those experiments; this resulted in a longitudinal temperature gradient and migration of a portion of the CsI to the cooler end, especially at the higher temperatures ($\geq 900^\circ\text{C}$). However, most of the cesium did not migrate in the experiments conducted at 900°C or lower, thus supporting observations of the probable reaction of CsOH with UO₂ that were made in the Knudsen cell-mass spectrometer study.⁴ Organic iodides, CsOH·H₂O, CsI, and I₂ were identified as part of the released material. These compounds were expected, based on the experiments performed in the Control Test Series.¹

In all the implant experiments that employed the TeO₂ simulant, the Zircaloy-4 cladding proved to be an effective getter of the tellurium. Visible tellurium deposition rings opposite the pellet interfaces gave evidence that tellurium reacted rapidly with the cladding. (TeO₂ was coated on the dished ends of the pellets from an aqueous slurry prior to the experiments.) A sample of the tellurium-cladding reaction product was determined by x-ray diffraction to contain primarily Te₂ZrO₅.

Limited Knudsen cell-mass spectrometer studies were made of the partial pressures of cesium-containing species [assumed to be primarily Cs(g)] over Cs₂CO₃ and over equilibrium phases involving

Cs-U-O compounds formed from mixtures that initially contained either Cs₂CO₃-UO₂ or CsOH-UO₂.⁴ Although additional work is required to further define the equilibria involved, the data unambiguously demonstrate a significant reduction in cesium partial pressure because of probable Cs-U-O compound formation and indicate essentially identical behavior with either CsOH or Cs₂CO₃ as the starting material with UO₂.

18.2 TRANSIENT RELEASE FROM LMFBR FUEL

The Transient Release Program is sponsored by the Nuclear Regulatory Commission Division of Reactor Safety Research. The objective of this program is to investigate the release and behavior of fuel and fission products in a hypothetical core disruptive accident (HCDA) of an LMFBR.

In order to develop a concept of the magnitude of the LMFBR radiological source term, an accurate characterization of the fuel aerosols, fission products, and volatile forms resulting from HCDA, must be derived experimentally by using actual highly irradiated fuel and subjecting the fuel to high-temperature hydrodynamic expansion while in the superheated liquid state. Incident transient chemical potentials provided by the mixture of fuel vapor,

fission products, cladding, and coolant in a high-radiation environment effectively discourage any attempt to predict these parameters from a simple thermodynamic approach.

An investigation of the behavior of highly concentrated fuel aerosols is being conducted in two parallel programs, both of which are limited to the use of unirradiated UO_2 as a simulant for LMFBR fuel. In one program, uranium oxide is vaporized as UO_2 or U_3O_8 , either by electric arc or by rapid oxidation of molten uranium. The resultant aerosols are characterized in terms of initial concentration, agglomeration rate, gravimetric and diffusional deposition, and particle size spectrum. In the other program the major emphasis is being placed on more accurately simulating the thermal transient of the HCDA by rapid electrical heating of short fuel rods.

Development of the Capacitor Discharge Vaporization Technique

A practical out-of-pile method for reaching the high fuel internal energy conditions has been developed by the use of direct heating via the discharge of electrical energy stored in capacitors.⁵⁻¹¹ This capacitor discharge vaporization (CDV) technique was developed to be used as a nonnuclear tool for studying fuel disassembly and the resulting radionuclide release and transport.

The CDV tests were carried out at the Arnold Engineering Development Center (AEDC), a U.S. Air Force facility operated by ARO, Inc., located at Arnold Air Force Station, Tennessee. Two capacitor bank configurations were used. One of these, when charged to 2600 V (74,000 J) delivered a nominal 15-MW power pulse with load currents of 10 to 12 kA

and a maximum energy delivery time of 3.3 msec. The other supplied a slower energy deposition rate. When charged to 2600 V (63,000 J), a nominal 5-MW pulse with load currents of 6 to 8 kA and a maximum discharge time of 10 msec is available.

About 23 tests using UO_2 as a fuel simulant were completed during CDV development in the last year. These experiments were performed to establish the feasibility of the technique and to provide a basis for design of the CDV equipment being constructed at ORNL.

Because of the high inverse resistance-temperature coefficient of fuel (and UO_2) and the lack of homogeneity expected in fuel samples, the technique also required the design of a constant-power preheater to bring test samples to desired thermal conditions prior to CDV firing. This regulator was developed and designed to control power in a resistive load to any selective level between 0 and 4000 W (100 A, maximum), using phase-fired silicon-controlled rectifiers (SCRs). A negative feedback loop automatically controls the SCR firing angles to equalize actual load power (which is measured electronically) with set-point power.

Typical fuel simulant sample assemblies used with the CDV system consist of a stack of LMFBR fuel pellets (UO_2) contained between spring-loaded tungsten electrodes and surrounded by loose UO_2 packing, all retained by an outer quartz sheath mounted in a flanged stainless steel housing. Spring loading compensates for expansion during the preheat cycle, and the quartz sheath provides electrical insulation as well as structural containment. The UO_2 packing serves as thermal insulation that prevents quartz melting and minimizes stresses from thermal expansion.

High-speed motion pictures of sample disassembly (20,000 frames/sec), electrical and pressure data, postshot serial filter samples, fallout samples, and plateau samples were obtained for analysis of each experiment. In addition, a computer simulation program was developed, using literature data and experimental results, to aid in design and operational improvements to increase aerosol yield.

In successful experiments, average power rates from 4.6 to 15.3 MW were observed. The computer simulation calculations¹² indicate that this range of rates is equivalent to 0.5 to 1.15 MW per gram of fuel pellet. A summary of the results of the most recent tests is given in Table 18.2. The time required for

5. T. S. Kress, G. W. Parker, and M. H. Fontana, *Work Plan: Transient Release from LMFBR Fuel*, ORNL TM-4875 (September 1975).

6. J. M. Rochelle, M. J. Kelly, and K. Rush, "Apparatus and Technique for Fast Vaporization of Simulated LMFBR Fuel," *Trans. Am. Nucl. Soc.* 22, 453 (November 1975).

7. M. J. Kelly, J. M. Rochelle, and G. W. Parker, "Experimental Results from Capacitor Discharge Vaporization Fuel Disassembly Tests," *Trans. Am. Nucl. Soc.* 22, 453-54 (November 1975).

8. *Quarterly Progress Report LMFBR Safety Programs October-December 1974*, vol. III, ORNL TM-4805 (April 1975).

9. *Quarterly Progress Report LMFBR Safety Programs January-March 1975*, vol. III, ORNL TM-4914 (July 1975).

10. *Quarterly Progress Report LMFBR Safety Programs April-June 1975*, vol. III, ORNL TM-5021 (October 1975).

11. *Quarterly Progress Report LMFBR Aerosol Release and Transport Program July-September 1975*, ORNL NUREG TM-8 (April 1976).

12. R. M. Train et al., *Modeling Resistive Heating of Powdered Uranium Dioxide*, ORNL MII-204 (December 17, 1974).

Table 18.2. Summary of test results for AEDC Tests 22 to 33

Shot No.	Energy deposited before arcing (J)	Load resistance to arcing (Ω)	Time to arc (msec)	Energy deposited after arcing (J)	Aerosol yield (g/m ³)	Deposition rate, $t_{1/2}$ (min)
22 ^a	7,200	0.046	1.4	12,500	0.51 UO ₂	75
23	15,900	0.041	3.2	5,300	0.67 UO ₂	44
24	23,200	0.048	4.0	9,300	0.05 stainless; 2.0 UO ₂	23
25 ^b	16,900	0.04	10 ^c	0	1.35 UO ₂ ; 0.64 ThO ₂ ; 0.10 stainless	~24
26	2,700	0.03	1.2	13,000		
27	None ^c					
28	17,400	0.072	40	4,560	0.84	26.3
29	3,600	0.144	~0.2	10,700		
30	25,126	0.095	4.6	6,470	2.09	17.7
31	21,740	0.073	4.2	2,880	1.51	37.3
32	9,925	0.160	2.0	15,550	0.76	39.7
33	22,910	0.066	4.6	4,980	0.37	102.6

^aBank energy split between load and preheater. Disassembly occurred.

^bWeight measurements on serial filter samples extrapolated to time zero gave 4.6 g/m³. Values in table are based on analytical data from the same filter samples.

^cQuartz containment cracked on preheat. Bank fired into preheater. No meaningful data.

sample disassembly has varied from 0.65 to 5.5 msec. These times and power rates are consistent with the energy input and time frame of postulated HCDAs.

Scanning electron microscope (SEM) examination of plateout samples (Fig. 18.2) indicated that a wide variety of particles are produced, including some which are apparently liquid droplets.¹¹ Condensed-phase primary particle sizes (the cottony phase) ranged from 0.0043 to 0.017 μm (D_{50}) when examined by transmission electron microscopy. Settling data from serial filter samples and the Stokes relation gave effective mass median diameters from 0.42 to 0.60 μm . In the SEM photomicrograph, the largest spheres are about 2 μm in diameter.

Present test sample design and operational procedures result in about 10% (~1 g) of the pellet stack forming persistent aerosol when disassembling into 1-atm ambient argon. Computer simulation calculations indicate a potential aerosol yield of about 25%.

Cold Proof Tests with U₃O₈ Aerosols

A continuing series of uranium oxide aerosol characterization tests are being performed in a 1200-gal (4542-liter) stainless steel vessel designated CRI-II. A number of tests conducted at the 1- to 2-g m⁻³ level have been used to illustrate the quality of fit of various particle input parameters to the master aerosol codes HAA-3B and HAARM-2. The aerosol produced by rapid oxidation of molten uranium metal is observed to consist of uniformly small primary particles which have agglomerated to 1 μm in aggregate size. No large spherical droplets, such as those seen in the electrically generated dispersion in Fig. 18.2, are evident. A comparison of the deposition behavior of the U₃O₈ aerosol at the 1-g m⁻³ concentration level with the behavior predicted by the aerosol code is illustrated in Fig. 18.3. The general behavior is in relatively good agreement; however, some obvious disagreement remains unexplained.

Much of the LMFBR HCDA interest in fuel-aerosol behavior is directed toward very high concentrations, which are beyond the capability of

13. Chem. Technol. Div. Annu. Prog. Rep. (Mar. 31, 1975, ORNL-5050, p. 89.

the metal oxidation method used in the CRI-II tests. We have constructed a 2500-A dc electric arc cold-hearth furnace to investigate behavior at the higher concentrations. In this device, UO_2 will be directly heated into a molten pool and then locally over-heated (essentially to boiling temperature) in order to produce large quantities of UO_2 vapor. This will be

rapidly quenched in argon and will be discharged into a vessel at rates up to about 100 g/min. At this rate, instantaneous peak concentrations of airborne oxide will approach 100 g m^{-3} , and at this level, according to the predicted agglomeration rate, deposition half-times of only 2 to 3 min will effectively impose a ceiling on the upper concentration level attainable.

ORNL DWG 75-5105RI

S-4576

Mag 5000 x

S-4577

Mag 1000 x

S-4578

Mag 200 x

S-4579

Mag 50 x

Fig. 18.2. Four successive magnifications (scanning electron microscope) of a plateout sample from test 9, showing both large droplets and submicron agglomerates.

Fig. 18.3. Rate of change in airborne UO_2 concentration at the 1-g m³ level in CRI-II.

19. Nuclear Regulatory Commission Programs

19.1 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. Two survey reports on the HTGR fuel cycle were prepared and issued, that is, on fuel fabrication¹ and fuel reprocessing.² A report on reprocessing LWR fuels, issued previously as ORNL TM-4901, was revised and reissued.³ A draft report on the conversion of yellow cake to UF_6 by the "dry" process was prepared and submitted to NRC for review.⁴ 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.

19.2 SAFETY REVIEW OF NUCLEAR FACILITIES

Federal regulations require that privately owned fuel reprocessing plants 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 NRC in reviewing the safety of these plants and in the preparation of safety evaluation reports and related generic reports. During this report period, we participated in the safety review of the Allied General Nuclear Services (AGNS), Barnwell Nuclear Fuel Plant Separations Facility (BNFP), the Exxon Fuel Recovery and Recycling Center Separations Facility, the Nuclear Fuel Services modified West Valley Reprocessing Plant, and the General Electric Morris Operation modified Fuel Storage Facility. Peripheral activities included: (1) providing assistance to the Environmental Sciences Division in assessing the environmental impact of solidifying radioactive wastes in the BNFP; (2) the analysis of the effect of a hydrogen explosion in the BNFP high-level waste tank; (3) the development of a model to enable computer solution of differential pressure across HEPA filters following an explosion in a space connected by duct to the filter unit; and (4) the preparation of testimony and the appearance as expert witnesses at the BNFP environmental hearing.

1. J. W. Roddy, R. E. Blanco, G. S. Hill, R. E. Moore, R. D. Seagren, and J. P. Witherspoon, *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 (in press).

2. 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 (in press).

3. B. C. Finney, R. E. Blanco, R. C. Fahlman, G. S. Hill, I. G. Kitts, 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 Light-Water Reactor Fuel*, ORNL NUREG TM-6 (first revision ORNL TM-4901) (in press).

4. 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).

19.3 SAFEGUARDS STUDIES

The Chemical Technology Division's safeguards work for 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.

In order to determine vault storage requirements and how they can be implemented in licensee facilities, ORNL personnel are reviewing the current state of the art in special nuclear material (SNM) storage vaults and the criteria to which they are built.

Funding for this project was received early in November 1975. During the first two months of the project, a draft of task 1 on the problem definition, problem areas, and proposed plan of action was developed. This draft indicated that the final product of the study will be the development of information to be included in guides and/or standards relative to vault systems used for the storage and protection of SNM. Such vault systems are typically found at fuel fabrication and reprocessing plants, and desirable characteristics of these systems include: (1) receiving and dispensing all SNM throughout the process, (2) preventing unauthorized people from removing material from the vault, (3) providing an immediate alarm in the event that unauthorized persons should attempt to remove SNM from the vault, (4) providing tamper-proof storage containers, (5) providing visual inventory methods to ensure container integrity, (6) providing real-time accountability as a backup for the physical protection of the SNM in the vault, and (7) protecting all SNM in the vault from direct overt attack.

In support of this program, trips were made to the Rocky Flats Plant (RFP), Denver, Colorado, for the purpose of studying their automated equipment in the RFP plutonium vault, and to the Kenway Engineering Company, Salt Lake City, Utah, for the purpose of discussing the RFP equipment with the engineers who designed and built it and who are now developing the software to operate it. The AGNS plant at Barnwell was visited to study their product storage area and safeguards program. At Babcock and Wilcox's Apollo facility, their mixed-oxide fuel pellet fabrication plant and their vault storage requirements were examined. The Hanford Engineering Development Laboratory was visited to discuss their proposed High Performance Fuel Laboratory and their vault storage plans.

Automated handling equipment has also been discussed with both users and manufacturers. Their knowledge of problem areas and equipment costs has been valuable.

Information received as a result of these contacts is being factored into the report covering task 2, which addresses the desirability and feasibility of automation of SNM handling equipment.

19.4 CARBON-14 PRODUCTION IN NUCLEAR REACTORS

A report was prepared on the origins of ^{14}C and the control of releases of ^{14}C in the nuclear fuel cycle.⁵ Quantities of ^{14}C that may be formed in light-water-cooled reactors (LWRs), high-temperature gas-cooled reactors (HTGRs), and liquid-metal-cooled fast breeder reactors (LMFBRs), both in fuel and in core structural materials, have been calculated by use of the ORIGEN code.⁶ The calculations are based on realistic estimates of 10 to 75 ppm nitrogen in the fuel, on specified maximum concentrations of nitrogen in core structural materials, and on an assumed nitrogen content in HTGR fuel graphite and reflector graphite of 30 ppm. Production of ^{14}C from oxygen in the oxide fuels (UO_2 , PuO_2 , ThO_2) and from carbon in HTGRs has also been calculated. Reference reactor burnups are 27,500 MWd per metric ton of uranium (MTU) for BWRs, 33,000 MWd MTU for PWRs, about 95,000 MWd MTU $^{235}\text{U} + \text{Th}$ for HTGRs, and 24,800 MWd MTU for an LMFBR with nuclear parameters pertaining to the Clinch River Breeder Reactor (CRBR). As the nitrogen content in BWR (Boiling-Water Reactor), PWR, and LMFBR fuels increases from 10 to 75 ppm, the ^{14}C content increases from 9 to 46, from 10 to 50, and from 2.6 to 19 Ci/GW(e)-year respectively; corresponding median values, based on 25 ppm nitrogen, are 18, 19, and 6 Ci/GW(e)-year. On the basis of 25 ppm nitrogen, 10 Ci of ^{14}C /GW(e)-year will be formed in HTGR fuel. All ^{14}C contained in the fuels may be released in a gas mixture (CO_2 , CO , CH_4 , etc.) during fuel dissolution at the fuel reprocessing plants. However, some small fraction may remain in aqueous raffinates and not be released until these are converted to solids. The gases would be released from the plant unless special equipment is installed to retain the ^{14}C -bearing gases.

⁵ W. Davis, Jr., *C-14 Production in Nuclear Reactors*, ORNL NUREG-1M-22 (in preparation).

⁶ M. J. Bell, *ORIGEN: The ORNL Isotope Generation and Depletion Code*, ORNL-4628 (May 1973).

Cladding metals and other core hardware will contain significant quantities of ^{14}C . Very little of this will be released from BWR, PWR, and MFBR hardware at fuel reprocessing plants; instead, the contained ^{14}C , 30 to 60 Ci (Ci) (Ci)/year for LWRs and about 13 Ci (Ci) (Ci)/year for a CFRBR, will remain within the metal, which will be retained on site or in a federal repository. The core structural material of HTRs will be graphite, which will contain less than 190 Ci of ^{14}C (Ci) (Ci)/year in fuel and reflector graphite if it initially contains 30 ppm nitrogen. All of this is available for release at a fuel reprocessing plant if the graphite is burned to release the fuel particles for further processing. Special equipment could be installed to retain the ^{14}C -bearing gases.

perform engineering and economic evaluations of alternative methods for management of nuclear wastes in the fuel cycle. Reprocessing of LWR fuels is being surveyed initially, and fuel fabrications and other facilities will be studied later. The study will include waste treatment at the reprocessing plant, on-site storage, transportation, and disposal in a burial ground or federal repository. All potentially feasible waste treatment methods are being evaluated to determine their efficiency and cost. This information will be incorporated in a computerized system analysis that can be used to determine the effect of a change in the system, such as the imposition of a new licensing regulation.

19.5 WASTE MANAGEMENT PARAMETRIC STUDIES

The Waste Management Parametric Studies Program was initiated in FY 1976. The objective is to

20. Diffusion of Adsorbed Species in Porous Media

The objectives of this investigation are to identify and to describe mathematically those mechanisms controlling the migration of sorbed species through porous media. The investigative efforts, which have focused on cesium-graphite systems, have involved theoretical mechanistic considerations and supplementary experimental activities designed to provide guidance and verification from both practical and academic points of view. An important aspect of this study is the search for techniques that will permit isolation of various dynamic interactions influencing the overall diffusion rates of the migrating cesium. This search has been implemented by comparing results for uniquely different graphite matrices, by comparing results for similar matrices that were subjected to dramatically different conditions of cesium exposure, and by comparing results for an identical system that was subjected to both static and flowing helium environments. Various graphite materials that were developed for high-temperature gas-cooled reactor (HTGR) applications have provided an interesting collection from which likely candidates for the present studies were selected. In addition, considerable cesium diffusion data generated under the auspices of various Peach Bottom HTGR surveillance programs have provided a valuable complement to those obtained in the present study.

An adequate description of the cesium migration patterns is given by the following system of equations for linear diffusive flow coupled with a net removal rate, r :

$$D' \frac{\partial^2 C''}{\partial x^2} = \frac{\partial C''}{\partial t} + r, \quad (1)$$

where

$$r = \frac{\partial C'}{\partial t} = k_1 C'' - k_2 C', \quad (2)$$

Primes are placed over the diffusion coefficient, D' , and the concentration of mobile cesium, C' , to signify that these parameters are referred to bulk dimensions of the graphite. The C'' variable represents the concentration of cesium that is strongly adsorbed and is practically immobilized relative to C' if k_2 is small. The remaining variables may be defined as follows: x is the length normal to the flow path, in cm; t represents time, in sec; τ has the value $(k_1 t)^{-1/2}$; and k_1, k_2 are constants, in sec^{-1} .

Solutions of this system of equations, which describe results of our bench-scale experiments, may be derived by assuming that the graphite specimen is initially devoid of cesium, the specimen is very long along x , and an initial amount of cesium (as ^{137}Cs), Q_0 (micromoles cm^{-2}), is pulsed onto the source surface normal to x at time zero. Thus, all information pertinent to D' , k_1 , and possibly k_2 is reflected in concentration profiles that are obtained by grinding-counting techniques.¹ If the removal rate r must be taken into account, the analytical procedure is to solve Eq. (1) for $C''(x,t)$ as a boundary-value problem and to insert this function into Eq. (2) to obtain $C'(x,t)$. Thus, for example, the total cesium concentration $C(x,t)$ as determined by the grinding-counting technique² is given by the equation

$$C(x,t) = C''(x,t) + k_2 \int_0^t C''(x,t) dt \quad (3)$$

when k_2 is small. This expression includes contributions of both mobile and immobile fractions.

Results for a fine-grain matrix containing a large fraction of carbon with a two-dimensional structure were unusual (with regard to typical graphite results), because the profiles indicated that the diffusion process was ideal. For the experiments, reasonable

1. R. B. Evans III, J. O. Steigler, and G. M. Watson, *J. Appl. Phys.* 41, 4808 (1970).

diffusion anneal times (ranging from hours to days) were employed. Also, the concentration profiles could be analyzed via classical mathematical formulations [with $r_s = 0$ in Eq. (1)] for diffusion from an impulse (thin-layer) source into a semi-infinite medium. The diffusion rates and activation energies were those indicative of surface transport. The equilibrium that controlled surface transport in this high-surface-area material was very elastic with respect to reversibility. In other words, rates of attainment of an equilibrium $K = C^*/C = k_1/k_2$ were very rapid such that the net adsorption rate was small relative to $\partial C/\partial t$. The possibility of direct control by either a gas or a solid-state mechanism was eliminated by various theoretical tests.

On the other hand, results for large-grain, coarse-texture, large-pore structures were significantly different from those described previously. Cesium transport rates along the low-area surfaces adjacent to the large pores were visualized as being much higher than the rate of approach to sorption equilibrium in or on the large-volume grains. The net result was the acquisition of profile shapes that were, at least initially, quite difficult to interpret. Nonetheless, for a theoretical treatment, the effects of the rate of approach to sorption equilibrium were assumed to be mathematically simulated by a first-order irreversible reaction rate term that could be added to the accumulation term in the transient diffusion equation. We substituted Eq. (2) into Eq. (1), assuming $k_2 = 0$. Admittedly, this heuristic approach was adopted for reasons of mathematical tractability; however, the resultant equations were quite adequate for correlation profiles from short-term laboratory experiments.

Analysis of cesium diffusion profiles in Peach Bottom HTGR fuel element components as reported by Vanslager et al.,² Haire and Zumwalt,³ and Dyer et al.⁴ were considered important for two reasons: (1) cesium diffusion coefficients based on laboratory experiments ($D = \sim 5 \times 10^{-10}$ cm²/sec at 700°C) were considerably higher than those reported for similar materials based on computer code and reactor

component data ($D = \sim 1.5 \times 10^{-10}$ cm²/sec at 700°C), and (2) any effects of a $k_1 C^*$ term, if present, should have been manifest in the fuel element component data by virtue of the relatively long-term cesium exposures involved (months to years vs minutes to hours in the laboratory experiments).

Examination of cesium concentration profiles in the graphite HTGR fuel element components indicated that the irreversible model ($k_2 = 0$) still held, even though the cesium exposure times for these components were very long. Typical results are shown in Fig. 20.1. The solid curves represent the predicted approach to a quasi-steady state that is attained when τ is 4.0 or greater and $k_1 = 0$. At this τ value the concentration ratios, referred to the surface concentration, appear to be static; however the entire profile $C(x,t)$ actually rises, even beyond $\tau = 4.0$, since

$$C(0,t) = C^*(1 + k_1 \tau),$$

where C^* is the fixed potential at $x = 0$. This result comes directly from Eqs. (2) and (3) with $k_2 = 0$, without recourse to Eq. (1). The effects of a back-reaction rate term were explored by taking $k_2 = 0.1k_1$. Attention is called to the 600°C dotted curves in Fig. 20.1. For the assumed value $k_2 = 0.1k_1$ at $\tau = 12$ (about 83 days), which is essentially steady state, the curve falls much above the data, indicating that the k_2 term must be much smaller than this—essentially negligible in present experiments and in the reactor data.

2. F. F. Vanslager, W. F. Bell, O. Seeman, and M. I. Morgan, "Fission Product Transport in HTGR Systems—A Summary," p. 361 in *Proceedings of Gas-Cooled Reactor Information Meeting at ORNL*, April 1970, CONF-700401 (1970).

3. M. J. Haire and I. R. Zumwalt, *Cesium Diffusion Coefficients and Other Results from the Analysis of Peach Bottom DT-405 Fuel Element Activity Profiles*, GA-A12492 (July 1973).

4. F. F. Dyer, R. P. Wachner, W. J. Martin, I. I. Fauchild, R. J. Keadl, and H. J. de Nordwall, *Postirradiation Examination of Peach Bottom HTGR Driver Fuel Element 1706-01*, ORNL-5126 (April 1976).

Fig. 30.1 Cesium concentration profiles in three sections of HLM-45 graphite in Peach Bottom fuel element DE3-05, core 1. This element operated for 452 effective full power days. Solid curves show the approach to the quasi-steady state condition represented by the $\lambda = 0$ curves which fit the data. Dashed curves in the upper right represent computed values for a relatively slow back reaction rate term.

21. Miscellaneous Programs

21.1 RESOURCE STUDIES

The Chemical Technology Division continued to contribute to ORNL interdivisional efforts on resources and energy analysis. The World Energy Conference, for which ORNL prepared *World Energy Conference Survey of Energy Resources, 1974*, has decided to update the statistical information on resources every 18 to 24 months. Since this work will be done in the United Kingdom to keep costs down, we have transmitted our files, computer tapes, and instructions to them. The first updated report is expected to be published in the summer of 1976.

J. H. Gibbons, read of the University of Tennessee Environment Center, sponsored a Citizens Energy Workshop at U-T-Nashville, May 16-17, 1975. H. F. Goeller delivered a talk on "Energy Resources". Other ORNL participants included G. G. Fee, S. F. Beall, and C. R. Richmond.

H. F. Goeller, as a member of the ORNL Program Planning and Analysis Office, has continued general studies on nonrenewable resources. Major work in this area has included his participation as a member of the ad hoc committee on Rational Use of Potentially Scarce Metals, a part of the Scientific Affairs Division of NATO. The findings of this committee, which will be issued this summer as a report of the Science Committee Study Group, 1976, is entitled *Rational Use of Potentially Scarce Metals*. This report examines the present and future world demand, production, consumption, and uses of 11 scarce metals (Cu, Pb, Sn, Hg, Co, W, Pt, Zn, Ag, Cd, and Sb) and provides recommendations for conservation through substitution and recycle. Goeller also coauthored a paper (with A. M. Weinberg) entitled "The Age of Substitutability,"

which was presented by Weinberg as the 11th Annual Foundation Lecture at the United Kingdom Science Policy Foundation Symposium on a Strategy for Resources at Eindhoven, the Netherlands, September 18-19, 1975.

Work on resource studies was interrupted by two subsidiary activities during this report period: (1) consultation on the design of the proposed Energy Systems Research Laboratory and (2) participation in an ad hoc committee [with C. F. Boes, Jr., I. S. Olson, and R. Rotty (Institute for Energy Analysis)] established in January 1976 to study the present national and international status of work on the CO₂ "greenhouse effect" on world climate and ERDA's possible role in this area.

21.2 STUDIES INVOLVING TESTS OF OBSOLETE CASKS

In recent years, there has been a great deal of interest in safety aspects of nuclear-related programs. The transportation of radioactive materials produced in the nuclear fuel cycle has generated considerable discussion, since some of these highly radioactive materials are moved through the public sector; these 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 the package behavior can be predicted with confidence. The ERDA Division of Environmental Control Technology has organized an advisory committee to provide guidance for the program.

In the past year, a 7000-lb (3182-kg) cask was tested twice by dropping it, once from a height of 30 ft (9 m) and once from a height of 90 ft (27 m), onto an armor-plate surface of a temporary reinforced concrete impact pad at the ORNL Tower Shielding

1. *Chem. Technol. Div. Annu. Prog. Rep.* Mar. 31, 1975, ORNL-5050, p. 96.

2. *Science* 191, 683 (Feb. 20, 1976), also published as IFA Report 76-1.

Facility (ISF). This facility has a capacity of lifting as much as 40 tons (36 metric tons) to a height of about 240 ft (73 m). These drops provided engineering data on the behavior of the temporary impact pad and the towers under drop conditions.

Following these initial tests, the 23-ton (21-metric-ton) Heavy-Water Components Test Reactor (HWCTR) cask was dropped 30 ft (9 m) at an oblique angle onto the temporary impact pad to demonstrate the damage that occurs in the secondary impact owing to the rotational energy. A second drop of the HWCTR cask was made from a height of 30 ft (9 m), with the center of gravity of the cask in a vertical plane over the point of impact to achieve the maximum deformation. The deformations measured compared favorably with those predicted by Los Alamos Scientific Laboratory's computer accident damage analyses.

A permanent impact pad will be installed at the ISF to serve as the "essentially unyielding surface" described in regulations. The structure will consist 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).

A subcontract was awarded to Battelle Columbus Laboratories (BCL) to design, analyze, and fabricate a prototype bulk impact limiter for the HWCTR cask. For the past several years, BCL has been involved with the design, development, and safety analysis of impact limiters that cushion a container or package to prevent large shock loads in crash-type accidents. This will be the first full-scale test of such a device. The impact limiter will be placed over the closure end of the cask and will serve as the impacting

surface in an end-on drop test from a height of 30 ft (9 m).

21.3 DISPOSAL OF ORNL RADIOACTIVE WASTE BY HYDRAULIC FRACTURING

A series of three injections of intermediate-level waste (ILW) solution was made in 1975. A total of 190,000 gal (~720,000 liters) of waste solution containing 86,700 Ci of radionuclides was injected; a summary of the volumes and activities is given in Table 21.1.

Injection ILW-12 was scheduled for October 1974, and preliminary preparations had almost been completed when the injection date was delayed. At this time, all of the solids to be used in the injection had been blended and stored. Preparations for the injection were resumed after a three-month interval, and at this time the suitability of the stored solids was questioned. A few nonconclusive tests were made which indicated some deterioration in flowability had occurred; however, there was no real evidence that the solids were unusable. In the absence of actual operating data on solids stored for lengthy periods, the decision was reached to attempt the injection with the old solids. The injection went very poorly; the solids would not flow out of one storage bin at all and flowed very erratically out of the others. This difficulty with solids flow caused great difficulty with mix control and resulted in very irregular operation of the injection pump. This was probably a major cause of a series of minor malfunctions that resulted. A total of 25,700 gal (~97,000 liters) of waste and 4,390 gal (~16,600 liters) of water was injected before the futility of continuing the injection under such

Table 21.1. Summary of intermediate-level waste injections

Injection	Date	Volume of waste (gal) [liters]	Volume of water (gal) [liters]	Volume of grout (gal) [liters]	Activity (Ci)
ILW-12	1-14-75	25,710 [~97,000]	4,390 [~16,600]	42,000 [~160,000]	14,076
ILW-13	4-29-75	81,000 [~306,000]	4,900 [~18,500]	126,100 [~480,000]	39,118
ILW-14	6-30-75	82,970 [~315,000]	9,500 [~36,000]	138,700 [~525,000]	33,466
Total		189,680 [~720,000]	18,790 [~71,000]	306,800 [~1,160,000]	86,660

conditions was acknowledged and the injection was ended. This somewhat abortive injection points up the importance of having solids that flow easily without clumping, sticking, and bridging.

Injection II W-13, which was made on April 29, 1975, went quite smoothly overall, although several minor difficulties were encountered. Failure of an air slide connection and plugging of a pump drain pan necessitated temporary shutdowns; in addition, cement bridging in the mixer bowl occasionally caused problems, particularly after any slowdown or shutdown of the injection. A total of 81,000 gal (~306,000 liters) of waste solution and 4900 gal (~18,500 liters) of water was injected at an overall solids:liquid mix ratio of 6.3 lb/gal (0.72 kg/liter).

Injection II W-14 was started on June 18, 1975. After 2 hr 20 min of operation, however, it was halted because the waste pumps were not delivering sufficient pressure. Following inspection and adjustment of the pumps, the injection was resumed. The injection was continued for an additional 2 hr 45 min; at that time, the packing of one of the pistons of the injection pump failed, allowing waste grout to leak past the piston into the pump cell. The injection was stopped, and the standby pump was used to clear the well of grout. The piping and the mix tub were subsequently washed, and cleanup operations were started to permit entry into the pump cell for repairs.

The injection pump was repacked on June 19. On June 20 the injection was restarted. Difficulty with the transmission of the injection pump prevented operation in the higher gears, and the remainder of the injection was made at an average waste flow rate of about 110 gpm (416 liters/min) [180 gpm (680 liters/min) is a normal flow rate]. The remaining solids were mixed with approximately 42,000 gal (~160,000 liters) of waste solution and 5700 gal (~21,600 liters) of water [overall solids:liquid mix ratio of 5.66 lb/gal (0.68 kg/liter)]. This part of the injection was uneventful and was terminated after about 7 hr 20 min, when the solids had been consumed.

The control of the mix ratio was more erratic in this injection than it had been in previous injections, primarily because of unreliable mass meter readings. The accuracy of these readings is routinely checked against the known weight of solids in the storage bins as each bin runs empty (four times during an injection). In injection II W-14, this frequency was not sufficient, and a large mass-meter bias went undetected for several hours. A more frequent check can be made by estimating the consumption of solids from the ratio of slurry volume to solution volume

and comparing this estimate with the mass meter readings. This procedure should be followed in future injections.

21.4 STORAGE, PURIFICATION, AND DISTRIBUTION OF ^{235}U

Oak Ridge National Laboratory serves as a national distribution center for ^{235}U . The facility includes shielded wells for storing up to 454 kg of ^{235}U in solid form (density, 1 g/cm³) and tanks (containing borosilicate glass for neutron poisoning) that can store 900 kg of ^{235}U in the form of uranyl nitrate solution at ^{235}U concentrations up to 250 g/liter. The Building 3100 vault, designed for storage of unirradiated fissile materials according to the latest ERDA specifications, has been used to store up to a maximum of 90 kg of fissile material (1.5 kg of ^{235}U , 1.0 kg of ^{239}Pu , and the remainder ^{233}U).

The storage facility accepts ^{235}U in the form of uranyl nitrate solution or as properly packaged solids. The solids may consist of uranium metal or uranium compounds that can be readily and safely dissolved in stainless steel equipment.

The purification facilities include a single-cycle solvent extraction system capable of purifying ^{235}U at the rate of 35 kg/week. An ion exchange and nitrate-to-oxide conversion line, with a capacity of 26 kg of ^{235}U per week, has been in operation for the light-water breeder reactor (LWBR) support program.

Receipts of ^{235}U during this report period [other than those involved in the LWBR program (Sect. 8.1)] consisted of four shipments totaling 4.4 kg of uranium as ^{235}U oxides. Four shipments made from the facility consisted of 2.5 kg of uranium as ^{235}U oxides.

As of March 31, 1976, 500.4 kg of ^{235}U and 801.7 kg of ^{235}U were stored at the facility. Of these, 101.6 kg of ^{235}U and 800.2 kg of ^{235}U as uranyl nitrate solution were stored in the Thorium Reactor Uranium Storage Tank facility. After storage for seven years, the uranium concentration remained constant. After addition of more cadmium and gadolinium, analysis showed the solution to contain more than the minimum concentration required. Plans are being made to convert this uranium to UO_2 in FY 1978 (see Sect. 21.7).

R. W. Horton and J. R. Parrott, *Criticality and Safety Analysis: Building 3100, a Storage Vault for Uranium and Plutonium* (ORNL TM 3029) (February 1973).

J. Chens, *Technical Data Annual Progress Report*, Mar. 31, 1977, ORNL 4794, pp. 52-53.

In addition to the ^{235}U and ^{238}U , a total of 2.7 kg of plutonium in the form of nitrate solution, oxide, and mixed oxides of thorium and uranium is also stored in the facilities.

21.5 PREPARATION OF TRAINING GUIDES FOR NUCLEAR FACILITY PERSONNEL

A *Guide to the Selection, Training, and Licensing or Certification of Reprocessing Plant Operators* was completed and was issued as ORNL TM-5323 (Vol. 1) and ORNL TM-5324 (Vol. 2). The first volume covers selection of candidates, training methods, licensing, accountability, and plant safety; the second volume covers process operations and control. This training guide, based on the Purex process for recovering spent nuclear fuel, offers generalized descriptions of the basic principles (theory) and the unit operations (mechanics) used in the entire reprocessing segment of the nuclear fuel cycle, from transportation of spent fuel to conversion of recovered uranium to its hexafluoride. The handling of radioactive wastes is also included. The guide contains over 100 illustrations. The generalized approach is intended to assist in the writing of manuals for training operators in specific reprocessing plants.

The preparation of this guide was funded by the ERDA Division of Operational Safety (DOS) with the objective of describing the recruiting, selection, and training actions necessary for providing competent operators to perform the duties required in present-day nuclear fuel reprocessing plants. The guide was prepared by the staff of the Pilot Plant Section assisted by several contributions from other ORNL divisions, Savannah River Laboratory, and Argonne National Laboratory. All the participants in this effort have had long careers in their respective areas of radiochemical operation. The draft of the guide was submitted for review to the DOS and to a number of training coordinators in the commercial sector as well as in government installations. The review comments were very favorable. The guide has been distributed to the safety and production branches of ERDA and the NRC, to the major research and operating contractors in the nuclear industry, and to a number of universities and vocational schools that offer training in the nuclear field.

The Chemical Technology Division and the Operations Division participated in organizing and conducting the Second Symposium on Training of

Nuclear Facility Personnel, which was held May 11-14, 1975, at Gatlinburg, Tennessee, and was sponsored jointly by ORNL and the American Nuclear Society. Over 200 people from the nuclear industry attended the five sessions, which included talks on a wide variety of aspects in the training of personnel in fuel fabrication plants, reprocessing plants, power plants, and other segments of the nuclear fuel cycle. Rough draft copies of *A Guide to the Selection, Training, and Licensing or Certification of Reprocessing Plant Operators* were available for inspection by the attendees, many of whom requested to be included on the distribution list. Requests for information about the *Guide* continued throughout the year.

21.6 ENVIRONMENTAL IMPACT STATEMENT ON THE U.S. NUCLEAR POWER EXPORT PROGRAM

An environmental impact statement (EIS) on the U.S. nuclear power export program was prepared by the ERDA Division of International Programs. The EIS covers the existing program, including all activities and commitments to date, as well as a range of estimates projected through the year 2000. Portions of this EIS prepared by the Chemical Technology Division last year and revised this year include the section that provides a general description of the nuclear fuel cycle and the sections that describe the impact of mining, milling, conversion, enrichment, fuel fabrication, and waste management. Environmental considerations include the radionuclides released by the associated dose commitments of the general population, nonradioactive effluents or wastes produced by these operations and their effect on the environment are also considered.

21.7 CONVERSION OF CONSOLIDATED EDISON URANIUM FROM A NITRATE SOLUTION TO UO_2

The Energy Research and Development Administration has funded a program that will provide design, fabrication, and installation of equipment to convert the Thorium Reactor Uranium Storage Tank (TRUST) uranium to an inert solid. This solution, from the Consolidated Edison Indian Point Reactor, was purified at the Nuclear Fuels Services Plant,

U.S. Energy Research and Development Administration,
U.S. Nuclear Power Export Activities, Final Environmental
Statement, ERDA-1542 (April 1976)

West Valley, New York, in January 1969 and was received at ORNL shortly thereafter. The isotopic content of the material is as follows:

Isotope	wt %
^{233}U	9.67
^{234}U	1.40
^{235}U	76.47
^{236}U	5.63
^{238}U	6.84

The ^{235}U content is 120 ppm (based on total uranium).

We propose to concentrate the solution, denitrate to UO_2 , and store in cans in a semipermanent storage facility. Flowsheet development, using synthetic solutions, and conceptual design of the conversion equipment are under way. We propose to design and install the equipment by the end of FY 1977, with actual conversion to take place in FY 1978.

Publications, Speeches, and Seminars

BIOCHEMICAL TECHNOLOGY

- Anderson, N. G.,¹ D. D. Willis,² D. W. Holladay,³ J. E. Caton,⁴ J. W. Holleman,⁴ J. W. Eveleigh,⁵ J. E. Attrill,⁶ F. L. Ball,⁷ and N. I. Anderson,¹ "Analytical Techniques for Cell Fractions. XX. Cyclic Affinity Chromatography: Principles and Applications," *Anal. Biochem.* **68**, 371 (1975).
- Anderson, N. G.,¹ D. D. Willis,² D. W. Holladay,³ J. E. Caton,⁴ J. W. Holleman,⁴ J. W. Eveleigh,⁵ J. E. Attrill,⁶ F. L. Ball,⁷ and N. I. Anderson,¹ "Analytical Techniques for Cell Fractions. XIX. The Cyclum: An Automatic System for Cyclic Chromatography," *Anal. Biochem.* **66**, 159 (1975).
- Bostick, W. D., "Simultaneous Determination of Molybdate-Reactive Silicon and Orthophosphate with a Miniature Centrifugal Fast Analyzer," presented at the 27th Southeastern and 31st Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Oct. 29-31, 1975.
- Bostick, W. D., M. L. Bauer,⁷ J. M. Morton,⁶ and C. A. Burtis, "Coagulation-Time Determination with Automatic Multivariable Analysis, by Use of a Miniature Centrifugal Fast Analyzer," *Clin. Chem.* **21**, 1288 (1975).
- Bostic, W. D., C. A. Burtis, and C. D. Scott, "Simultaneous Determination of Silica and Phosphate in Water from a Single Experiment Using a Miniature Centrifugal Fast Analyzer," *Anal. Lett.* **9**(1), 65 (1976).
- Burtis, C. A., "Advances in Centrifugal Fast Analyzer Development," presented at the Symposium on Emerging High-Sensitivity Analytical Techniques, Ninth International Congress on Clinical Chemistry, Toronto, July 13-18, 1975.
- Burtis, C. A., "Historical Development and Concept of the Centrifugal Analyzer," presented at the Centrifugal Analyzer Workshop, Fall Meeting of the American Society of Clinical Pathologists, Chicago, Sept. 20, 1975.
- Burtis, C. A., "Recent Advances in Centrifugal Fast Analyzers," presented to the Miami Section of the American Association of Clinical Chemists, Miami, Fla., June 3, 1975.
- Burtis, C. A., "Recent Development in Centrifugal Analyzer Technology," presented at the Centrifugal Analyzer Workshop, Fall Meeting of the American Society of Clinical Pathologists, Chicago, Sept. 20, 1975.
- Burtis, C. A., "The Analytical Effect of Sample Evaporation in the Clinical Laboratory," presented to the Miami Section of the American Association of Clinical Chemists, Miami, Fla., Nov. 14-15, 1975.
- Burtis, C. A., "The Centrifugal Analyzer: A New Tool in the Clinical Laboratory," presented at a Continuing Education Program for Veteran Administration Personnel, Veteran Administration Hospital, Birmingham, Ala., Oct. 29, 1975.

1. Medical University of South Carolina, Charleston.

2. MAN Program.

3. Analytical Chemistry Division.

4. Information Division.

5. Instrumentation and Controls Division.

6. Health Division.

7. Center for Disease Control, Atlanta, Ga.

- Burtis, C. A., "The Centrifugal Fast Analyzer Program at the Oak Ridge National Laboratory," presented to the Dade Chemical Company, Miami, Fla., June 4, 1975.
- Burtis, C. A., "The Effect of Sample Evaporation on Analytical Accuracy," presented at the Spring Meeting of the Southeastern Section of the American Association of Clinical Chemists, Charleston, S. C., Apr. 30, 1975.
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April 9	Coal Conversion	Royce Salmon
April 23	Flowsheet Calculations for the Molten-Salt Breeder Reactor Processing Plant	C. W. Kee
May 7	Introduction and General Overview Voloxidizer and Dissolver Development Iodex Process Development	W. S. Groenier W. D. Holland ³⁹ B. A. Hannaford
May 21	Status of Hot-Cell Support for LMFBR Reprocessing Plant Design	V. C. A. Vaughen J. H. Grode
May 28	Storage and Release of Gamma-Ray Energy in Halite and Other Geologic Formations	G. H. Jenks

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June 11	Coal Pyrolysis	P. R. Westmoreland
June 18	Recirculating Fluidized Beds for Coal Conversion	R. E. Barker
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January 21	Actinide Removal from Waste Solutions by Ion Exchange Treatment of Spent Ion Exchange Resin	D. O. Campbell J. M. Chilton
January 28	Ion Exchange Separation of ^{233}U from Thorium and Daughter Activity - Experience in 3019 Pilot Plant	A. M. Krichinsky
February 11	Vaporization of LMFBR Fuel by a Capacitor Discharge Technique	M. J. Kelly
February 25	Feed Preparation, Recovery, and Refinement, and Special Separations for Separated Isotopes Preparation of High-Purity Crystal Bars of Hf, Ti, and Zr Recovery of Enriched Hg Isotopes	H. R. Gwinn J. O. Younghanse H. H. Caudili
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March 10	Aspects of the ^{14}C Problem, Including Local and Global Exposure	S. V. Kaye ²⁷
March 17	LWR Program Status Recent Advances in Iodine Process Development PuO_2 Dissolution Studies Isolation of Radioiodine as Insoluble Iodate in Cement	B. L. Vondra J. C. Mailen O. K. Tallent W. E. Clark
March 24	KALC Operation Experience ^{14}C Disposal by Fixation as Carbonate	A. D. Ryon D. W. Holladay
March 31	Separation of Solids from Coal Conversion Liquids	B. R. Rodgers

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