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Chemical Technology DIVISION

Annual Progress Report

PERIOD ENDING MARCH 31, 1975

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for Plutonium and Uranium

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CHEMICAL TECHNOLOGY DIVISION
ANNUAL PROGRESS REPORT
for Period Ending March 31, 1975

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OCTOBER 1975

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Preface

This progress report is a summary of the research and development efforts conducted in the Chemical Technology Division during the period April 1, 1974--March 31, 1975. Further information regarding work in the various programs can be obtained from the topical reports and journal articles cited in the references.

Contents

PREFACE	iii
1. DEVELOPMENT OF AQUEOUS PROCESSES FOR LMFBR FUELS	1
2. HTGR FUEL RECYCLE DEVELOPMENT PROGRAM	2
3. MOLTEN-SALT REACTOR PROGRAM	3
4. WASTE MANAGEMENT	4
4.1 Geologic Disposal Evaluation Program	4
4.2 Processing Modifications for Improved Waste Management	6
4.3 Leaching of Radionuclides from Waste Solids	11
4.4 Methods for Management of ORNL Liquid Wastes	14
4.5 Projections of Radioactive Wastes from the Nuclear Fuel Cycle	19
5. TRANSURANIUM-ELEMENT PROCESSING	20
5.1 TRU Operations	20
5.2 Special Projects	21
6. HTGR TECHNOLOGY AND SAFETY PROGRAMS	24
7. PREPARATION OF $^{233}\text{UO}_2$	25
7.1 Recovery of ^{233}U from Waste UO_2 and Scrap UO_2 - ThO_2 Pellets	25
7.2 ^{233}U Purification Systems	25
7.3 Conversion of ^{233}U from Nitrate Solution to Ceramic-Grade Dioxide Powder	26
8. SEPARATIONS CHEMISTRY RESEARCH AND DEVELOPMENT	27
8.1 New Separations Agents	27
8.2 Separation of Radium from Uranium Ore Tailings	28
8.3 Separation of Alpha Emitters from Fuel Reprocessing Wastes	30
8.4 Waste Stream Processing Studies	31
8.5 Distribution Equilibria, Kinetics, and Mechanisms	33
9. BIOMEDICAL TECHNOLOGY	36
9.1 Advanced Analytical Techniques	36
9.2 Centrifugal Fast Analyzer Development	42

10. ENVIRONMENTAL STUDIES	49
10.1 Automated Analysis of Pollutants	49
10.2 Environmental Effects of Antifoulants	54
11. BIOCHEMICAL ENGINEERING	57
11.1 Enzyme-Catalyzed Production of Hydrogen	57
11.2 Bioreactor Development	59
11.3 Bioprocess Development	61
12. COAL TECHNOLOGY PROGRAM	65
12.1 Hydrocarbonization Research	65
12.2 Separations Technology	66
12.3 Experimental Engineering Support of an In Situ Gasification Process	68
13. ACTINIDE OXIDES, NITRIDES, AND CARBIDES	70
13.1 Estimation of Thermodynamic Data	70
13.2 Nitride Phase Equilibria	70
14. STUDIES IN CHEMICAL ENGINEERING SCIENCE	72
14.1 Mass Transfer Rates in Open Bubble Columns	72
14.2 Permeation-Oxidation Studies	72
14.3 Flooding Studies in Columns Filled with Goodloe Packing	74
14.4 Salt-Metal Contactor Development: Experiments with a Mechanically Agitated Nondispersing Contactor Using Water and Mercury	75
14.5 Preparation of Small-Particle Sorbents	75
14.6 Adiabatic Combustion of Graphite	77
15. CONTROLLED THERMONUCLEAR PROGRAM	79
15.1 Scoping Studies of a Tritium Handling System for an Experimental Fusion Power Reactor	79
15.2 Preparation for Tests of Cryosorption Pumping for Fusion Reactors	81
15.3 Tritium Sorption Studies	81
15.4 Tritium Sorption in Lithium-Aluminum and Lithium-Bismuth Alloys	81
16. IODINE STUDIES	82
16.1 Iodine Sorption on Charcoal Ignition and Desorption	82
16.2 Reaction of Organic Iodides with Hyperazeotropic Nitric Acid	84
17. REACTOR SAFETY RESEARCH	86
17.1 Fission Product Release from LWR Fuel	86
17.2 Transient Release from LMFBR Fuel	87

18. NUCLEAR REGULATORY COMMISSION PROGRAMS	91
18.1 Development of "As Low as Practicable" (ALAP) Guides for the Nuclear Fuel Cycle	91
18.2 Safety Review of Nuclear Facilities	91
18.3 Safety Review of Transport Casks	92
19. DIFFUSION OF ADSORBED SPECIES IN POROUS MEDIA	93
20. MISCELLANEOUS PROGRAMS	96
20.1 Resource Studies	96
20.2 Studies Involving Tests of Obsolete Casks	96
20.3 Disposal of ORNL Radioactive Waste by Hydraulic Fracturing	97
20.4 Storage, Purification, and Distribution of ^{233}U	98
20.5 Chemical Applications of Nuclear Explosives	99
20.6 Preparation of Training Guides for Nuclear Facility Personnel	99
20.7 Environmental Impact Statement on the U.S. Nuclear Power Export Program	100
PUBLICATIONS, SPEECHES, AND SEMINARS	101

1. Development of Aqueous Processes for LMFBR 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 the Period April 1 to December 31, 1974* (ORNL-TM-4836). Some areas of the work have also been discussed in documents of a topical nature.

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 will be summarized in the *Gas-Cooled Reactor Programs Progress Report for the Period January 1, 1974, to June 30, 1975* (to be published).

3. Molten-Salt Reactor Program

The Chemical Technology Division's activities under the Molten-Salt Reactor Program are 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. This work is not reported 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.³⁻⁶

1. *MSR Program Semiannu. Progr. Rep. Aug. 31, 1974*, ORNL-5011, p. 99.
2. *MSR Program Semiannu. Progr. Rep. Feb. 28, 1975*, ORNL-5047 (in preparation).
3. J. R. Hightower, Jr., et al., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 18*, ORNL-TM-4698 (March 1975).
4. J. R. Hightower, Jr., et al., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 19*, ORNL-TM-4863 (July 1975).
5. J. R. Hightower, Jr., et al., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 20*, ORNL-TM-4870 (in preparation).
6. J. R. Hightower, Jr., et al., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 21*, ORNL-TM-4894 (in preparation).

4. Waste Management

4.1 GEOLOGIC DISPOSAL EVALUATION PROGRAM

The Geologic Disposal Evaluation (GDE) Program, as now constituted, has two objectives: first, to evaluate the suitability of all potential geologic formations and rock types in the continental United States as permanent receptacles or repositories for any category of radioactive waste, using any appropriate emplacement technique; second, for those promising geologic formation--waste-type--emplacement technique systems, to carry out the research and development activities that could eventually lead to the establishment of actual waste repositories using one or more of these systems. During the current report period, emphasis has been focused on (1) geologic and hydrologic studies of a number of rock types, to evaluate their fundamental suitability for use as waste receptacles, and (2) developmental studies, in particular those concerned with rock mechanics, rock properties, and radiation effects on rocks and borehole plugging.

Major changes have occurred in the GDE engineering programs during the past year. The Bedded-Salt In-Situ Experimental Program to support the high-level waste repository design effort at the New Mexico site was terminated in late August 1974. With the assignment of primary responsibility for the design, construction, and operation of an alpha repository to Sandia Laboratories in February 1975, all ORNL engineering efforts directed toward the design of an alpha repository at the New Mexico site were terminated (or will be by the end of FY-1975). Engineering efforts are now directed solely toward evaluating and assessing promising waste disposal systems developed by the GDE Program.

Geology and Hydrology

The objective of the geologic and hydrologic studies is to investigate the general characteristics, features, and occurrence of a number of rock types so that their fundamental suitability for use as radioactive-waste receptacles can be evaluated. The principal characteris-

tics to be examined for this purpose relate to stability (both short-term mechanical stability for the operations and long-term stability for preservation of waste containment) and tightness (i.e., isolation from the circulating waters of the biosphere). This will be accomplished largely through the study of mines and other underground openings constructed in the various rock types throughout the country. The geologic formations or rock types under investigation include: (1) rock salt (interior salt domes of the Gulf Coast area; Salt Valley anticline and other structures in the northwest portion of the Paradox Basin; and deep bedded salt deposits of the Williston, Supai, and Salina Basins); (2) argillaceous rocks (shales and especially the Pierre Shale formation); (3) carbonate rocks (limestones in northern Ohio and Kansas City areas, and the Selma Chalk in Alabama and Mississippi); (4) volcanic rock (basalts and tuffs); (5) crystalline rocks (granitic intrusives and high metamorphics); and (6) porous and permeable formations for disposal of fluids.

Bedded salt, salt domes, and salt anticlines. The stratigraphy of the southeastern New Mexico repository site developed from cores taken from exploratory boreholes AEC 7 and 8 indicates that marginal commercial potash ore zones occur in the McNutt potash zone of the Salado Formation that overlies the three candidate salt horizons which are at depths of 1900, 2100, and ~2700 ft. A single-unit seismograph operating at the site since January 1, 1974, sensed one significant seismic event which is being studied to determine whether it might have been a small earthquake or a rock fall in a nearby potash mine. Based on geologic and engineering studies, it was concluded that no economically significant oil and gas fields are likely to be discovered in or around the site. Several studies are under way to determine tectonic stability, hydrologic stability, and location of salt domes suitable for waste storage facilities. Preliminary analysis of the data indicates that several domes appear to be suitable. A preliminary geologic investigation of the salt anticlines in Paradox Valley, Utah, indicated that the deposits at

the northernmost portion of the Salt Valley anticline have the greatest potential for a waste repository site.

Argillaceous rock. A survey study was completed which explains and illustrates the critical geologic and hydrologic characteristics of several rock types, such as shale and mudstones, which would be instrumental in their containment of radioactive wastes. Since the most affirmative evidence of hydrologic tightness and mechanical stability of rock exists in subsurface excavation, a survey was conducted of the more than 80 caverns that have been constructed for storage of liquid petroleum gas. Those regions of the United States that appeared most favorable for a waste storage cavern were delineated. Studies were initiated to evaluate the suitability of the Pierre shale formation and the Green River oil shale formations as waste repositories.

Carbonate rock. Studies are in progress to evaluate the suitability of the essentially dry limestone formations near Barberton, Ohio, and Kansas City, Kansas, as waste repositories.

Volcanic rock. Studies are under way to provide information about the geologic and hydrologic factors affecting the utility of basaltic rocks and tuff for waste disposal. Specifically, information about the rock underlying the Hanford Plant Site and Nevada Test Site is being evaluated.

Crystalline rock. A study was initiated to evaluate the information available from geologic studies at the Savannah River Reservation and to extrapolate it to other areas in the eastern coastal plains with the same type of rocks. A similar study was initiated of the rock in the Minnesota, Michigan, Wisconsin, and neighboring Canadian areas to establish the geologic and hydrologic conditions that cause mines in this area to be dry or wet.

Arenaceous rock. Studies are under way to evaluate small and "enclosed" basins containing rock formations of adequate porosity and permeability to receive liquid waste.

Developmental Studies

Various studies are in progress to provide the experimental and developmental information necessary to support both the geologic and hydrologic studies and the engineering assessment studies, in particular, and to evaluate the impact of the waste disposal operations per se and other works of man on the long-term containment provided by any geologic formation. These studies include the development of borehole plugging techniques, mine stability and rock mechanics analysis, rock property measurements, and rock-waste interactions.

Rock property measurements. The coefficient of thermal expansion (CTE) for pure NaCl crystals and natural rock salt from the Lyons mine has been measured. The CTE of the pure crystal agreed well with the reported literature values and fits the expression

$$\text{CTE} = \alpha \times 10^{-6} \text{ } ^\circ\text{C}^{-1} = 41.03 - 2.984 \times 10^3 / t^2 + 1.015 \times 10^{-2} t + 3.352 \times 10^{-5} t^2.$$

Natural rock salt CTE measurements differed greatly in that the sample expanded rapidly and irreversibly on first heating to 140°C; this was probably due to the expansion of the brine inclusions exceeding the plastic limit of the salt lattice, thereby causing plastic strain or deformation. Thus, the results obtained on heating the sample are only valid for this particular time-temperature history. The results obtained on cooling, however, show that the true CTE of natural rock salt is essentially that of pure NaCl after the induced stress is relieved.

A device, the "plane probe," for rapidly measuring the thermal conductivity and thermal diffusivity of rock samples has been developed and tested and is now operational. The results will be used in thermal analyses studied to determine the effect that heat released from radioactive waste will have on various waste disposal systems of interest to the GDE Program.

Rock mechanics. The rock mechanics analysis effort is divided into two parts: a finite-element analysis technique using both thermoelastic-plastic and thermo-viscoelastic laws to model the stability of mine excavations, and a complementary semiempirical model to simulate a full-sized repository. Both models are being validated using appropriate actual mine stability data.

Stored-energy studies. The stored-energy studies on salt and solidified wastes were essentially completed. It was concluded that the storage of radiation energy in salt will not present any barrier to the safe operation of a salt mine repository. Data obtained with solidified wastes in a cooperative program with Pacific Northwest Laboratory are still being analyzed. A review of the general aspects of radiation damage and energy storage in solids, and of pertinent physical and chemical properties of rocks (in particular, silicate minerals and limestone), does not indicate any significant amounts of stored energy or any significant radiation-induced chemical effects at the gamma dose and the fast-neutron fluences ($< 10^{17}$, > 3.4 keV) that will prevail in the rock immediately adjacent to buried waste. This program is being redirected into a broad study of rock-waste interactions to obtain information, such as the migration of radionuclides from waste through the

geologic formation; the effects of radiation on physical and chemical properties of rock; chemical interactions between waste and rock; the effects of high temperatures, including melting (on both waste and rock); and methods for effectively isolating waste packages from the rock and the circulating groundwater.

Borehole plugging – salt dissolution studies. Because boreholes that have been or will be drilled at all prospective waste repository sites must be plugged, it is necessary, particularly for a salt mine repository, not only to study the dissolution of soluble rock historically and theoretically but also to develop materials and techniques for emplacing and testing the borehole plugs. Studies are under way (1) to determine the history of salt dissolution around boreholes in the Hutchinson salt formation in Kansas; (2) to develop and validate a mathematical model of salt dissolution around a borehole in a salt bed which would predict the size and shape of the cavity that would develop if fresh water enters the top of the formation with brine removal at the bottom; and (3) to develop and validate a mathematical model of convective-diffusive flow in a static-water column in an open borehole.

In addition, several ongoing programs are in progress: (1) to develop methods for mechanically forming a borehole plug with natural materials, such as shales; (2) to chemically emplace a borehole plug by hydrothermal transport (usually by aqueous solutions at temperature and pressures different from the ambient), and (3) for rock salt, to grow a molten-salt plug in situ. Civil engineering grouting techniques and commercial borehole plugging programs were also reviewed, and a survey of the literature pertaining to naturally occurring borehole plugs was carried out.

Most of these studies will be completed early in FY-1976. The information obtained will be evaluated and used in developing a program to field-test promising materials and emplacement techniques in situ.

Engineering Assessment Studies

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. These engineering assessment studies are carried out under five broadly defined programs: (1) analyses of techniques for emplacing gaseous, liquid, or solid wastes in a geologic formation; (2) waste characterization; (3) waste disposal system evaluation; (4) development of promising waste disposal systems; and (5) repository design. Emplacement techniques being analyzed include the rock-melt capsule concept, the

deep rock disposal concept for high-level waste, and a generalized study of the emplacement of heat-generating encapsulated waste in a mined cavity.

Studies of the Bedded-Salt Pilot Plant. To document the Bedded-Salt Pilot Plant (BSPP) design effort, a Conceptual Facility Design Description report was assembled and given limited distribution in May 1974. This report is a file compilation of the work done by Kaiser Engineers, Inc., under the technical supervision of ORNL; the work was terminated in November 1972. Some updated information and design alternatives were added.

The BSPP in situ experimental program was terminated in August 1973. A report documenting the planned experiments, the preliminary equipment design, the mine layouts, and the initial contacts with potash mine operators in the southeastern New Mexico potash field was placed in ORNL Central Files.

Alpha repository studies. In July 1974 the GDE Program was directed to develop "in-house" concepts and mine arrangements for the disposal of alpha waste and spent-fuel hulls in a suitable geologic formation. Further guidance in August 1974 specified that the conceptual designs developed for the Lyons, Kansas, repository and the BSPP should be reviewed, evaluated, and, based on current alpha repository design criteria, used to develop a concept for the surface facilities by "fitting" them to the New Mexico site. This study was completed, and 15 drawings showing the location of the facilities on the site, as well as their conceptual design features, were prepared.

Stratigraphic data for the New Mexico site indicate that potential salt horizons exist at 1900, 2100, and ~2700 ft below the surface. Engineering studies are in progress for the preliminary analyses of: (1) the stability of a mine layout in each of the three horizons; (2) the methods and equipment required for drilling spent-fuel hull canister emplacement holes; and (3) the various methods for excavating storage rooms, etc., and for transporting excavated salt to the hoisting facility. The studies will be completed by the end of FY-1975.

Early in February 1975, Sandia Laboratories was given the overall direction for the design, construction, and operation of the alpha repository, and ORNL was directed to provide Sandia with all pertinent information. Any further alpha repository design effort at ORNL will be at the request of Sandia Laboratories.

4.2 PROCESSING MODIFICATIONS FOR IMPROVED WASTE MANAGEMENT

This program for the improvement of waste management by additional removal of actinides, using modified

reprocessing methods, replaces the Waste Fractionation Program, for which we reported activities and progress last year. In the latter program, only the fractionation (or partitioning) of actinides from the high-level waste stream from a conventional Purex plant was considered. However, the investigation quickly revealed that the program needed to be expanded in scope.^{1,2} In addition to the development of processes to partition the high-level waste, it was concluded that significant advantages could be attained by improvements and modifications of present-day reprocessing methods.

The objective of this program is to determine the technical feasibility of removing actinides from all the radioactive wastes generated during the commercial reprocessing of nuclear reactor fuels. During this report period we investigated the possibility of recovering uranium, plutonium, neptunium, americium, and curium from spent fuels to such a degree that the calculated radiological toxicity of wastes after about 1000 years of storage would be comparable to the toxicities of naturally occurring uranium minerals. The recovered actinides would receive special treatment for disposal, and might be recycled to power reactors where they would be burned to form fission products. The study was limited to the development of methods for removing actinides from light-water reactor (LWR) fuels. Removal of 99.99% of the plutonium, 95% of the neptunium, and 99.9% of the uranium, americium, and curium from LWR fuel (with plutonium recycle) would reduce the potential hazard of high-level waste at 1000 years to about 5% of that for pitchblende (assuming that 99.9% of the ¹²⁹I is also removed during reprocessing and is managed as a separate waste).³ At these levels of actinide and ¹²⁹I removal, the actinide contribution to the long-term hazard potential would be comparable to that from the long-lived fission products.

The concept of actinide removal is based on a combination of modified Purex processing and secondary processing of the high-level waste. According to this concept, the necessary removal of uranium and neptunium and most of the plutonium is accomplished by extra extraction stages in the Purex process and by

recycle of the aqueous wastes from the actinide purification cycles. Secondary processing of the high-level waste is used to remove americium, curium, and any residual plutonium. Insoluble residues from fuel dissolution or solids generated in processing would be separated in feed clarification steps and treated, where necessary, to reclaim the actinide values. An important requirement is the capability for removing the actinides without significantly increasing the volumes of high-, low-, and intermediate-level wastes. This requirement prohibits the use of processes that discharge large quantities of chemical reagents in the wastes. If processes that depend on large quantities of reagents are to be used — and they are probably necessary for the removal of americium and curium — reagents that can be recycled or converted to acceptable nonradioactive chemical wastes must be chosen.

The studies comprising this program have not yet progressed to the point where the feasibility (or infeasibility) of chemical flowsheets for the satisfactory removal of actinides from reprocessing wastes can be determined. On the basis of tracer-level studies with synthetic wastes and conceptual material-balance flowsheet studies, the chemistry required for the actinide separations (with the possible exception of plutonium) appears to be theoretically possible. However, a vast amount of work remains to be done in order to select the best combination of chemical steps and to prove that the desired chemistry can be carried out in workable, integrated processes under conditions involving high levels of radiation. Our work strongly suggests that recycle methods might be developed for Purex plants which would substantially reduce the quantities of the miscellaneous low- and intermediate-level wastes. The actinide-bearing wastes currently require relatively large-area sites for disposal or storage. Such wastes appear to be amenable to recycle if appropriate chemical reagents are used for treating used solvent and for adjusting the neptunium and plutonium valences in the Purex separations.

The most troublesome chemical problems encountered in actinide removal are associated with plutonium and americium-curium. The chief difficulty with plutonium lies in the need to maintain it in an extractable form at a very low concentration. Scouting experiments showed that about 0.01% of the plutonium was inextractable when a solution of Pu(IV) in nitric acid was repeatedly extracted with tributyl phosphate (TBP). Interferences from fission products in the waste may increase the fraction of inextractable plutonium (see Sect. 8.4). The major difficulty in americium-curium processing is in effecting the removal of these elements without generating radioactive wastes that

1. W. D. Bond and R. E. Leuze, *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).

2. W. D. Bond, H. C. Claiborne, and R. E. Leuze, "Methods for Removal of Actinides from High-Level Wastes," *Nucl. Technol.* **24**, 362-70 (December 1974).

3. H. C. Claiborne, *Effect of Actinide Removal on the Long-Term Hazard of High-Level Waste*, ORNL-TM-4724 (January 1975).

contain large quantities of chemical reagents. In addition to the problem of the inextractability of plutonium from waste solutions, sufficient information has not been obtained relative to the plutonium content and nature of the solids generated in the processing of spent fuels. A considerable amount of work is still required to define the scope of the solids problem and to develop methods for preventing plutonium losses to these solids.

Material-balance flowsheet studies show that actinide removal according to our concept -- or any concept -- will require extensive recycle. Demonstrating that this recycle can be accomplished is a major undertaking. For example, conclusive proof will be required that none of the steps involved will lead to a buildup of impurities which could cause process failure. Unfortunately, no previous experience is available concerning the operation of a large-scale radiochemical plant which utilizes extensive recycle of the waste streams.

Activities carried out this year included: (1) laboratory and bench-scale experiments with tracer-level activity in synthetic waste solutions to determine the chemical feasibility of selected process methods, (2) investigation of solids formation in waste solutions, (3) conceptual flowsheet studies of alternative separations processes, and (4) scoping studies relative to recycle and transmutation of the actinides.

Reprocessing Modifications

We prepared a conceptual material-balance flowsheet for a modified Purex process that includes the recycle of nitric acid as well as the aqueous, actinide-bearing waste streams generated in the partitioning and purification cycles for uranium, neptunium, and plutonium.¹ In addition, we carried out some experimental studies on the extractability of neptunium from synthetic wastes and its subsequent partitioning. Studies of plutonium extractability are reported in Sect. 8.4.

In our conceptual flowsheet, the uranium, neptunium, and plutonium are recovered in a primary Purex plant in which the uranium and neptunium concentrations are reduced to the required levels by additional stages of Purex extraction. The Purex process has the capability for accomplishing the required uranium and neptunium recovery and for removing perhaps as much as 99.8% of the plutonium. Our conceptual flowsheet includes the recycle of the nitric acid and actinide values from all of the intermediate- and low-level aqueous waste streams, except those wastes from solvent purification and off-gas treatment. Recycle of the aqueous waste streams is based on the use of a

partitioning reductant other than ferrous sulfamate, which would add sulfate to the high-level waste. The sulfate also interferes with recycle of the actinide values from the partitioning and purification cycle wastes. A considerable amount of experimental work remains to be done on the recycle steps of the flowsheet to determine whether they will lead to an accumulation of impurities that could inhibit recovery of actinides. Also, experimental work needs to be done preparatory to developing a conceptual flowsheet for recycling actinides from the solvent purification wastes.

Laboratory batch extraction tests showed that greater than 98% of the neptunium was removed by two stages of TBP extraction when tracer-level neptunium was maintained as Np(VI). Qualitative rate measurements showed that ferrous nitrate reduces Np(VI) to Np(IV) at a satisfactory rate for partitioning plutonium from neptunium and uranium. The required reduction times, 10 to 20 min, appear to be compatible with the holdup time of production-size solvent extraction columns. The variables affecting the reduction rate of Np(VI) were determined in a fundamental investigation (see Sect. 8.4).

Recovery of Americium and Curium

Several processes for the recovery of americium, curium, and transcurium elements from high-level waste are being evaluated in the Laboratory, using tracer-level activity in synthetic wastes. All of the processes involve isolating the chemically similar trivalent lanthanide fission products and trivalent actinides (americium, curium, and transcurium elements) from the other waste elements and then separating the trivalent actinides from the lanthanides by cation exchange chromatography or by the Talspeak solvent extraction process. Experimental studies on the Talspeak process are being carried out under the Separations Chemistry Program (see Sect. 8.3). The processes being studied for the separation of the trivalent actinides and lanthanides (trivalent elements) include: (1) cation exchange, (2) oxalate precipitation coupled with cation exchange, and (3) TBP extraction from solutions heavily salted with aluminum or lithium nitrates. Each of these processes has certain advantages and disadvantages. Additional experimental studies are needed to permit selection of the optimum overall process for removing americium and curium from high-level radioactive waste. Involved in this selection is the preparation of detailed flowsheets with recycle or satisfactory handling of every waste stream, including waste solvents and spent resins.

Cation exchange, the method we studied most extensively for removing the trivalent elements, appears

promising. In this process the trivalent elements and certain of the fission products (primarily zirconium and some palladium) are loaded on cation resin from 1 M HNO₃ solutions of waste, and the trivalent elements are then eluted selectively with 3.5 M HNO₃. We have demonstrated greater than 99.9% recovery using americium, europium, cerium, and erbium tracers in synthetic waste. Aside from ion exchange resin, nitric acid is the only chemical reagent added in the processing.

Coupling oxalate precipitation with ion exchange may be an attractive alternative to an all-ion-exchange process for removing the trivalent elements. This process has been demonstrated in the laboratory, using synthetic wastes. A single oxalate precipitation was used in a first step to remove about 95% of the trivalent elements and also to complex the zirconium; then a cation exchange column was used as a final "polishing" step to remove the residual trivalent elements and any solids or colloidal material remaining after the precipitation step. Considerably less ion exchange capacity is required in these operations than in the all-ion-exchange process. Measurements with radiotracers showed greater than 99.9% recovery of the trivalent elements. The separation of oxalate precipitate need not be accomplished in the first step to be quantitative, since any residual precipitate will be retained by the ion exchange column and will be dissolved when the trivalent elements are eluted from the resin column with 3.5 M HNO₃. A question yet to be resolved with regard to the oxalate precipitation step is whether the precipitation and solids removal step is feasible in remote operations.

Tributyl phosphate extraction from heavily salted solutions may be a viable method for the recovery of the trivalent elements.⁴ If satisfactory methods can be developed for recycling the salting agents, Purex-type technology might be extended to remove americium-curium and transcurium elements along with the heavy lanthanides at the time of fuel reprocessing. In nitrate-salted systems, the light lanthanides (about 80 mole % of the lanthanide fission products) can be partitioned from the trivalent actinides and heavy lanthanides. Laboratory studies with synthetic wastes have shown that about 95% of the salting agent, Al(NO₃)₃, can be recovered for recycle by precipitating it from 15 M HNO₃ solution. The extra acid required to precipitate the salting agent could then be recovered by distillation and reused.

4. J. M. McKibben et al., *Partitioning of Light Lanthanides from Actinides by Solvent Extraction with TBP*, DP-1361 (August 1974).

Ion exchange chromatography appears attractive as a method for separating the trivalent actinides from the lanthanides in both conceptual flowsheet and laboratory studies. Emphasis of the laboratory work has been directed to the use of a hydrogen ion barrier for elution rather than a metallic ion barrier such as zinc, because this would diminish the addition of nonvolatile solids to the waste streams. Laboratory studies show that a barrier-ion composition of 80% H⁺--20% Zn²⁺ yields good separations. This composition considerably reduces the quantity of zinc required and simplifies the treatment of waste streams from the separations process.

We have completed conceptual material-balance flowsheets for the recovery of americium-curium by an all-ion-exchange process and for recovery of the trivalent elements by oxalate precipitation coupled with ion exchange. We view these flowsheets as tentative and preliminary, since many of the process steps require experimental verification at full activity level and in regard to performance of recycle concepts and minor fission product behavior. A great deal of work remains to be done to confirm the overall flowsheets. The conceptual flowsheets for the all-ion-exchange process are shown in Figs. 4.1 and 4.2. Material balances are based on the high-level waste from reprocessing 1 metric ton of LWR fuel irradiated to a burnup of 33,000 MWd/metric ton.

Formation of Solids in Waste Solutions

Studies are being carried out to identify the solids present in waste solutions and, ultimately, to determine their actinide content. In most of our work, we used synthetic waste solutions; however, we recently obtained solid residues from the dissolution of irradiated LWR fuel (burnup, 33,000 MWd/metric ton). Synthetic waste solutions contain a small amount of solids when they are prepared. These solids consist primarily of zirconium, tin, silver, halides, and some selenium. On aging the waste solutions, small amounts of solids containing predominantly zirconium and molybdenum continue to precipitate. Small quantities of colloidal material are also formed during the aging and can be detected by a Tyndall beam. Although analyses of the residues from fuel dissolution are incomplete, qualitative spectrographic analysis indicates that such residues consist mainly of technetium, ruthenium, palladium, silicon, and rhodium, plus small amounts of zirconium, molybdenum, nickel, and iron. The retention of plutonium by synthetic waste solids is discussed in Sect. 8.4.

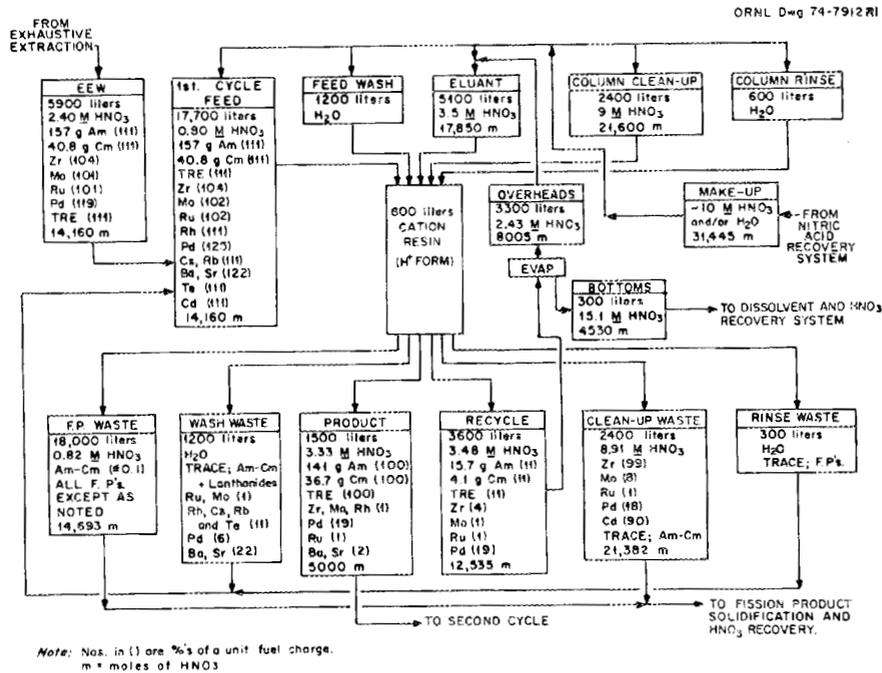


Fig. 4.1. Conceptual material-balance flowsheet for the ion exchange separation of americium-curium and the rare earths from high-level waste.

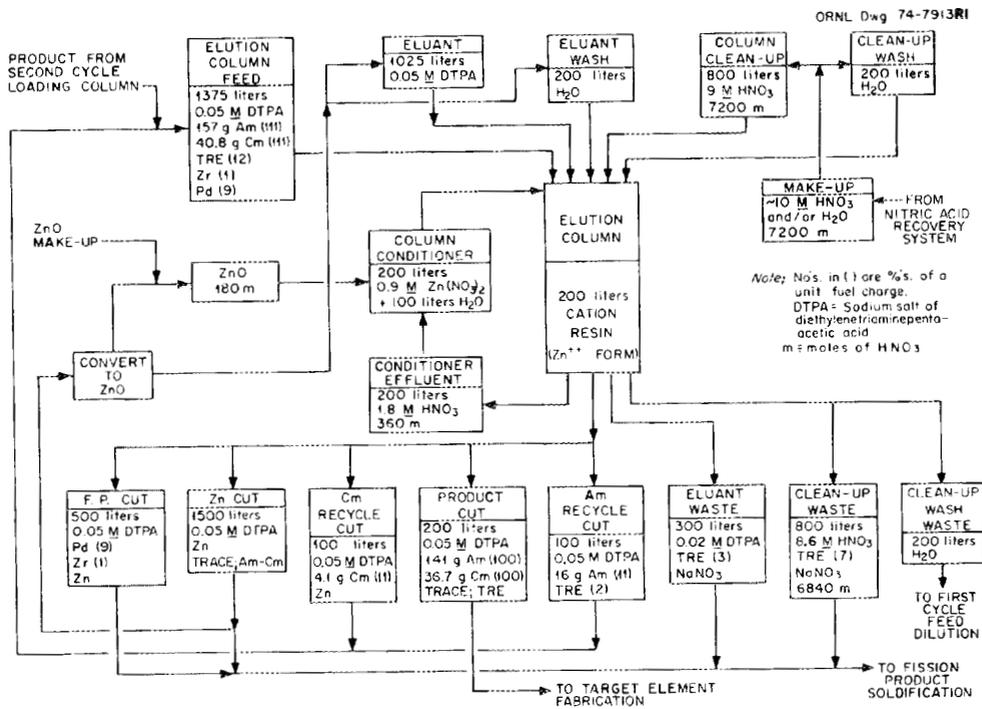


Fig. 4.2. Conceptual material-balance flowsheet for the ion exchange chromatographic separation of americium-curium from the rare-earth elements.

Conceptual Scoping Studies of Actinide Transmutation and Recycle

Transmutation in commercial power reactors is one of the potential waste management alternatives for reducing the long-term hazard of the actinides removed from fuel reprocessing wastes. During the past year, scoping studies have been performed to determine some of the potential impacts on the commercial fuel cycle industry that might result from the transmutation of these waste actinides, and to establish the trends in transmutation rates that result from variations of both the type of reactor producing the waste actinides and the type of reactor transmuted the waste actinides. All of the comparisons in our studies are made at conditions approximating steady-state recycle of the waste actinides. The amounts of the various actinides, on a spent-fuel basis, that were recycled for transmutation were as follows:

U-Pu fuel: 0.4% U; 0.49% Pu; 95% Np; and 99.9% Am, Cm, Bk, Cf, and Es.

U-Th fuel: 0.49% U; 0.4% Th; 0.49% Pu; 95% Np and Pa; and 99.9% Am, Cm, Bk, Cf, and Es.

Some of the most important results obtained from these studies are as follows:

1. The average annual transmutation rates of the waste actinides in the four types of transmutation reactors are: PWR-Pu, 3.2%; LMFBR, 4.3%; PWR-U, 4.9%; HTGR, 7.8%.
2. The recycled waste actinides being transmuted occupy, on the average, approximately 0.7% of a PWR-U or PWR-Pu core, 1.4% of an LMFBR core, and 2.6% of an HTGR core.
3. The infinite neutron multiplication factor (k_{∞}) of the waste actinides ranges from 0.7 to 0.9 for thermal transmutation reactors and from 0.9 to 1.4 for an LMFBR transmutation reactor. Since the recycle waste actinides represent only a small fraction of the reactor core, the overall reactivity of any of the reactor types is changed only slightly.
4. The neutron activity of fresh thermal transmutation reactor fuel, containing actinides to be transmuted, is very high due to the presence of ^{252}Cf ; typical values range from 10^{11} to 10^{13} neutrons sec^{-1} (metric ton) $^{-1}$. The neutron activity of fresh LMFBR transmutation reactor fuel is much lower, about 10^8 to 10^9 neutrons sec^{-1} (metric ton) $^{-1}$.

Results of the initial studies indicate that one of the most potentially serious impacts on the commercial fuel cycle is the additional shielding required for fabrication

and shipment of the highly neutron-active transmutation reactor fuels. Our results show that remote fabrication of the fuel would be required.

4.3 LEACHING OF RADIONUCLIDES FROM WASTE SOLIDS

Grouts similar to those used in the Hydrofracture Facility at ORNL were made by blending simulated intermediate-level waste solution containing ^{85}Sr , ^{137}Cs , ^{239}Pu , or ^{244}Cm with a dry mixture of cementitious materials and selected clays, and the products were tested for retention of these isotopes in the International Atomic Energy Agency (IAEA) type of leach tests.^{5,6} The "fraction of isotope leached" varied with the square root of time if leachant replacement was more frequent than once per day, but was inhibited, or depressed, if changed less often. Curing a grout specimen up to 28 days in humid air before leaching decreased the amount leached from the specimen. When Grundite clay (for cesium retention) was present, the isotope leach rates followed the order: $\text{Cs} > \text{Sr} > \text{Cm} > \text{Pu}$, with overall results indicating that grouts can give leach rates comparable to those obtained for wastes incorporated into borosilicate glasses (Figs. 4.3 and 4.4).

To obtain data more rapidly, the proposed IAEA leach test was successfully modified by using specimens with a smaller volume, a much larger surface-to-volume ratio, and a larger volume of leach water per volume of specimen, and by replacing leach water more frequently. The leach rate for cesium was decreased by the addition of Grundite, pottery clay, or Conasauga shale. These additives, as listed, are in the order of increasing effectiveness with respect to cesium retention. The leach rates of cesium from grouts made with pottery clay and containing one, two, and four times the normal weight percent waste salts (6 wt %) showed that these higher salt concentrations had no significant effect on the leach rate of cesium.

Theoretical relationships that consider diffusion and instantaneous reaction (an equilibrium or time-independent relationship between mobile and immobile forms of a species) gave good agreement with the data

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

6. International Atomic Energy Agency, "Leach Testing of Immobilized Radioactive Waste Solids, a Proposal for a Standard Method," ed. by E. D. Hespe, *At. Energy Rev.* 9(1), 195-207 (1971).

WASTE PRODUCTS

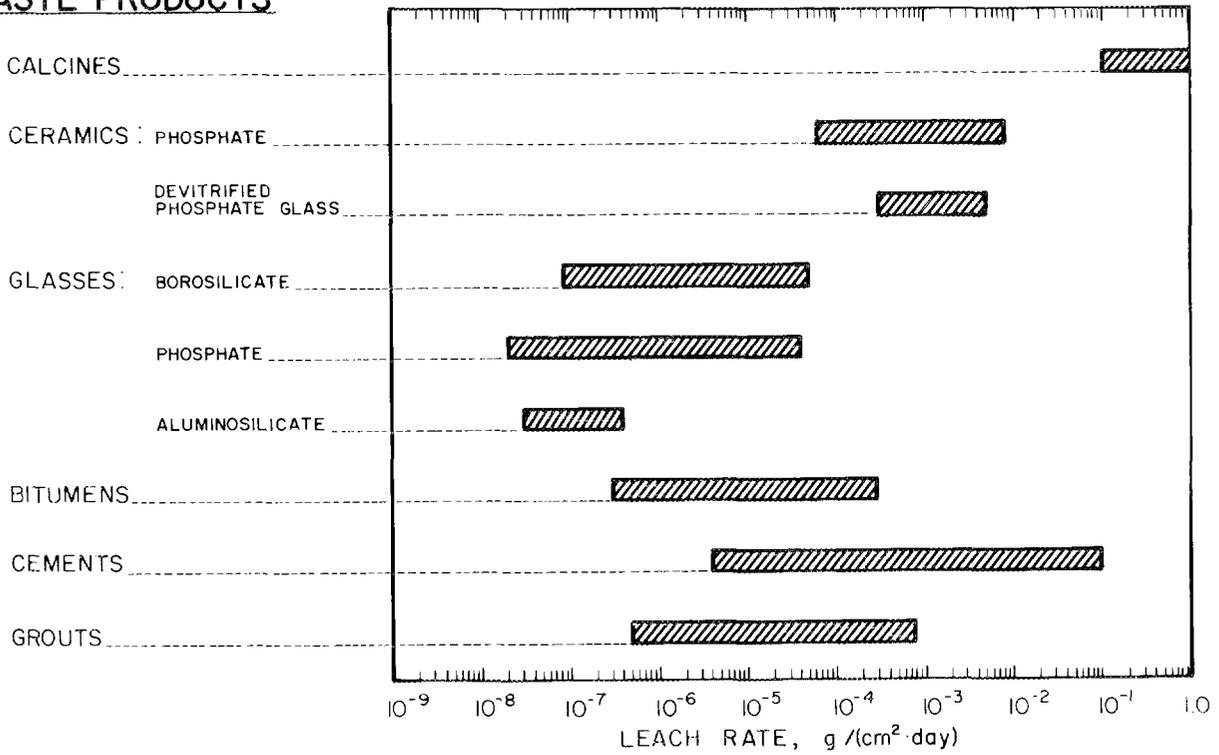


Fig. 4.3. Comparison of leach rates for alkali and alkaline-earth elements from various waste products.

- CERIUM
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WASTE PRODUCTS

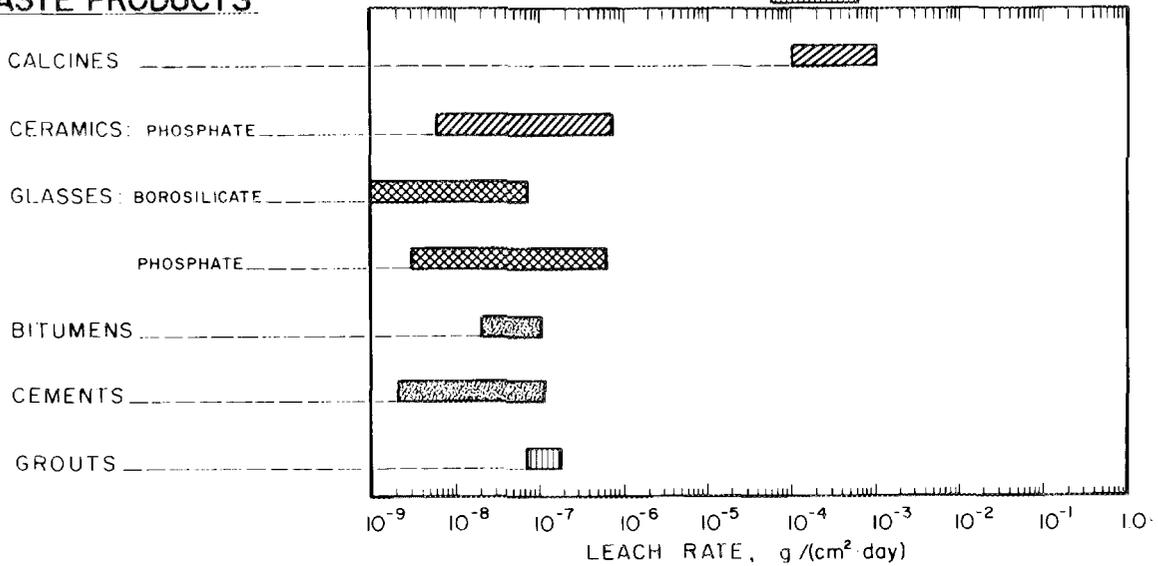


Fig. 4.4. Comparison of leach rates for rare-earth and actinide elements from various waste products.

for the 28-day-cured grouts when the leachant was initially replaced twice per day (Fig. 4.5). In contrast, the amounts leached from many borosilicate glasses appear to be explained by diffusion and time-dependent dissolution processes. The predicted amounts of cesium leached from a grout containing Conasauga shale are compared with those for a borosilicate glass in Fig. 4.6. The theoretical relationships used in these calculations are given in ref. 7. The comparison of fractions leached (Fig. 4.6) shows that, during short time periods, a slightly smaller fraction of cesium is leached from the

glass product than from the grout; however, during longer time periods, a smaller fraction of cesium is leached from the grout product than from the glass. Using the modified effective diffusivities (D_e) derived from the data, comparisons were made of the amounts leached from a 55-gal drum of grout, assuming two different forms for the drum — a semi-infinite medium and a finite cylinder. These calculations show that the drum approximates a semi-infinite medium for a few years if the D_e is approximately 1×10^{-9} cm²/sec and for more than 3000 years if the D_e is approximately 6×10^{-16} cm²/sec. They also show that the projected amounts leached from a waste product that is assumed to approximate a semi-infinite medium are conservative (on the side of safety), since they are equal to or greater than the amounts predicted by a mathematical solution based on the actual geometry of the finite product.

7. H. W. Godbee, J. G. Moore, A. H. Kibbey, and D. S. Joy, "Leach Behavior of Cementitious Grouts Incorporating Radioactive Wastes," presented at the 77th Annual Meeting of the American Ceramic Society, Washington, D.C., May 3-8, 1975.

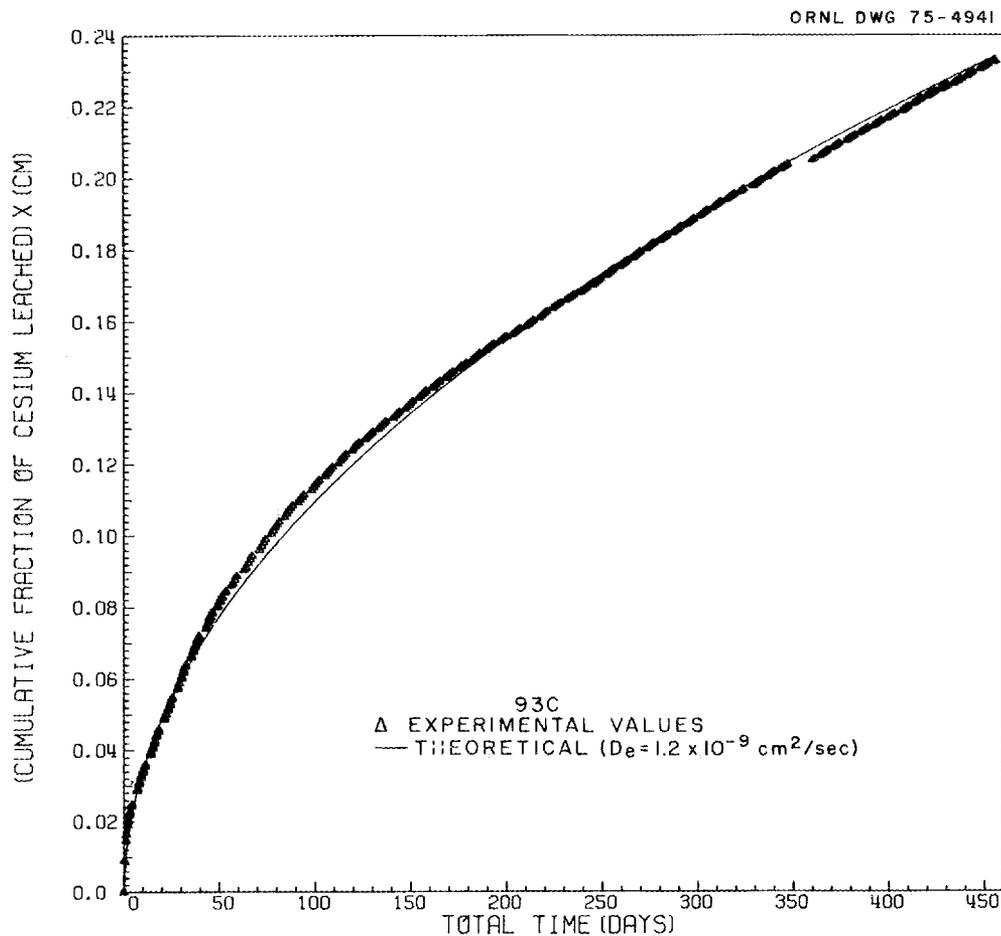


Fig. 4.5. Comparison of the cumulative fraction of cesium leached to that predicted by diffusion equation for 28-day-cured grout specimen 93C.

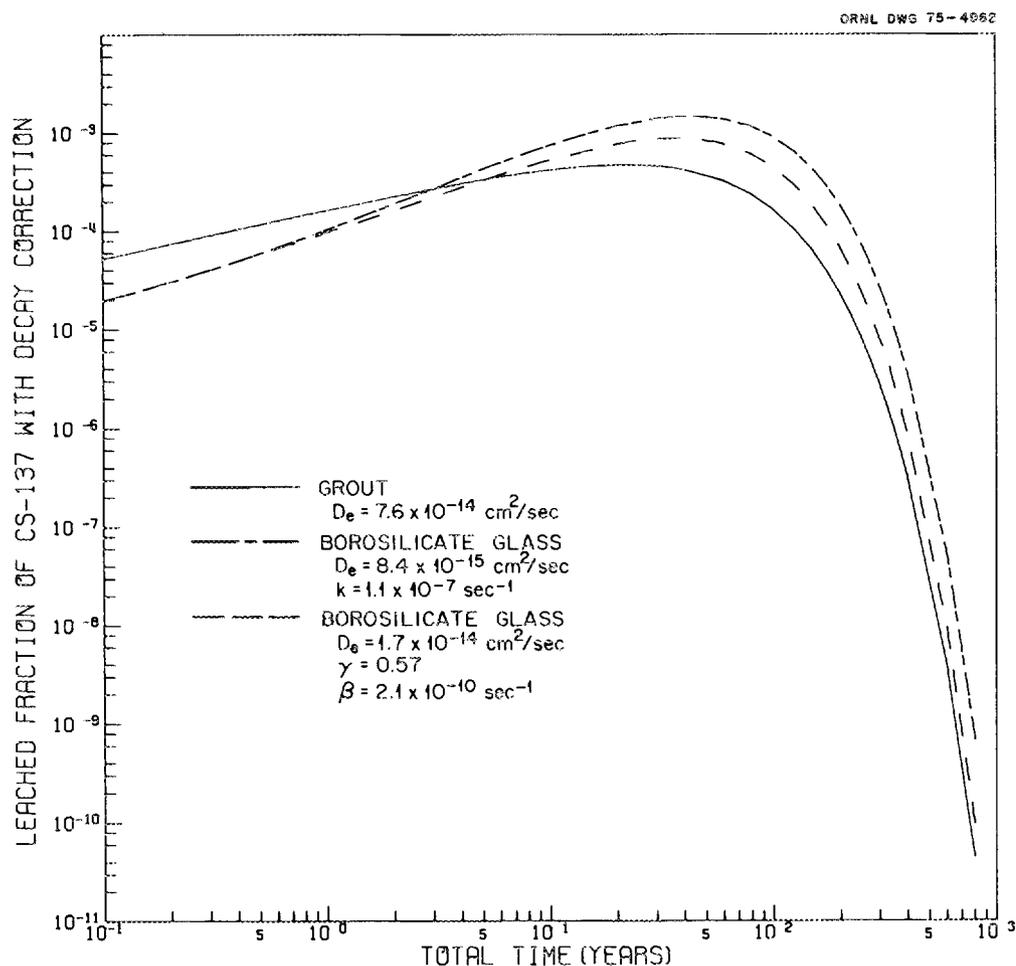


Fig. 4.6. Comparison of the amounts of ^{137}Cs ($t_{1/2} = 30$ years) leached from a borosilicate glass and a cementitious grout as predicted by equations based on mass transport phenomena.

4.4 METHODS FOR MANAGEMENT OF ORNL LIQUID WASTES

The shale fracturing process is a proven, economical method for the permanent disposal of intermediate-level waste (ILW) solution at ORNL; over the past eight years, about 1,000,000 gal of waste solution containing 500,000 Ci of radionuclides has been mixed with cement and injected into the impermeable shale beds that underlie the ORNL area. Recent national emphasis in waste disposal technology, however, 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 is being 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 for disposal 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 desirable

characteristics of the process include operational simplicity, compatibility with alkaline nitrate solutions, low operating cost, and a minimum of required development. A qualitative estimate of the "fit" of selected processes and product waste forms with the desired characteristics is given in Table 4.1. None of the known waste forms or processes meets all criteria; therefore, some desirable characteristics must be sacrificed or compromised so that other, more desirable characteristics can be achieved.

The most promising of these methods are summarized for reference in the flow diagrams in Fig. 4.7. Processes for the treatment of ILW, ILW sludge, and effluents from the Process Waste Treatment (PWT) facility are included. All processes are based on the same weekly load (100% load factor), and all storage volumes are given in terms of 55-gal drums so that comparison of different processes will be simplified.

An average composition and annual volume have been assumed for each of the several waste streams of

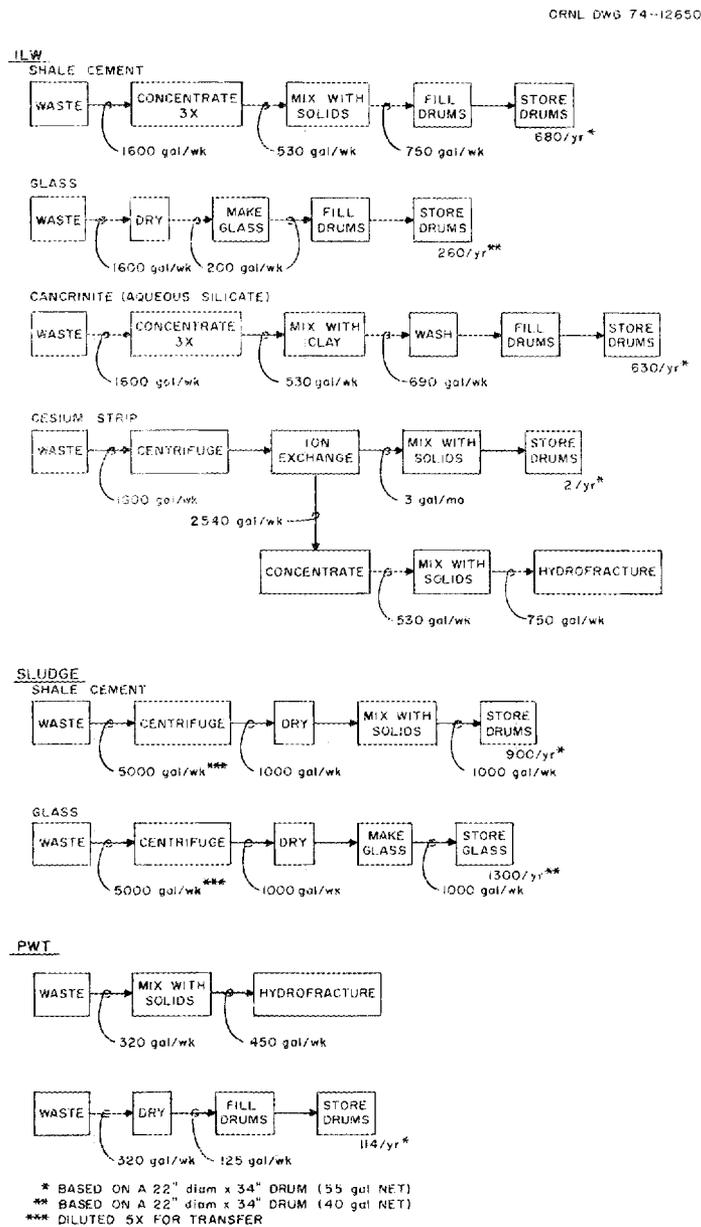


Fig. 4.7. Processes for waste fixation.

Table 4.1. Qualitative evaluation of various waste processes

Process	Waste form characteristics					Process characteristics		
	Leach rate	Structural strength	Volume	Flammability	Radiation damage	Operational complexity	Required development	Compatibility with nitrate alkaline wastes
Shale cement	Very low	Low to moderate	High	None	Very low	Low	Low	Yes
Glass	Very low	Moderate	Moderate	None	Very low	Very high	Very high	Yes
Aqueous silicate	Moderate	Low to moderate	High	None	Very low	Moderate	Moderate	Yes
Cesium stripping	<i>a</i>	<i>a</i>	Low ^{<i>b</i>}	<i>a</i>	<i>a</i>	High	High	Yes
Scavenging	<i>a</i>	<i>a</i>	Low ^{<i>b</i>}	<i>a</i>	<i>a</i>	High	High	Yes
Calcining	High	None	Moderate	None	Very low	Low	Low	No
Asphalt	Low	Moderate	Moderate	Yes	Appreciable	Low	Low	Doubtful
Polyethylene	Low	Moderate	Moderate	Yes	Very low	Low	Moderate	Yes
Titanate	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
Urea-formaldehyde	High	Low	Moderate	<i>c</i>	<i>c</i>	Low	Moderate	No
VR-20 ^{<i>d</i>}	<i>c</i>	<i>c</i>	Moderate	<i>c</i>	<i>c</i>	Low	Moderate	Doubtful

^{*a*}Not applicable.

^{*b*}Not including separated nitrate waste.

^{*c*}Unknown; insufficient information.

^{*d*}Commercially available process from the Aerojet Energy Conversion Company.

concern to this study — the ILW, the PWT waste, the currently generated ILW sludge, and the ILW sludge in inventory. These values are listed in Table 4.2. The sludges will have to be diluted by a factor of 4 or 5 before they can be resuspended and transported through the waste handling system; however, the volumes of sludges given in Table 4.2 are for undiluted material. A ten-year processing period is assumed for the 400,000 gal of sludge presently in inventory.

Of the 11 processes given in Table 4.1 for ILW fixation, only four — shale cement fixation, glass formation, aqueous silicate (cancrinite), and cesium stripping — have suitable final waste forms and have been studied in sufficient detail for most of the significant process parameters to be known. The calcining, asphalt, and polyethylene fixation processes produce inferior waste forms. The urea-formaldehyde and the VR-20 processes yield waste forms that have not yet been sufficiently evaluated; in addition, the compatibility of these processes with nitrate waste solutions has not been demonstrated. The scavenging and titanate fixation processes need further development work before serious study is attempted.

A brief investigation was made of the suitability of the four processes for handling ORNL waste solution and sludge. Several tentative conclusions were reached:

1. The fixation of ORNL waste in shale cement grout is probably the best of the alternatives to the shale

fracturing process. The cement fixation process is a simple low-temperature operation that produces a waste form of high durability and excellent leach resistance. It is probably also the least expensive of the alternatives considered.

2. The glass formation process is complex and involves the use of high temperatures; therefore, its suitability could be established only by carrying out a major development program. The off-gas problems and disposal of by-product waste streams would require particular attention.
3. The cesium strip process is a complicated process that offers the possible advantage of a major reduction in waste volume.
4. The aqueous silicate process provides no obvious advantage over cement fixation and results in a product that is apparently much more leachable.
5. The cement fixation process appears to be clearly superior for the processing of sludges. The volume of waste that would be produced is somewhat smaller than that required for glass formation; in addition, the complexities inherent in high-temperature operation are avoided.

An engineering study of cement fixation, glass formation, and cesium stripping processes has been started. The results of this study will be used to prepare comparative cost estimates that will be used in the selection of one process for more-detailed future consideration.

Table 4.2. Composition and volume of significant waste streams

	Waste stream			
	ILW concentrate	PWT	Current sludge	Inventory sludge
Volume, gal/year	80,000	16,000	10,000	40,000
Salt concentration, <i>M</i>	1.2	3.5		
Suspended solids, wt %	0.5		40	50
Radionuclide content, Ci/gal				
⁹⁰ Sr	0.1	6×10^{-5}	1.6	2.0
¹³⁷ Cs	1.0	2×10^{-4}	0.16	0.2
²⁴⁴ Cm	1×10^{-3}	None	2.4×10^{-2}	3×10^{-2}
⁶⁰ Co	2×10^{-3}	8×10^{-6}	0.08	0.1
²³⁹ Pu	2×10^{-5}	None	6.4×10^{-4}	8×10^{-4}
¹⁰⁶ Ru	0.035	1.5×10^{-5}	0.04	0.05
²³³ U			2×10^{-4}	

Table 4.3. Fuel cycle wastes projected for the year 2000

Category	Annual generation			Accumulated inventory in the United States					
	Volume (10 ³ ft ³)	Activity (MCi)	Annual shipments	Volume (10 ³ ft ³)	Activity (MCi)	Thermal power (kW)	Metric tons of actinides	Toxicity (m ³ at RCG) ^a	
								Air	Water
High-level waste, solidified	36	43,000	220 ^{b,c}	109	14,000	63,000	330	2.4 × 10 ²¹	8.8 × 10 ¹⁵
Transuranium wastes									
Cladding hulls	39	130	380 ^{c,d}	370	560	6,000	77	1.8 × 10 ¹⁹	3.1 × 10 ¹³
Miscellaneous α, β, γ solids	230	5.5	2,800 ^{d,e}	2,400	22	84	0.5	3.5 × 10 ¹⁸	8.8 × 10 ¹²
Alpha solids	810	22	640 ^{c,d}	6,600	121	160	14	9.6 × 10 ¹⁹	1.6 × 10 ¹²
Beta-gamma wastes									
Noble gases	1.1 ^f	190	170 ^{c,d}	10 ^f	1,200	2,000	0	4.0 × 10 ¹⁵	
Iodine	0.06	0.0007	15 ^{d,e}	0.6	0.006	~0	0	3.0 × 10 ¹⁴	1.0 × 10 ¹¹
LWR tritium	1,900	0.26	3,400 ^{d,e}	21,000	1.9	0.07	0	9.7 × 10 ¹²	6.5 × 10 ⁸
Fission product tritium	7.5	11	10 ^{d,e}	70	75	2.6	0	3.7 × 10 ¹⁴	2.5 × 10 ¹⁰
Miscellaneous β, γ solids	2,600	3	49,000 ^{d,e}	2,400	15	180	~0	3.8 × 10 ¹⁶	4.7 × 10 ¹¹
Ore tailings	1,200,000	0.4		1.7 × 10 ⁷	5.4	120	77,000	7.6 × 10 ¹⁸	2.3 × 10 ¹³

^aCubic meters of air or water required for dilution to Radiation Concentration Guides (RCG) values (Appendix B, Table B, of 10 CFR 20).

^bSolidified immediately and shipped ten years after generation.

^cRail shipments are assumed.

^dShipped one year after generation.

^eTruck shipments are assumed.

^fNumber of cylinders pressurized at 2200 psi.

4.5 PROJECTIONS OF RADIOACTIVE WASTES FROM THE NUCLEAR FUEL CYCLE

In order to obtain waste management data that are more realistic in light of current knowledge, new projections were made of the volumes and nuclear characteristics of wastes to be shipped and stored through the year 2000. The new projections were based on a recent projection of nuclear power growth in the United States.⁸ The conservative estimate (case A) was modified to delay commercial LMFBRs until 1993. The resulting contribution of each reactor type to total installed nuclear electric capacity is shown in Fig. 4.8.

To estimate the future magnitude of waste management operations, calculations were made using ORIGEN⁹ subroutines for the ten types of wastes described previously.¹⁰ However, the assumptions were modified to allow compaction for beta-gamma solid wastes to parallel the compaction of alpha solid wastes. A summary of these projections for the year 2000 is given in Table 4.3. A comparison of Table 4.3 with the previous projections shows a general decline of projected waste volumes. However, the delay of breeders

8. *Nuclear Power Growth 1974-2000*, WASH-1139(74) (February 1974).

9. M. J. Bell, ORIGEN - The ORNL Isotope Generation and Depletion Code, ORNL-4628 (May 1973).

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

caused an increase in the projected volume of ore tailings in the year 2000.

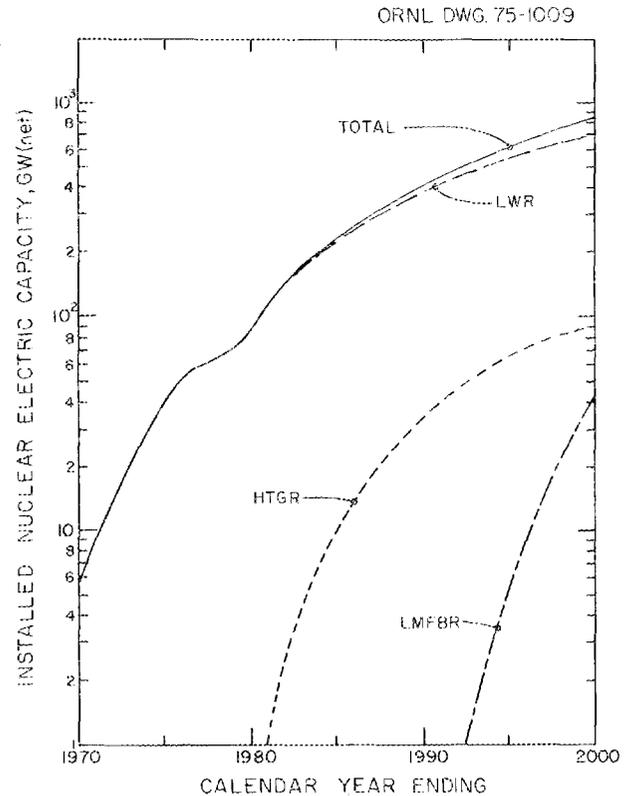


Fig. 4.8. Projected installed nuclear capacity in the United States (case A, 1993 LMFBR).

5. 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 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 upon request, and hot-cell space is 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.

The phases of the program under the direction of the Chemical Technology Division, including the operation of TRU, isolation and purification of products, and development of chemical processes, are reported here. Target fabrication work directed by the Metals and Ceramics Division is described in detail in reports issued by that division.

5.1 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 being used in TRU. More detailed information is presented in a series of semiannual reports on production, status, and plans.^{1,2}

Status and Progress

During the first four years that TRU was in operation, processed materials 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 sponsored by the AEC Division of Production and Materials Management. There has been no further request to process Cf-1 materials during the past two years. 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 meaningful levels by irradiating isotopically heavier curium, most of which had been recovered from the Cf-1 campaigns at TRU.

The primary role of TRU as supplier of research materials has continued; about 60 shipments were made this year to researchers throughout the country.

1. L. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June 30, 1974*, ORNL-4991 (February 1975).

2. L. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1974*, ORNL-5034 (in press).

Production and Processing

During this report period, two target processing campaigns were conducted, and a total of 23 HFIR targets were processed. Twelve of these targets had been prepared from Cf-I curium. Key isotopes in the campaign products are listed in Table 5.1.

Product finishing operations include (1) final purification and packaging of the transcurium elements; (2) separation, purification, and packaging of daughter products (^{248}Cm , ^{249}Cf , and ^{253}Es); and (3) final purification of the americium-curium product followed by conversion of the actinide elements to the oxide form for use in HFIR targets. This year we purified some of the products from target campaigns 47 and 48, from previous campaigns, and from various rework materials. The amounts of materials undergoing product finishing operations included 2 g of ^{243}Am , 82 g of curium, 24 mg of ^{249}Bk , 408 mg of ^{252}Cf , 1250 μg of ^{253}Es (mixed isotopes), 1.3 μg of ^{254}Es , and about 0.5 μg of ^{257}Fm . Daughter products recovered and purified included 139 μg of isotopically pure ^{253}Es and 90 mg of ^{248}Cm (34 mg contained 0.0007% ^{244}Cm , and 56 mg was a lower quality material containing 4% ^{244}Cm).

Fabrication of Targets

Twenty-six targets were fabricated in order to recycle curium to the HFIR. Of these targets, 15 contained curium from regular TRU stock, 5 contained Cf-I curium, and 6 contained curium recovered from previous irradiation of Cf-I curium in the HFIR.

Processes and Equipment

Flowsheets used at TRU remain unchanged. However, we have continued to incorporate new techniques to minimize the processing time and to maximize product yields.

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 two tubing bundles that connect processing equipment in cubicle 4 to tanks in the cell pits. Also, five of the cubicle equipment racks were replaced. Two more racks have been built and are being tested; another is being designed.

5.2 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. Five sources containing from 0.9 μg to 13 mg of ^{252}Cf were fabricated this year; three of these were doubly encapsulated in type 304L stainless

Table 5.1. Amounts of materials recovered in major campaigns in the Transuranium Processing Plant during the period April 1, 1974, through March 31, 1975

	Campaign 47	Campaign 48	Total
Completion date	10/74	3/75	
Material processed	11 TRU Cm- HFIR targets plus rework	12 Cf-I Cm- HFIR targets plus rework	
Amount recovered			
^{243}Am , g ^a	1.5	0.7	2.2
Total Cm, g ^a	87	71	158
^{244}Cm , g ^a	45	32	77
^{249}Bk , mg	24	26	50
^{252}Cf , mg	252	225	477
^{253}Es , mg	1.25	1.2	2.45
^{257}Fm , μg	0.5	0.5	1.0

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

steel in a standard configuration (NSD).³ Two sources other than NSD's were prepared. One of these was another of the special sources prepared for the National Bureau of Standards.⁴ The californium content of this source was 1.65 mg of ^{252}Cf .

The other special source was a neutron source prepared for Aerojet Nuclear Company in the standard NZS configuration (i.e., a singly encapsulated Zircaloy-2 source capsule). The experimenter needed a configuration in which a low-neutron cross section was an important consideration. An interesting feature of this source (NZS-90) is the novel method of loading the ^{252}Cf . Instead of using ion exchange resin, the pellet liner was loaded with a layer of loose aluminum powder to provide a large surface area. A small volume (100 μl) of the californium solution was pipetted directly into the pellet liner, where it sorbed on the aluminum powder. The powder was dried under a heat lamp, and the liner was then filled with fresh aluminum powder. The pellet pressing and fabrication proceeded in the usual manner.

Sources Returned

An increasing number of neutron sources are being returned as the projects for which they were requested are completed or as replacement sources are ordered to make up for decay of the ^{252}Cf . The returned sources are available for reassignment until the appropriate time for reprocessing to recover the ^{248}Cm daughter. Eleven

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*, ORNL-4718 (January 1972), p. 13.

4. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1972*, ORNL-4794, p. 38.

sources that contain from 48 to 1548 μg of ^{252}Cf are now in this category. During the report period, two sources were returned and four were reassigned.

Special Rabbit Irradiations

Production of ^{250}Cf by irradiation of ^{249}Bk in the HFIR hydraulic rabbit has become a standard procedure. During the reporting period, seven rabbits, each containing 1.2 to 1.5 mg of ^{249}Bk in three pellets, were fabricated, irradiated, and processed using the magnesium diluent technique.⁵ This technique facilitates the physical handling of milligram quantities of material, producing good yields of $^{249}\text{BkO}_2$ in a form that can be readily fabricated into rabbit capsules and which later can be readily dissolved and processed. A speedy schedule is necessary to minimize the contamination of the ^{250}Cf product with ^{249}Cf , which is continually growing into the ^{249}Bk regardless of whether the sample is in the reactor or not.

Six of the seven rabbits were irradiated for 16 hr at a thermal flux of 3×10^{15} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. Separation of ^{250}Cf from ^{249}Bk was made in a high-pressure ion exchange run within 30 hr after reactor discharge. These are the conditions that maximize the concentration of mass 250 in the product. Approximately 1.2 mg of ^{249}Bk and 220 μg of ^{250}Cf were recovered from each rabbit and purified. Yields and compositions of the material recovered from the six rabbits are shown under sample A (one rabbit) and sample C (five rabbits) in Table 5.2.

5. L. J. King, J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1973*, ORNL-4965 (November 1974), p. 14.

Table 5.2. Yields and properties of ^{250}Cf samples

	Sample A	Sample B	Sample C
Date of analysis	May 10, 1974	May 15, 1974	March 26, 1975
Isotopic analysis	Atom %	Atom %	Atom %
^{249}Cf	4.22	17.24	3.62
^{250}Cf	88.86	81.85	89.22
^{251}Cf	6.22	0.850	6.48
^{252}Cf	0.689	0.059	0.678
^{253}Cf	<0.003	<0.005	<0.002
^{254}Cf	<0.003	<0.005	<0.002
Total ^{250}Cf	204 μg	79 μg	1.14 mg
Percent of spontaneous fission activity due to ^{252}Cf	59.8%	12.1%	59.3%

The other rabbit (sample B) was irradiated at the same neutron flux but for only 4.5 hr. This irradiated target was processed by the same technique. Approximately 1.0 mg of ^{249}Bk and 80 μg of ^{250}Cf were recovered and purified. The isotopic composition of this californium is also shown in Table 5.2. The shorter irradiation time resulted in a significant reduction in the contribution to the spontaneous fission activity from the heavier californium isotope, ^{252}Cf .

Special HFIR Targets

A series of calculations has been made for the purpose of determining the optimum procedure for irradiating ^{252}Cf to produce ^{253}Es . The calculations showed that the best yield of ^{253}Es would be obtained from the central portion of a californium-loaded target that is given two cycles of irradiation in the Control-Rod Access Plug Facility in the HFIR. The calculated yields of ^{253}Es were confirmed by the irradiation and processing of a special target, ST-9 (T29), which was fabricated with three pellets, each containing about 2 μg of ^{252}Cf .

The next step in the evaluation involves a scale-up to the order of 1 mg of ^{252}Cf . At this level, we need to develop and demonstrate the technology of fabricating mixed ^{252}Cf -Al pellets, and also to check the irradiation to determine the possible effects of resonance self-shielding at higher nuclide concentrations. The ultimate objective would be to load as much as 20 mg of ^{252}Cf per pellet (the approximate limit for heat removal) and irradiate ten pellets at a time near the reactor midplane; this could produce over 1 mg of ^{253}Es per target rod.

In an earlier set of experiments, two Phoenix capsules had been irradiated in three different target rods (ST-4, -5, and -6) over a total irradiation period of about one year with the objective of producing ^{250}Cm . The capsules were small Zircaloy-2 cans, 0.25 in. in diameter by 1 in. long with threaded end plugs, containing quartz ampuls loaded with a total of 150 μg of ^{248}Cm . During this report period, the capsules were processed for recovery of the actinide elements. A californium prod-

uct containing 0.4 μg of ^{252}Cf , and a curium product containing 2.6 μg of ^{244}Cm , 6.7 μg of ^{248}Cm , and 125 μg of ^{250}Cm were obtained.

A series of computer calculations was made, using the exact irradiation history of the capsules and the measured product composition, to determine the best value for the ^{249}Cm capture cross section. Most of the ^{249}Cm decays to ^{249}Bk with a 64-min half-life. Only a small fraction (about 5×10^{-5}) captures a neutron and becomes long-lived ^{250}Cm .

The destruction of the ^{250}Cm by absorption of a neutron was accounted for by assuming values of σ_c for ^{250}Cm varying from 2 to 200 b. The corresponding values for $\sigma_c(^{249}\text{Cm})$ required to conform to the results of the experiment were calculated to range from 1.25 to 24 b. These are remarkably low values by comparison with the next lighter odd isotope of curium. For example, if $\sigma_c(^{250}\text{Cm})$ is assumed to be 8 b [comparable to $\sigma_c(^{248}\text{Cm})$], then the computed value for $\sigma_c(^{249}\text{Cm})$ is 1.6 b, which is only 2% of the capture cross section of ^{247}Cm . Additional irradiations (of varying length) will be required to determine the cross sections of ^{249}Cm and ^{250}Cm .

Recovery of ^{126}Sn

Several years ago, a researcher requested that we investigate the possibility of recovering some of the fission product isotope ^{126}Sn for use in accelerator experiments. As time permits, we are developing a recovery and purification procedure. Analytical measurements made at TRU indicated that much of the fission product tin from HFIR targets was dissolved in the aluminum dejacket solution (3 *M* NaOH, 1.5 *M* NaNO₃). During this report period, we processed some of the dejacket solution by means of a procedure which included acidification followed by extraction of the tin with di(2-ethylhexyl)phosphoric acid. The product analyses indicated that we might expect a yield of 100 to 200 mg of tin, containing about 5% ^{126}Sn , from a typical HFIR target campaign (10 to 12 targets). Additional amounts may be obtainable from other process solutions.

6. 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 will be summarized in the *Gas-Cooled Reactor Programs Progress Report for the Period January 1974–June 1975* (to be published).

7. Preparation of $^{233}\text{UO}_2$

The ORNL contract with Bettis Atomic Power Laboratory (BAPL) to prepare $^{233}\text{UO}_2$ involves (1) purifying several hundred kilograms of ^{233}U (currently stored in the facility) at the rate of approximately 20 kg of ^{233}U per week, (2) converting the purified uranyl nitrate to ceramic-grade UO_2 powder at the rate of about 20 kg of ^{233}U per week, (3) packaging and shipping the UO_2 to BAPL for blending with thoria and pressing into pellets, and (4) recovering ^{233}U from the $^{233}\text{UO}_2$ scrap generated at ORNL and the $^{233}\text{UO}_2$ - ThO_2 scrap generated at BAPL. The routine production of UO_2 powder at a plant capacity of 100% was continued throughout the year.

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

During this report period, the oxide dissolver was operated to recover 78.1 kg of ^{233}U from recycle UO_2 and ammonium diuranate in 24 dissolutions. This recycle material consisted of: (1) material rejected because of overheating in the microwave oven (i.e., ammonium diuranate) and incomplete reduction in the calcining furnace (i.e., UO_2); (2) recycle UO_2 accumulated from cleanup of the glove boxes after each week's operation; and (3) one entire lot of product powder that BAPL could not receive because of problems in their facility. In addition, some unused $^{233}\text{UO}_2$ (5.2 kg) returned by BAPL and small accumulations of analytical samples at ORNL were dissolved.

All of the pure UO_2 was dissolved in slightly more than the stoichiometric amount of HNO_3 at 80°C so that the nitrate solution, after being analyzed 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. Four of the dissolutions were essentially "cleanout" operations made in an effort to account for all uranium charged previously. Eight dissolutions of Savannah River oxide (39.1 kg of

U) were made to produce feed for conversion to low-phosphorous-content UO_2 .

We received 34 shipments (10.1 metric tons) of binary (UO_2 - ThO_2) scrap generated at BAPL. This scrap, which contained 233 kg of uranium and 8.7 metric tons of thorium, included 30 kg of baked grinder sludge. One hundred ninety-seven dissolutions were made in the scrap dissolver to recover 229 kg of ^{233}U and 8.4 metric tons of thorium from this material. The amount of scrap charged to the dissolver in each case varied from 50 to 250 kg of mixed oxide, and a dissolvent of the composition 12 M HNO_3 -0.04 M F^- -0.1 M $\text{Al}(\text{NO}_3)_3$ was used. The dissolvent 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. About 14 kg of baked grinder sludge was also dissolved along with normal scrap to determine dissolution rates. A motorized self-cleaning filter in the dissolver drain line proved to be effective for removing insolubles (primarily Al_2O_3) from the solution.

7.2 ^{233}U PURIFICATION SYSTEMS

Twenty runs were conducted in the solvent extraction system to recover and to purify 336 kg of 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 5000 ppm.

Approximately 706 kg of uranium was purified in 31 runs made in the ion exchange equipment. Nonrecoverable losses totaled 0.02%. The effectiveness of the resin (200- to 400-mesh AG-50W-X12) column was observed to decrease markedly after a total throughput of 370 kg of uranium, which corresponded to approximately 20 loadings and 20 elutions. This loss in effectiveness was attributed to the ^{224}Ra , a thorium decay product, that had "grown into" the uranium solution during the five years it had aged in the storage tanks. We then diluted

the remaining ^{233}U (120 kg) with water to a concentration of 150 g/liter and pumped the resulting solution through the ion exchange system in a single run. The resin sorbed nearly all the ^{228}Th but little of the ^{224}Ra . However, rapid decay of the ^{224}Ra will yield a solution exhibiting the radioactive emission spectrum of recently purified ^{233}U .

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

During the year, a total of 627 kg of UO_2 (31 lots) was prepared and 556 kg (30 lots) was transferred to

BAPL in 27 shipments; nonrecoverable losses totaled 0.16%. One lot (20.8 kg of UO_2) was recycled, at BAPL's request, after storage for an extended period. Except for one lot in which we exceeded the allowable level for aluminum, all the material met specifications. The material is processed through the conversion system in 1.0- to 1.1-kg (uranium) batches. We rejected three batches due to an accidental loss of hydrogen to the furnace and two batches due to ignition in the microwave oven. The latter was attributed to failure of the rotating mechanism for the Teflon liner.

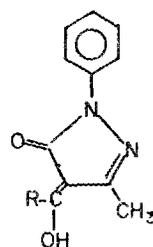
We have met every production commitment requested by BAPL.

8. Separations Chemistry Research and Development

While the development of new separations methods continues to be oriented largely toward the needs of nuclear power, increasing attention has been given to separations problems in other energy fields. The activities reported here, however, are chiefly concerned with radiochemical processing because of the preliminary nature of the nonnuclear investigations. Fewer fundamental studies of separations systems were conducted, since increased emphasis was placed on the descriptive chemistry of separations systems and process development. Descriptive chemistry includes studies of the reactions of substances to be separated and of separations agents, sufficient to establish the controlling variables in related separations processes, and investigation of the chemistry of potential new separations agents and methods, sufficient to evaluate their usefulness. In process development, a selected method is developed into a complete process and tested at the scale needed to evaluate its performance and/or economics and to predict its large-scale performance. Although there is considerable interdependence and overlap between descriptive chemistry and process development, Sects. 8.1, 8.2, and 8.5 represent primarily the former, while Sects. 8.3 and 8.4 represent primarily the latter.

8.1 NEW SEPARATIONS AGENTS

A number of reagents have been examined in our search for selective extractants for plutonium and the transplutonium actinides from acidic reprocessing waste solutions. One class of compounds, the acylated pyrazolones in mixture with donor additives such as tri-*n*-octylphosphine oxide (TOPO) or tributyl phosphate (TBP), has been used in analytical applications.¹ A representative compound used in our studies, 1-phenyl-3-methyl-4-benzoyl-2-pyrazolin-5-one (Φ MBP) [Fig. 8.1(a)] was found to have excellent



ORNL DWG 75-8422

- (a) Φ MBP: R =
- (b) Φ MBBP: R =
- (c) Φ MDP: R =

Fig. 8.1. Acylated pyrazolones (enol form).

extraction characteristics for americium and other trivalent actinides from dilute acids; unfortunately, however, it has limited solubility ($<0.05 M$) in aliphatic diluents such as *n*-dodecane and undesirably high aqueous solubility. We have synthesized two new acylated pyrazolones with more favorable solubility properties: 1-phenyl-3-methyl-4-*p*-*tert*-butylbenzoyl-2-pyrazolin-5-one (Φ MBBP) [Fig. 8.1(b)] and 1-phenyl-3-methyl-4-decanoyl-2-pyrazolin-5-one (Φ MDP) [Fig. 8.1(c)]. When used in synergistic combination with TOPO at the optimum ratio of one mole of acylated pyrazolone to two moles of TOPO, the two new compounds show much higher solubility in *n*-dodecane; Φ MDP is the more soluble, $>0.2 M$. Neither compound shows any measurable distribution to aqueous phases. All of these compounds, Φ MBP, Φ MBBP, and Φ MDP, have higher solubilities in aromatic diluents such as diethylbenzene than in *n*-dodecane, but give lower americium distribution (extraction) coefficients. Even in diethylbenzene, however, the americium coefficient with Φ MBBP may be high enough to be useful. Table 8.1 contains data on the extraction of americium by Φ MDP-TOPO and Φ MBBP-TOPO mixtures from Talspeak-process effluent (Sect. 8.3) adjusted to pH 1.5. The americium distribution coefficients are much lower than the maximum values that could be obtained with higher TOPO concentrations.

1. B. F. Myasoedov, N. E. Kochetkova, and M. K. Chmutova, *Zh. Analit. Khim.* **28**, 1723 (1973).

Table 8.1. Synergistic extraction of americium from Talspeak solution by Φ MDP-TOPO and Φ MBBP-TOPO mixtures

(Composition of Talspeak solution: 1 M glycolic acid, 0.05 M Na₅DTPA, adjusted to pH 1.5)

TOPO (M)	Φ MDP ^a (M)	Φ MBBP ^b (M)	Am distribution coefficient, D_a^o
0.1	0.2		1020
0.05	0.1		160
0.025	0.05		16
0.01	0.02		0.62
0.1		0.2	830
0.05		0.1	19
0.025		0.05	0.41
0.01		0.02	0.0037

^aDiluent: *n*-dodecane.

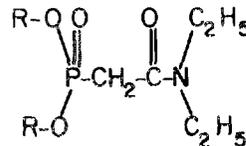
^bDiluent: diethylbenzene.

Bifunctional phosphonates, first investigated by Siddall,²⁻⁴ extract americium, curium, and rare earths fairly strongly from highly acid solutions (4 to 6 M HNO₃) and, when pure, are easily stripped by dilute acids (<1 M). These compounds have potential applicability to separating americium, curium, and rare earths from all of the other fission products in fuel reprocessing wastes without prior destruction of the HNO₃ (Sect. 8.3). In two commercially prepared compounds, dibutyl-*N,N*-diethylcarbamylenephosphonate (DBDECMP), [Fig. 8.2(a)], and dihexyl-*N,N*-diethylcarbamylenephosphonate (DHDECMP), [Fig. 8.2(b)], impurities prevented stripping of americium in the desired way. These impurities may be strongly extracting neutral compounds. Our present efforts relative to these compounds are directed toward developing methods of purification.

Cyclic "crown" ethers are reported to complex many metal ions, especially alkali metals and alkaline earths, presumably with the metal ion within the ether ring. It has been suggested that the size of the "host" ring affects the specificity as a function of the size of the metal ion. If so, one would hope to be able to synthesize compounds that are highly selective for a specific ion or group of ions — an exciting prospect. An arrangement has been made with D. J. Cram of UCLA⁵ to supply certain of these compounds to us for testing. We are currently investigating several compounds sup-

2. T. H. Siddall III, *J. Inorg. Nucl. Chem.* 25, 883 (1963).
3. T. H. Siddall III, *J. Inorg. Nucl. Chem.* 26, 1991 (1964).
4. T. H. Siddall III, U.S. Patent 3,253,259 (1964).
5. AEC Contract AT(04-3)34, P.A. 218.

ORNL DWG 75-8421



(a) DBDECMP: R = -(C₃H₇)CH₃

(b) DHDECMP: R = -(C₅H₁₁)CH₃

Fig. 8.2. Aliphatic *N,N*-Diethylcarbamylenephosphonates.

plied by Dr. Cram and also some commercially available ones for possible applications as extractants.

8.2 SEPARATION OF RADIUM FROM URANIUM ORE TAILINGS

The objectives of this project to investigate the leaching characteristics of radium from uranium ores and sulfate-leached ore tailings are: (1) to determine if there is an economically practicable method for removing the radium (and other radionuclides), and (2) to find a means by which the leachability of the radium due to weathering can be significantly reduced. Previously reported tests,^{6,7} which were directed toward the determination of the leaching characteristics of the "slimes solids" fraction of the sulfate-leached tailings, indicated that effective removal of radium was probably not practical, since it required the use of fairly concentrated HNO₃ or HCl solutions (3 M), or excessively large volumes of selected salt solutions.

In more recently reported data,⁸ pertinent to possible reduction of radium leaching due to weathering, leaching tests were made on sea sand that had been ground to -325 mesh, washed successively with 0.1 M HCl solution and water to prevent adsorption of radium on the freshly exposed surfaces, and then coated with either RaSO₄ alone or RaSO₄ in combination with CaSO₄ and/or BaSO₄. In an attempt to further eluci-

6. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973*, ORNL-4883, pp. 57-58.

7. S. D. Shearer, "The Leachability of Radium-226 from Uranium Mill Solids and River Sediment," Ph.D. thesis, University of Wisconsin, Madison, 1962.

8. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1974*, ORNL-4966, pp. 25-26.

date the leaching mechanism, recent tests have been directed toward a study of the interrelation of the effective solubilities (S') of calcium, strontium, barium, and radium sulfates. Mixtures of these alkaline-earth sulfates were precipitated on the surface of sand prepared as above and then leached with 1 M NaCl--0.1 M HCl solutions. Results of leaching tests made in this fashion (Fig. 8.3) suggest the following tentative generalization for the minor component effective solubility (S'_{\min}) in such mixtures: When the inherent solubility, S_{\min} , of the minor component is greater than that of the major component, S_{maj} , then

$$S'_{\min} \propto S_{\min} \frac{\{\text{min}\}}{\{\text{maj}\}}, \quad (1)$$

where $\{\text{min}\}/\{\text{maj}\}$ denotes the mole ratio of minor to major component in the solid phase. When S_{\min} is less than S_{maj} , then

$$S'_{\min} \propto S_{\text{maj}} \frac{\{\text{min}\}}{\{\text{maj}\}}, \quad (2)$$

with S'_{\min} always $\leq S_{\min}$. Equation (2) is consistent with the solubilities of barium and radium as a function of the barium/radium ratio reported by Lind.⁹

9. S. C. Lind, J. E. Underwood, and C. F. Whittemore, "The Solubility of Pure Radium Sulfate," *J. Amer. Chem. Soc.* 40, 465--72 (1918).

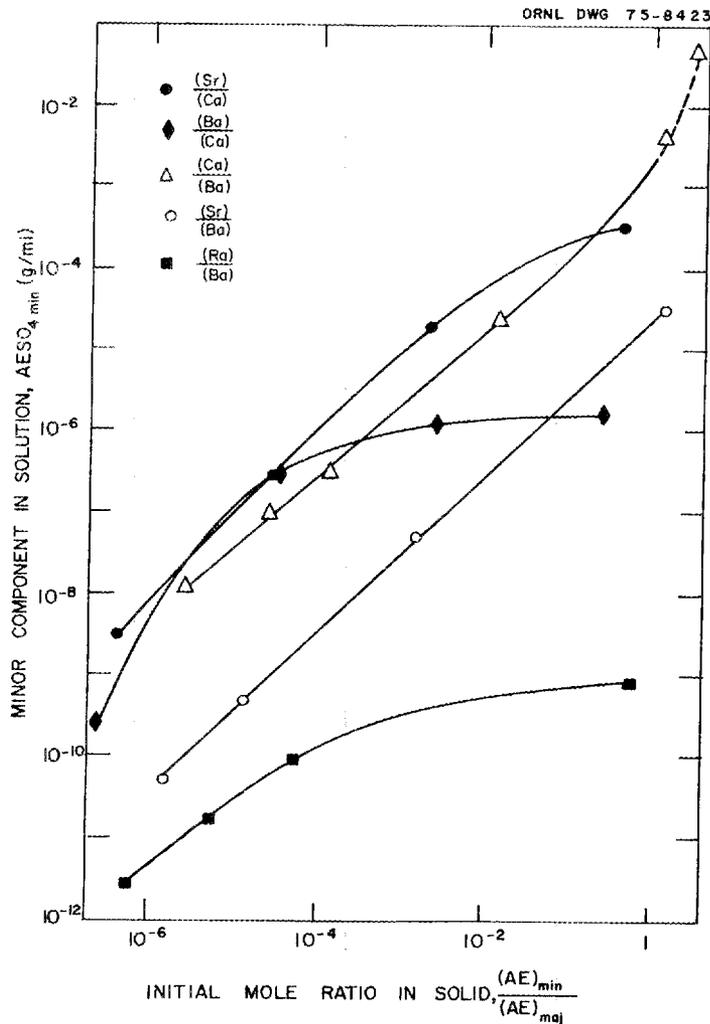


Fig. 8.3. Effect of varying ratios of alkaline-earth sulfates (AESO_4) on the effective solubilities, S'_{\min} . AESO_4 mixtures were precipitated onto finely ground sand and then leached with 1 M NaCl--0.1 M HCl solution. Solubility (in g/ml) of unmixed AESO_4 : $S_{\text{Ca}} \approx 0.02$, $S_{\text{Sr}} \approx 10^{-4}$, $S_{\text{Ba}} \approx 2 \times 10^{-6}$, $S_{\text{Ra}} \approx 2 \times 10^{-8}$.

These data suggest the possibility of reducing the leaching of radium from ore tailings by the addition of BaSO_4 ; however, such a procedure would probably require impracticably large quantities of BaSO_4 .

8.3 SEPARATION OF ALPHA EMITTERS FROM FUEL REPROCESSING WASTES

In support of the program on Process Modifications for Improved Waste Management (Sect. 4.2), we devised an improved process flowsheet for removal of americium and curium from reprocessing wastes. The new version (Fig. 8.4) eliminates most of the difficulties encountered with a previously published flowsheet that was based chiefly on solvent extraction.¹⁰ Several extraction steps are excluded by using conventional oxalate precipitation followed by scavenging of residual amounts of americium and curium with small amounts of rare earths. These operations are applicable both to

the original waste solution containing the americium, curium, and fission product rare earths and to the americium-curium-bearing effluent from the Talspeak process. In the current version of the Talspeak process, the rare earths are separated from the trivalent actinides by preferential extraction with di(2-ethylhexyl)phosphoric acid (HDEHP) in diethylbenzene from an aqueous solution containing glycolic acid and sodium diethylenetriaminepentaacetate.

The composition of the feed solution is based on standard values assigned to typical LWR fuel reprocessing wastes from 1 metric ton of uranium fuel as modified by the present concept of processing to remove uranium, neptunium, and plutonium to acceptable levels (Sect. 4.2). The values for distributions of americium and curium in the various processing steps are based on results obtained in tracer-level laboratory experiments with simulated fuel-reprocessing solutions under a set of conditions which are not necessarily optimum. For example, removing more HNO_3 would make possible a decrease in volume, with a consequent decrease in cost and improved performance; however,

10. Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1974, ORNL-4966, pp. 26-27.

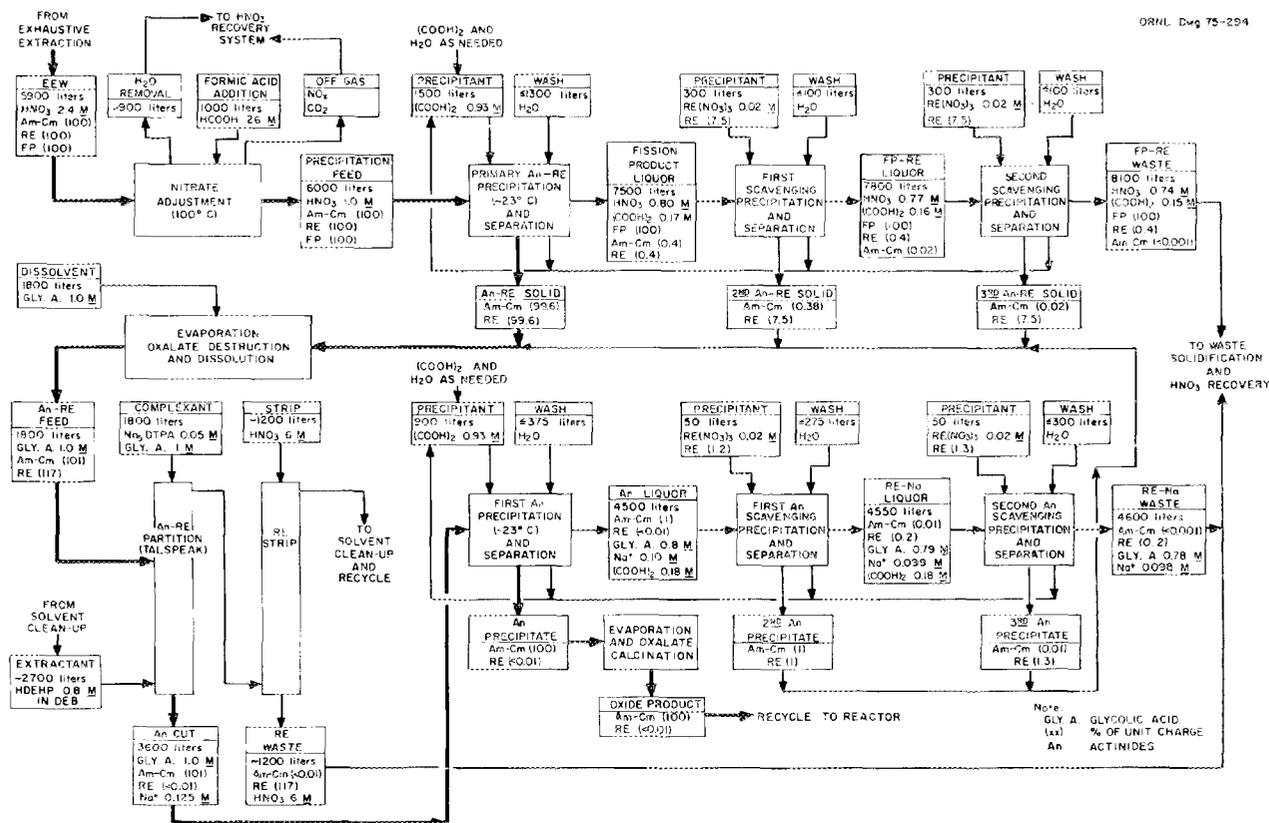


Fig. 8.4. Americium-curium recovery from Purex waste by oxalate precipitation of rare earths and actinides, Talspeak partitioning, reprecipitation, and calcination.

the specific conditions in terms of results expected have not been determined yet. The terms "HNO₃ removal," "solid-liquid separations," and "oxalate decomposition" designate operations for which various alternative, feasible methods exist.

8.4 WASTE STREAM PROCESSING STUDIES

The purpose of this program is to provide certain fundamental information required for the satisfactory treatment of waste streams in nuclear fuel reprocessing plants. A number of problems have already become apparent in studies¹¹ of processes for removing long-lived actinides from wastes, and 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 removal of actinides from the high-level waste stream from fuel reprocessing plants. These studies include:

1. an investigation of the nature of the plutonium in high-level waste streams that is inextractable by TBP, its mechanism of formation, and methods for its removal;
2. control of neptunium valence by the use of reagents that are more amenable for recycle of waste streams from the separations process;
3. application of fused-salt processing methods for treatment of insoluble residues in the wastes.

Last year the principal emphasis was on studies of inextractable plutonium in high-level waste. In addition, an investigation of the kinetics of the reduction of Np(VI) to Np(IV) by ferrous nitrate was carried out. Studies on fused-salt methods for dissolution of solid residues were initiated late in the year.

Plutonium Behavior in Synthetic Wastes

Difficulties in achieving high plutonium recoveries (99.99%) during reactor fuel reprocessing are anticipated due to the formation of inextractable plutonium species. Therefore, studies were initiated to investigate reactions that can result in plutonium losses and to determine the basic mechanism involved.

Since plutonium will be recovered from spent reactor fuels by the Purex process, in which Pu(IV) is extracted

into TBP from HNO₃ feed solution, experiments were designed to determine the stability of Pu(IV) in HNO₃ and in synthetic fission product solutions at various temperatures and acidities of interest. Some of these conditions are conducive to hydrolysis and precipitation of several of the fission products, and efforts were made to determine the effects of this behavior on plutonium extractability.

To date, we have identified three principal problem areas that can result in plutonium losses prior to or during Purex processing. These include: (1) a decrease in the plutonium distribution coefficients with successive TBP extraction stages, (2) the Pu(IV) interaction with the ruthenium-rhodium-palladium components of synthetic feed, and (3) plutonium losses associated with precipitates of zirconium and zirconium-molybdenum. The basic mechanisms involved in these reactions have not, as yet, been determined.

A small but significant amount of plutonium does not extract into 30% TBP-dodecane from a 3 M HNO₃ feed solution. This effect involved about 0.01% of the present plutonium feed concentration and resulted in a decrease in plutonium distribution coefficients from 17.0 to 0.2 in seven consecutive extraction stages. The initial plutonium was highly purified, and spectrophotometric analysis indicated that it was composed entirely of ionic Pu(IV); however, the limits of detection for other species are well above 0.01%. The nature of this inextractable plutonium has not yet been identified; identification will be difficult because of the very low concentration.

A second type of reaction observed involves Pu(IV) instability when synthetic feed solutions are aged or heated. This instability was found to be due primarily to interaction with the ruthenium component, although similar effects were observed to a smaller degree with rhodium and palladium. At room temperature, Pu(IV) is not stable in the presence of ruthenium, rhodium, and palladium at acid concentrations of 2 M or less. As much as 50% of the Pu(IV) can convert to other species in about ten days. A significant feature of this interaction is that the affected plutonium is slowly lost from solution, although visible precipitates are not generally involved. When such solutions are heated, the change occurs very rapidly, and greater than 90% of the Pu(IV) can be converted at 80°C even in fairly concentrated acid solution (3 to 7 M). In preliminary efforts to identify the species to which the Pu(IV) is converted, it was determined spectrophotometrically that the Pu(IV) was oxidized to Pu(VI); HDEHP and TBP extraction behavior also indicated that the species was Pu(VI). The principal effect of the ruthenium-plu-

11. W. D. Bond and R. E. Leuze, *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).

onium interaction on plutonium extraction behavior in the TBP-HNO₃ system was the reduction of distribution coefficients by a factor of 2 to 3, although in some experiments small third-phase losses occurred due to solids formation.

Since plutonium losses can result from the formation of solids in feed or waste solutions, the hydrolytic and precipitation behavior of zirconyl nitrate is being studied at various conditions of aging and heating. At 60 to 80°C, a consistent trend exists in the dependence of zirconium hydrolytic behavior on HNO₃ concentration, and this trend was not altered by the presence of Pu(NO₃)₄. At low acid concentrations (1 M or less), colloidal solutions of very small zirconia particles (20 to 40 Å) are formed. These colloidal solutions are very stable, and formation appears to be irreversible in that the particles do not readily dissolve even in concentrated acid solutions. Hydrolysis of ZrO(NO₃)₂ in more-concentrated acid media (≥ 2 M) results in the formation of zirconia precipitates instead of colloidal solutions. Maximum precipitation occurs at 2 M HNO₃, and the amount of precipitate that forms decreases with increasing acid concentration. A small amount of precipitate is formed even in 6 M HNO₃. Although the nature of such precipitates has not been fully resolved, electron micrographs show that they contain distinctive rodlike structures that are typically about 1000 Å wide and many thousands of angstroms long.

The effect of zirconium hydrolysis on plutonium-TBP extraction behavior was evaluated in two experiments. In the first, Pu(NO₃)₄ was heated at 80°C with ZrO(NO₃)₂ in 3 M HNO₃ until precipitation occurred. Some plutonium is undoubtedly associated with the zirconia precipitate, but the amount is too small to be detected by gross alpha analysis of the feed solution. The effect on plutonium extraction behavior is also quite small, although plutonium losses are a factor of 3 greater than for solutions of Pu(IV) alone after five extraction stages.

In the second experiment, 1 M HNO₃ containing both Pu(NO₃)₄ and ZrO(NO₃)₂ was heated at 80°C. This gave rise to a major plutonium loss mechanism in which 2% of the plutonium became completely inextractable in TBP from 3 M HNO₃.

Reduction Kinetics of Np(VI)

A study of the kinetics of the reduction of Np(VI) to Np(IV) in nitric acid solution by ferrous nitrate was made using spectrophotometric methods.¹² The rate-

determining step was found to be the reduction of the intermediate species, Np(V). The reduction reaction was first order with respect to Np(V) and Fe(II) concentrations and about 3/2 order with respect to hydrogen ion concentration. The complexing of Np(IV) with nitrate ion appears to explain the modest increase in rate observed with nitrate ion concentration. The energy of activation was measured to be 9.8 kcal. We also studied the kinetics of the back reaction of the reduction [i.e., oxidation of Np(IV) to Np(V) by ferric ion]. The reaction rate appears to explain the moderate slowing of the reduction rate after about 75% of the reduction has been completed. The oxidation reaction, which is first order with respect to Np(IV) and Fe(III) concentrations and negative third order with respect to hydrogen ion concentration, has an activation energy of 35 kcal. The relative effect of temperature on reaction rate constants is shown in Fig. 8.5. Based on the results of this study of chemical kinetics, a 10- to 20-min holdup time would be required to reduce Np(VI) to Np(IV) in a partitioning column.

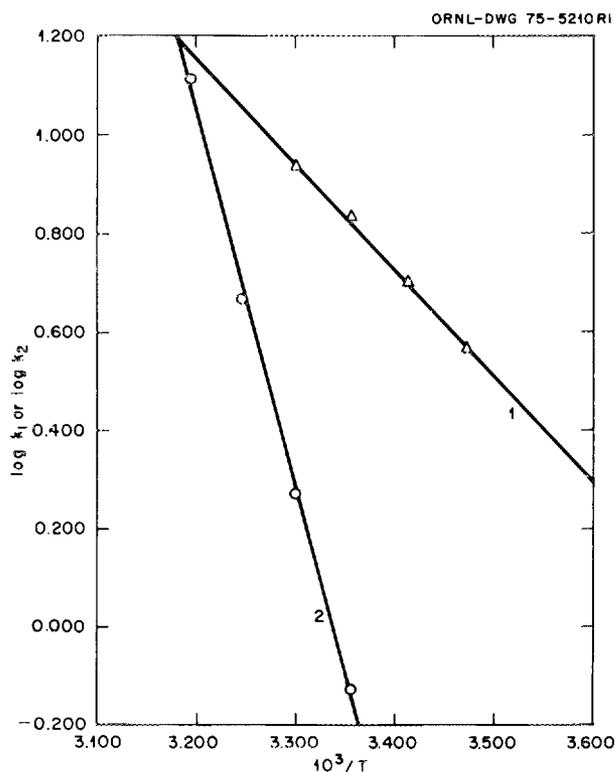
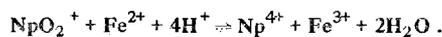


Fig. 8.5. Effect of temperature on the specific rate constant in the reversible reaction



Δ = forward reaction; ○ = backward reaction.

12. Work performed in collaboration with J. R. Peterson and Y. Jao of the University of Tennessee, Knoxville.

Molten-Salt Processes

A review of the literature was made to determine the feasibility of a molten-salt extraction process for removing actinides from the solid residues that result from the aqueous dissolution of spent fuels. These residues consist primarily of plutonium oxides and noble-metal fission products but may contain trace quantities of other actinides. In principle, the recovery of the actinides should be possible by dissolving the residues in molten salts and then extracting the actinides into a liquid-metal phase. Studies were initiated regarding the chemical reactions required for dissolution of the residues in molten salts and the chemistry of the molten-salt-liquid-metal transfer process.

8.5 DISTRIBUTION EQUILIBRIA, KINETICS, AND MECHANISMS

"Single-Atom" Chemistry

The adaptation of separations chemistry techniques to rapid handling and to small volumes has allowed successful completion, in cooperation with members of the Chemistry Division, of three separate studies of the chemistry of nobelium, element 102, using the cyclotron-produced isotope ^{255}No ($t_{1/2} = 223$ sec). The first paper, "Comparative Solution Chemistry, Ionic Radius, and Single-Ion Hydration Energy of Nobelium," has been published;¹³ the other two are in preparation. The abstract of the second paper follows:

"Nobelium Chemistry: Aqueous Complexing with Carboxylate Ions," by W. J. McDowell, O. L. Keller, P. F. Dittner, and J. R. Tarrant. *Abstract:* The tendency of divalent nobelium to form complexes with citrate, oxalate, and acetate ions in an aqueous medium of $0.5\text{ M NH}_4\text{NO}_3$ has been examined by solvent extraction techniques and compared with the complex-forming ability of calcium and strontium under the same conditions. In general, for each anion, the complexing tendency of nobelium is between that of calcium and strontium, being more nearly like that of strontium. The data allow the estimation of a concentration quotient for the formation of NoHCit and NoOx . There is some suggestion of a difference in nobelium chemistry from that of calcium and strontium.

The paper describing the third study will be entitled "Determination of Half-Wave Amalgamation Potential of Nobelium." In this work, nobelium was placed in a small electrolysis cell and electrolyzed into a mercury cathode. By analysis of the nobelium solution before and after electrolysis at each of several selected potentials and by repeating the experiment a number of times

at each potential, a fraction-reduced-vs-potential curve was obtained. From this curve, the half-wave amalgamation potential from $0.1\text{ M NH}_4\text{Cl}$ was determined to be $-1.60 \pm 0.05\text{ V}$ relative to the standard hydrogen electrode potential. This is similar to the values for calcium ($E_{1/2} = -1.97\text{ V}$) and strontium ($E_{1/2} = -1.86\text{ V}$), again demonstrating the similarity noted above.

Liquid Scintillation Alpha Spectrometry

Outside interest in liquid scintillation alpha spectrometry increased greatly during the past year. This interest and our own use of this alpha counting method resulted in investigations leading to significant improvements in it and in the related separations methods for alpha-emitting nuclides.

In cooperation with the School of Engineering of Arizona State University, Tempe, a short study of reflector and electronics configurations was made and reported. The abstract follows:

"Some Studies of Reflector Construction and Electronics Configurations for Optimizing Pulse-Height and Pulse-Shape Resolution in Alpha Liquid Scintillation Spectrometry," by John W. McKlveen, School of Engineering, Arizona State University, Tempe, Arizona, and W. J. McDowell, Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. *Abstract:* Various sample sizes, reflector sizes and shapes, and reflector materials were examined to determine their effect on pulse-height and pulse-shape resolution in alpha liquid scintillation spectrometry. A section of metal sphere coated with a diffuse-white reflective material was found to have the best characteristics for both pulse-height and pulse-shape resolution. Although sample volumes as large as 10 ml could be tolerated when used with reflectors to accommodate them, the best results were obtained with 1-ml samples and smaller reflectors. Comparison of two types of pulse-shape discrimination circuitry for separating alpha and beta-gamma pulses indicated that a zero-crossover method was superior to a constant-fraction-timing method. The combination of these improved detectors with solvent extraction methods of incorporating the sample in the scintillator and pulse-shape discrimination allows alpha spectrometry with a background as low as 0.01 count/min and an energy resolution as good as 5.5%.

Other work was directed toward adapting liquid scintillation alpha spectrometry to a wider range of applications. A program being carried out in cooperation with the Health Physics Division has the objective of improving both the instrumentation and the chemical separations aspects of the system. Efforts in instrumentation development are aimed at improving alpha-energy resolution and pulse-shape resolution, that is, the capability for electronically separating alpha-produced pulses from beta-gamma-produced pulses. Chemical systems improvements have included increased light output and stability of the scintillator solution as well

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

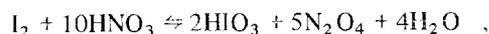
as more effective and more dependable methods of extracting the alpha-emitting nuclide into the scintillator. Progress was made in the development of a procedure for stripping the alpha-emitting nuclide from the extractive scintillator used in a commercial beta liquid scintillation counter and reextracting it into the high-resolution scintillator. This procedure could be used to scan a large number of samples, selecting only those requiring the better energy resolution or the lower background of the high-resolution detector for further treatment.

Iodine Chemistry

In the Iodex process, concentrated nitric acid is used to scrub or remove volatile iodine from air streams encountered in various parts of a nuclear fuel reprocessing facility. The nitric acid serves as an oxidizing agent to convert the iodine to the nonvolatile pentavalent form (i.e., to a form of iodic acid). The iodic acid or its equivalent form of I_2O_5 or HI_3O_8 is then stored or disposed of as radioactive waste (^{131}I , ^{129}I). Oxidation of iodine leads to the production of reduced nitrogen in the HNO_3 . In oxidizing iodine to the pentavalent state, the use of HNO_3 in the 16 to 20 M range is most important, since at these concentrations the reaction rates are much faster and the chemical equilibrium favors formation of pentavalent iodine.

Previously, we reported studies of the chemical equilibria made by spectrophotocemical methods in the HNO_3 concentration range of 14 to 18 M .¹⁴ This report summarizes tracer studies of the Iodex equilibria in 17 to 20 M HNO_3 . In order to approach the operating conditions to be used in the actual gas scrubbing process, experiments were designed to measure the liquid-gas partition of iodine between 17, 18, 19 and 20 M HNO_3 solutions and air.

Some understanding of the partition behavior of iodine can be obtained if we assume that we are dealing primarily with a two-species equilibrium (namely, I_2 and HIO_3). Studies made on the HNO_3 - NO_2 - NO system indicate that the NO_2/NO ratio becomes large, at least 100, for HNO_3 concentrations above 17 M .¹⁵⁻¹⁷ Thus it appears that the reduced species will be either NO_2 or its dimer, N_2O_4 . Further, on the basis of other work on the NO_2 - N_2O_4 equilibrium, the predominant species at high equivalent nitrite concentrations will probably be N_2O_4 .¹⁸⁻²¹ The corresponding redox reaction is



and, with $[H_2O]$ and $[HNO_3]$ approximately constant, the equilibrium quotient expressed in liquid-phase concentrations is

$$Q = \frac{[HIO_3]^2 [N_2O_4]^5}{[I_2]} \quad (1)$$

We define the distribution coefficient H as the ratio of tracer iodine count rate in the liquid to that in the gas, C_L/C_G . Since HIO_3 exists only in the liquid state and $\approx 99.9\%$ of the iodine is in the form HIO_3 in these tests, $C_L \approx [HIO_3]$. The only species in the gas is I_2 , so that assuming I_2 distribution to follow Henry's law with proportionality constant k gives $C_G \approx 2k[I_2]$. Equation (1) then becomes

$$Q = 2k \frac{C_L}{C_G} [HIO_3] [N_2O_4]^5 \quad , \quad (2)$$

$$\begin{aligned} \log \frac{C_L}{C_G} + \log [HIO_3] &= -5 \log [N_2O_4] + k_1 \\ &= -5 \log [HNO_2]_{st} + k_1 \quad , \quad (3) \end{aligned}$$

where $k_1 \equiv \log [Q/2k]$, since the concentration of the actual predominant reduced nitrogen species, $[N_2O_4]$, is equal to the equivalent stoichiometric concentration of nitrous acid, $[HNO_2]_{st}$. Further, $[HIO_3]$ was held approximately constant in these tests (H varied only when C_G varied), so that Eq. (3) reduces to

$$\log H \equiv \log \frac{C_L}{C_G} \approx -5 \log [HNO_2]_{st} + k_2 \quad , \quad (4)$$

where $k_2 \equiv k_1 - \log [HIO_3]$. A plot of $\log H$ vs $\log [HNO_2]_{st}$ would thus be expected to show a slope of -5 .

14. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1974*, ORNL-4966, pp. 29-31.

15. L. Ya. Tereshchenko et al., *Zh. Prikl. Khim.* **41**, 487-92 (1968).

16. M. E. Pozin et al., *Zh. Prikl. Khim.* **36**, 16-24 (1963).

17. L. Ya. Tereshchenko et al., *Zh. Prikl. Khim.* **41**, 702-9 (1968).

18. V. I. Atroshchenko et al., *Kors Tekhnologhii Sviazonovo Azota*, Izd. Khimia, Moscow (1968).

19. L. H. Mishina et al., *Vestn. Akad. Belarusk. S.S.R., Ser. Fiz. Tekn. Navuk*, **4**, 23 (1967).

20. R. F. T. Wayland, *J. Phys. Chem.* **72**, 1626 (1968).

21. C. Matasa and E. Tonca, *Basic Nitrogen Compounds*, 3d ed., Chem. Publishing Co., Inc., New York, 1973.

If the predominant reduced nitrogen species were NO_2 instead of N_2O_4 , the corresponding relation would be

$$\begin{aligned} \log H \equiv \log \frac{C_L}{C_G} &\approx -10 \log [\text{NO}_2] + k_3, \\ &\approx -10 \log [\text{HNO}_2]_{\text{st}} + k_4. \end{aligned}$$

Figure 8.6 shows the equilibrium iodine distributions obtained at the four nitric acid concentrations as a function of the stoichiometric nitrite concentration in the system (added nitrite plus nitrite-equivalent produced by oxidation of iodine). The results are similar to those from the spectrophotometric work¹⁴ in that the slopes vary between -2.5 and -5 . As noted previously, slope values of -2.5 could suggest reduction to NO and

N_2O . However, such a reduction would be counter to the evidence cited above;¹⁵⁻¹⁷ hence it is more likely to reflect, for example, changing activity coefficients. While the slopes per se thus cannot yet be interpreted with confidence, the close agreement of these tracer distribution measurements with the spectrophotometric measurements gives confidence in the validity of both. Consequently, the results allow calculation of the partition coefficients required for practical application of the Iodex process to be made in both high and low nitrite concentration regions by use of the appropriate apparent concentration dependences. Note from Eq. (2) that the distribution coefficient, H , is inversely proportional to the total iodine concentration, $\approx [\text{HIO}_3]$. At lower HIO_3 concentrations than used in these tests ($2 \times 10^{-3} M$), the distribution coefficient would be correspondingly higher.

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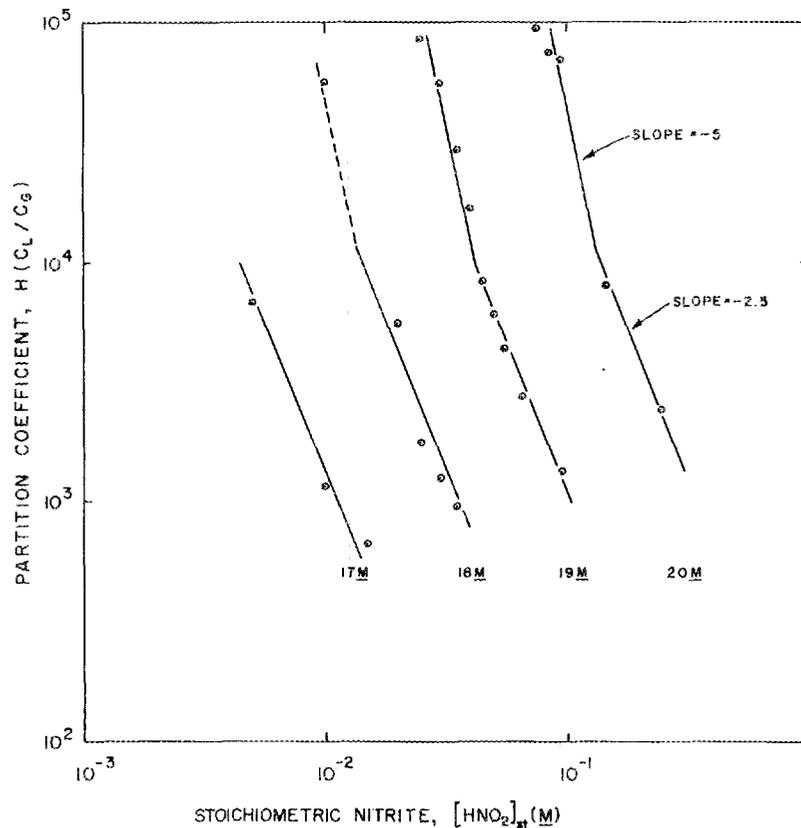


Fig. 8.6. Dependence of the iodine partition coefficient in the Iodex process on the nitrite-equivalent concentration at constant HIO_3 concentration ($0.002 M$) and differing nitric acid concentrations.

9. Biomedical Technology

9.1 ADVANCED ANALYTICAL TECHNIQUES

Various disease states may give early warning of their onset or their continuing presence by subtle changes in excretion levels of molecular constituents in physiologic body fluids. Prompt medical treatment based on these early symptoms may prevent the disease from developing; retard the progress of the disease; or, at the very least, minimize its debilitating effects. Detection and monitoring of these early symptoms will require that research and clinical laboratories be equipped with

automated high-resolution analytical systems that can identify and quantitate many molecular constituents. New analytical concepts are being developed by the Biomedical Technology Group; some of these will lead to the fabrication of prototype analytical systems for use in clinical and biomedical research laboratories.

Engineering Development

Three major analytical concepts are undergoing development and may be categorized as: high-resolution

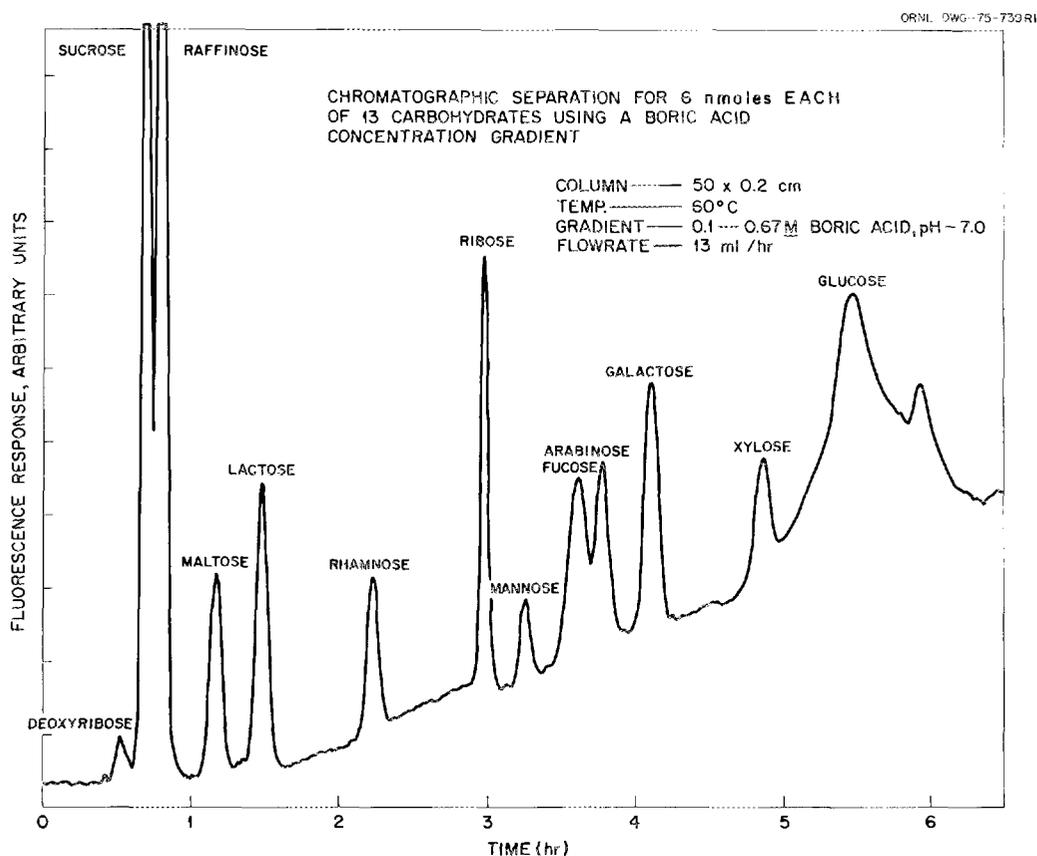


Fig. 9.1. Rapid separation of 13 carbohydrates by anion exchange chromatography, using a neutral boric acid concentration gradient. High sensitivity of the cerate oxidimetric detector shows the baseline rise due to an increase in borate concentration.

liquid chromatography, centrifugal elution chromatography, and elution electrophoresis.

High-resolution liquid chromatographic systems. The high-resolution liquid chromatographic system receiving the most developmental attention in the past year was the glycoprotein carbohydrate analyzer. The application of the cerate oxidimetric detector system to carbohydrate analysis was discussed previously.¹ This detector system has been improved and coupled with a liquid chromatographic system² for the analysis of neutral carbohydrates in serum glycoproteins. The sensitivity of the cerate oxidimetric system for carbohydrates was increased, and the analysis time for protein-bound carbohydrates in serum was reduced. Figure 9.1 illustrates the separation of 13 carbohydrates in 6 hr, using the improved glycoprotein carbohydrate analyzer.

Centrifugal elution chromatographic system. A prototype centrifugal system was developed to permit photometric monitoring of eluate streams from multiple chromatographic columns.³ The major components, shown in Fig. 9.2, include: a means for sample and

eluent introduction, a rotor with up to eight chromatographic columns terminating in flow cuvetts, a stationary light source and photodetector, and a digital logic circuit which synchronizes the cuvet signal with the appropriate recorder trace.

In operation, the sorption medium is loaded into the columns dynamically in the form of a slurry. A steady eluent flow rate is established, and the sample is injected into the eluent stream. The eluate monitoring system is operated throughout the run, and a multi-channel strip-chart recorder is used for data display.

1. C. D. Scott et al., *Experimental Engineering Sect. Semi-annu. Progr. Rep. Sept. 1, 1973, to Feb. 28, 1974*, ORNL-TM-4602 (December 1974).

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

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

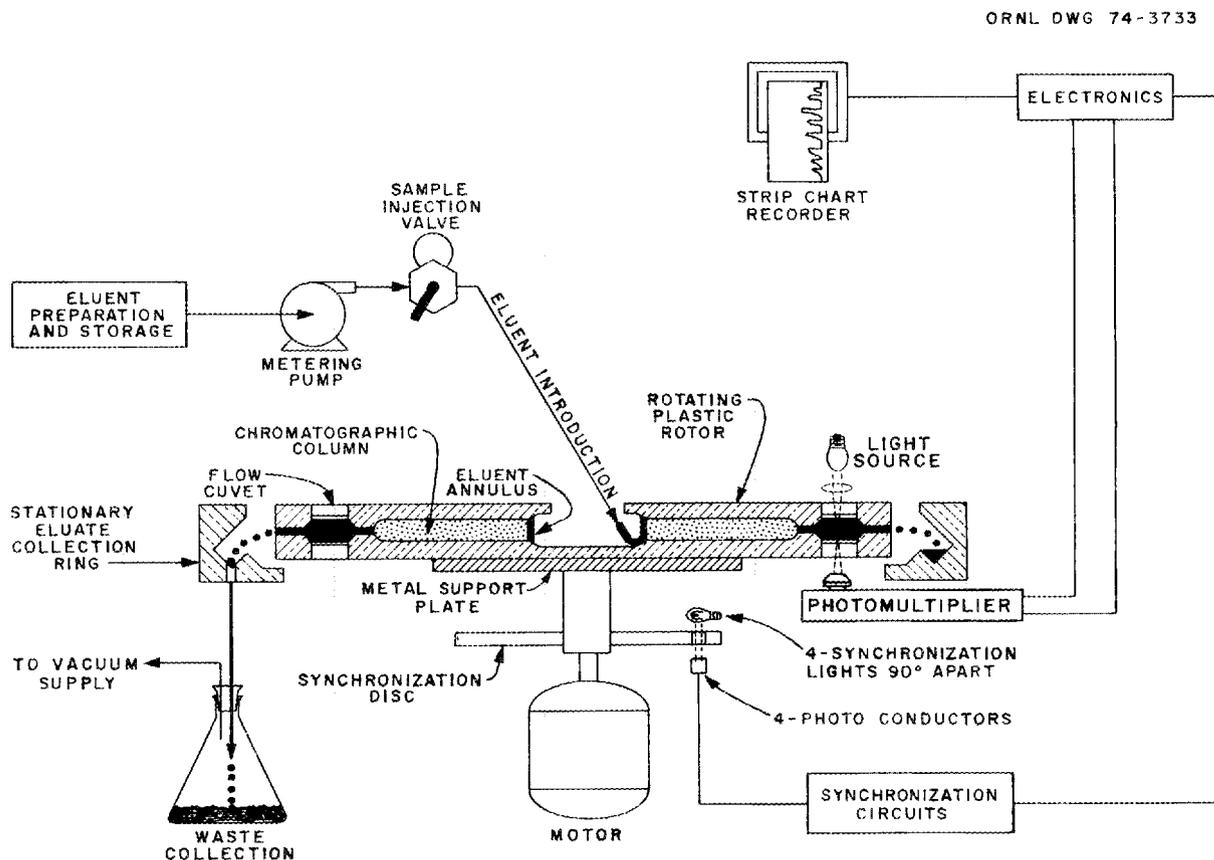


Fig. 9.2. Centrifugal elution chromatograph with eluate monitoring.

Experiments with simple gel filtration separations have shown that the apparent efficiency of the entire system can be represented by about 30 theoretical plates. The comparable chromatographic peaks from each channel had very close elution times, indicating that the eluent flow rates for the various channels were quite similar.

Elution electrophoresis system. The usual high-resolution electrophoresis for biological macromolecules requires a series of manual manipulations to achieve best results. Consequently, the entire operation can require a relatively long time (hours), and the many manual steps result in poor quantitation that can be very operator dependent. A new concept for electrophoresis is under development that, hopefully, will result in a highly automated analytical system which will be accurate, reproducible, and require a short analytical time. This concept is that of elution electrophoresis in which the eluate stream is continuously monitored by a flow photometer or colorimeter.

The elution electrophoresis system utilizes a horizontal glass column (typically 3 mm in diameter by 40 cm long) loaded with a packed bed of particulates and jacketed for forced-liquid cooling (Fig. 9.3). Samples are introduced at the midpoint through a septum, and column entry points are arranged to allow a continuous flow of eluent sweeping past each electrode chamber into the column or column exit. Eluent can be introduced directly into the system at either electrode side during or subsequent to the electrophoresis separation, and the eluate stream progresses through a continuous-flow uv photometer or colorimeter. A reagent development system can also be used wherein one or more reagent streams are continuously mixed with the eluate stream and the resulting reaction products are continuously monitored photometrically.

The entire system, excluding the 5-kV power supply, is enclosed in an acrylic plastic housing. Double-interlocking safety switches are installed at each point of entry to the column area. As a result, electrical current can be applied only if and when all switches are closed.

Analytical Applications

Analytical separations studies on human physiologic fluids continue to demonstrate useful applications of high-resolution liquid chromatographic systems and detectors developed by the Biomedical Technology Group. Emphasis is continuing on the separation and analysis of protein-bound carbohydrates in serum. Feasibility separations of human serum immunoglobulins, using the centrifugal elution chromatograph, have shown a potential for the development of a prototype clinical analyzer. Preliminary results obtained with the elution electrophoresis system indicate that clinical utility includes the separation of serum proteins with detection by uv photometry, the separation of various hemoglobins in the hemolysate from red blood cells (RBC) with colorimetric detection, and the separation of serum isoenzymes of lactic dehydrogenase (LDH) with reagent development followed by colorimetric detection.

Analysis of neutral carbohydrates in serum glycoproteins. A sensitive and reproducible chromatographic

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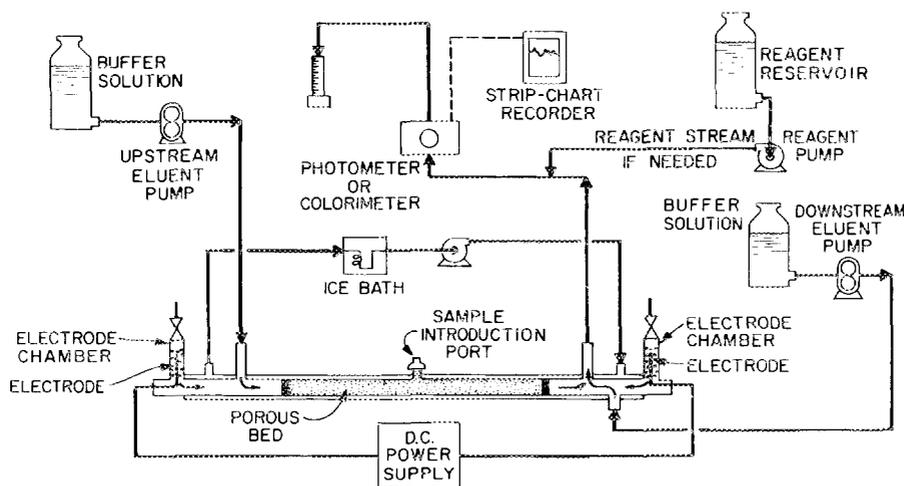


Fig. 9.3. Elution electrophoresis system.

procedure was developed for the analysis of neutral carbohydrates in glycoproteins. Separation is effected by elution of a high-resolution anion exchange column with a pH 7 concentration gradient of boric acid (0.067 to 0.672 M); high-sensitivity detection is provided by a cerate oxidimetric system² which monitors the fluorescence of Ce³⁺ produced by the oxidation of eluted constituents with Ce⁴⁺. Sensitivity to nanomole amounts of the carbohydrates galactose, fucose, and mannose was demonstrated. The separation of a reference standard containing 16 neutral carbohydrates is shown in Fig. 9.4 and is illustrative of the separations that can be achieved with this system.

Levels of glycoproteins in human serum were estimated by using hydrolysis and analysis of the protein-bound carbohydrates. Elevated levels of serum glycoproteins were observed in human subjects with malignant diseases and in laboratory animals with induced tumors.^{4,5} An elevation of serum protein-bound fucose was reported for patients with malignant breast masses.⁶ In general, nonspecific colorimetric procedures were used to analyze neutral carbohydrates in serum glycoproteins even though the methods were shown to be subject to interference.⁷⁻¹⁰ Chromatographic separation enables a specific analysis of each of the three neutral carbohydrates (mannose, fucose, and galactose) that are bound to serum glycoproteins.

Protein-bound mannose, fucose, and galactose were measured in 12 normal female subjects. Our average fucose analysis (Table 9.1) was substantially lower than the values determined by means of the nonspecific colorimetric procedure and reported in the literature. The latter generally ranged between 8.2 and 9.5 mg/100 ml.^{11,12} However, Sobocinski et al.,⁸ analyzing the same pooled normal serum by means of the nonspecific colorimetric method and a specific enzymatic procedure, found that results by the nonspecific method were 44% higher than those obtained by the enzymatic method (9.5 mg/100 ml vs 6.6 mg/100 ml). Our results would tend to verify the failure of the colorimetric method to measure accurately true fucose levels.

The three protein-bound neutral carbohydrates were measured in sera from 29 patients with metastatic breast cancer. Twenty-three of these patients had fucose values above the range of values found for the normal female subjects. Levels of the three carbohydrates were all within normal ranges for the six patients having normal fucose levels. In general, elevation in fucose was accompanied by elevation in the two hexoses; however, a proportionately larger increase was apparent in the levels of fucose (Table 9.1).

The results showing that 79% of the patients have elevated fucose are interesting, but the high percentage of these patients displaying normal values is somewhat disappointing. Additional studies are needed for pa-

4. R. A. L. Macbeth and J. G. Bekesi, "Plasma Glycoproteins in Malignant Disease," *Arch. Surg.* **88**, 633 (1964).

5. S. Harshman and G. Bryant, "Serum Mucoid Levels in Rats Bearing Walker Carcinoma 256 and the Effect of Surgical Extirpation of the Malignance," *Cancer Res.* **24**, 1625 (1964).

6. F. E. Rosato, M. Seltzer, J. Muller, and E. F. Rosato, "Serum Fucose in the Diagnosis of Breast Cancer," *Cancer* **28**, 1575 (1971).

7. A. S. Evans, M. F. Dolan, P. Z. Sobocinski, and F. A. Quinn, "Utility of Serum Protein-Bound Neutral Hexoses and L-Fucose for Estimation of Malignant Tumor Extension and Evaluation of Efficacy of Therapy," *Cancer Res.* **34**, 538 (1974).

8. P. Z. Sobocinski, W. J. Canterbury, and K. M. Hartley, *Determination of L-Fucose in Glycoproteins. I. Effect of Nonfucose Moieties of Serum Glycoproteins*, SR 72-6, Armed Forces Radiobiology Research Institute Scientific Report, Bethesda, Maryland (1972).

9. G. Gyorky and J. C. Houck, "The Determination of Terminal Protein-Bound Fucose," *Can. J. Biochem.* **43**, 1807 (1965).

10. R. J. Winzler, "Determination of Serum Glycoproteins," *Methods Biochem. Anal.* **2**, 279 (1955).

11. J. J. Barlow and P. H. Dillard, "Serum Protein-Bound Fucose in Patients with Gynecologic Cancers," *Obstet. Gynecol.* **39**, 727 (1972).

12. A. Saifer and S. K. Weintraub, "Serum Protein-Bound Fucose Levels in Certain Chronic Diseases: A Clinical-Statistical Study," *Clin. Chim. Acta* **6**, 174 (1961).

Table 9.1. Chromatographic analysis of protein-bound carbohydrates in sera from normal females and those with metastatic breast cancer

Type of subject	No.	Average analysis (mg/100 ml)						Range (mg/100 ml)		
		Mannose	C.V. ^a	Fucose	C.V. ^a	Galactose	C.V. ^a	Mannose	Fucose	Galactose
Normal	12	44.4	17.6	4.8	25.7	43.6	19.5	34.5-62.6	2.8-7.6	30.2-57.5
Breast cancer	29 ^b	69.0	26.8	10.0	39.2	73.5	30.9	45.0-107.3	3.9-21.1	39.1-125.1

^aCoefficient of variation in %.

^bSix patients had all analyses within the range of normal values.

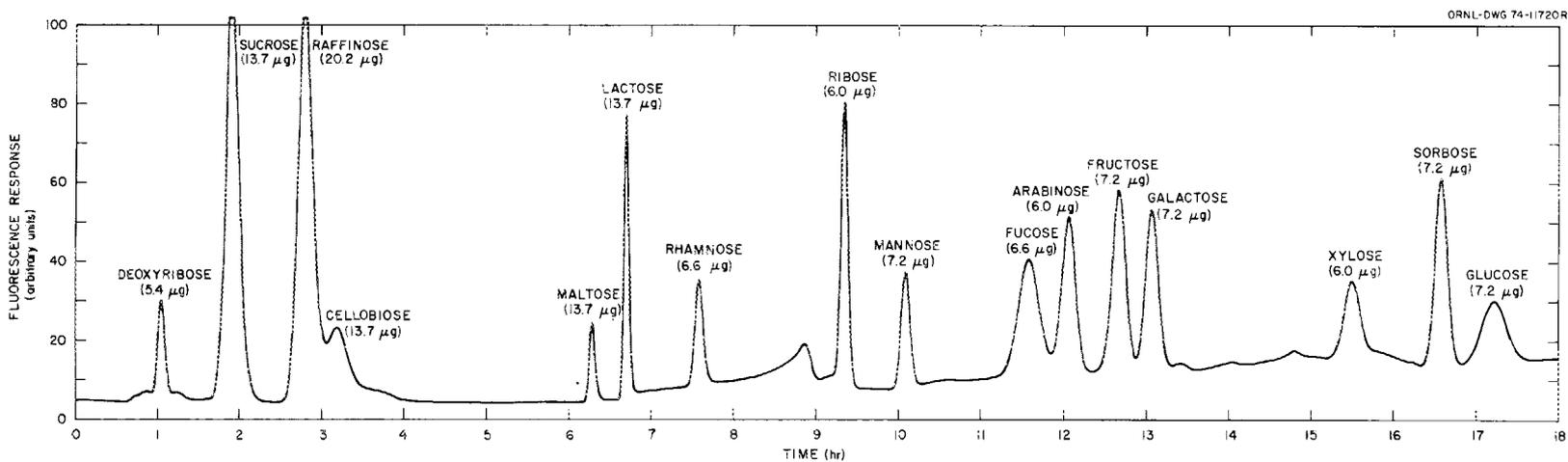


Fig. 9.4. Anion exchange separation (150×0.22 cm column) of 16 carbohydrates, using a pH 7 concentration gradient of boric acid generated with a nine-chamber gradient box.

tients in the latter category to determine if the normal levels are maintained.

Centrifugal elution chromatography of serum immunoglobulins. A separation of the protein IgG from normal human serum is representative of the affinity chromatography experiments using the centrifugal elution chromatograph. The eight-place, fixed-column rotor previously described was used for this investigation. The columns are dynamically loaded with a slurry of Sephadex G-25, 100- to 300- μ size range, onto which anti-(human)-IgG had been immobilized. When a steady-state flow rate of eluent was established, the sample volume of 25 μ l of human serum per column (a total of 200 μ l for eight columns) was dynamically introduced into the eluent annulus. The resulting

chromatogram is shown in Fig. 9.5. As expected, the chromatographic pattern had a large peak for all of the nonsorbed species, followed (after changing the eluent to 3 M NaSCN) by a much smaller peak for the specific protein, IgG. The rotor speed was 400 rpm; monitoring was done at a wavelength of 280 nm.

The results of these preliminary experiments led us to believe that the system is capable of performing determinations of several different serum proteins simultaneously from a single sample in less than 10 min. Proteins of specific interest include the human immunoglobulins.

Elution electrophoresis of serum proteins, hemoglobins, and serum isoenzymes of LDH. As many as 12 electrophoretic peaks, detected by a flow uv photometer operating at 280 nm, were separated from 10 μ l or less of human serum. A typical electrophoretogram of human serum shows a separation in which the normal serum protein pattern (i.e., the pattern usually observed by cellulose acetate electrophoresis) is observed but with an indication of additional resolution. The peaks were tentatively identified by elution position and by reelectrophoresis on an analytical gel electrophoresis system.

Operation of the same system with a flow colorimeter monitoring at 410 nm but with other operating conditions similar to those used with the serum separation gives an indication of seven hemoglobin peaks from 1 μ l of a 4:1 (distilled water:packed RBC) RBC hemolysate. This compares with the usual four to five bands that are more completely isolated with a cellulose acetate separation.

Separation of serum LDH isoenzymes was achieved using the same operating conditions as those above; however, a reagent development system was used to detect the separated enzymes. A colorimetric determination of isoenzyme activity was made continuously by monitoring the lactate-to-pyruvate conversion with a flow colorimeter measuring absorbance at 510 nm.

Five major electrophoretic peaks and several smaller peaks were evident in the resulting LDH separation (Fig. 9.6). This pattern was in good agreement with the typical separation of the five common LDH isoenzymes on cellulose acetate. The separated enzymes were tentatively identified by elution position and cochromatography of two of the isoenzymes.

An elution electrophoresis that can be applied to routine clinical analyses has not yet been developed, but the operating concept for such a system has been demonstrated by a first prototype system.

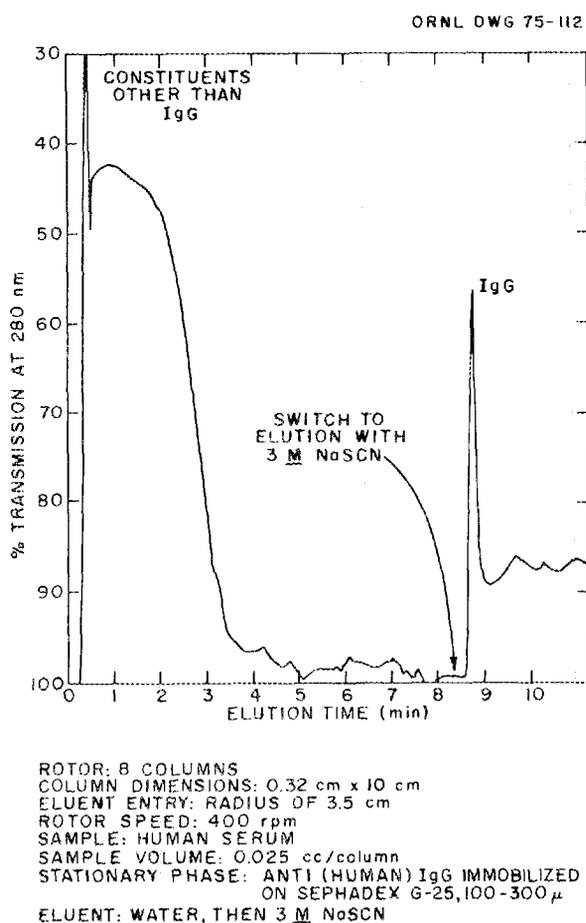


Fig. 9.5. Affinity chromatogram for separation of IgG from normal human serum, using prototype centrifugal elution chromatograph.

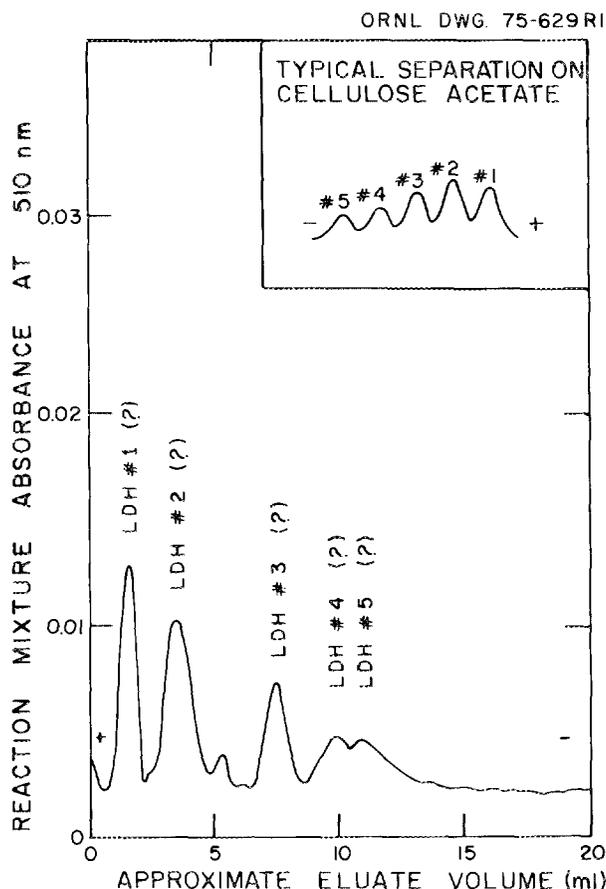


Fig. 9.6. Separation of LDH isoenzymes in 10 μ l of pooled serum by elution electrophoresis at 1200 V for 30 min with a 5-ml/hr buffer (0.25 M sodium phosphate, pH 8.6) flow at each end of the column. Eluate monitoring is by reagent development.

9.2 CENTRIFUGAL FAST ANALYZER DEVELOPMENT

The basic objective of this effort is the development of fast analytical systems for clinical, small animal, genetic monitoring, environmental, and other related uses. The first system developed under this program was the GeMSAEC Centrifugal Fast Analyzer (CFA), which features the use of a centrifugal field to simultaneously initiate and transfer several parallel reactions into their respective cuvetts, where they are rapidly and sequentially monitored by a stationary photometer or fluorometer and an on-line digital data system.¹³⁻¹⁶ These analyzers have been commercially developed, and approximately 400 to 500 of them are now operating in clinical laboratories located around the world. In general, their acceptance has been good, and although the technology is new, a sizable source of reference

literature is now available with over 85 articles or chapters published on the subject.

Engineering Development

During the past year, primary efforts included the continued development of an analytical system based around a miniaturized prototype of a CFA. A system comprised of an automated sample-reagent loader, an analyzer, a computerized data system, a rotor cleaning station, and several rotors has been evaluated and routinely operated for the past two years in the clinical laboratory of the Health Division. To obtain another independent evaluation, two additional systems were fabricated and are being assessed in the clinical laboratories of the NASA Johnson Space Center, Houston, Texas, and the National Institutes of Health (NIH), Bethesda, Maryland. Three additional systems are being fabricated for future evaluation in several diverse laboratories such as a blood bank laboratory, a small-animal laboratory (National Center for Toxicological Research, Jefferson, Arkansas), and a genetic screening laboratory (University of Michigan, Ann Arbor).

To broaden the application of CFAs, a multipurpose optical system has been developed (see Fig. 9.7). The same basic system can be used to obtain either

13. N. G. Anderson and C. A. Burtis, "GeMSAEC Fast Clinical Analyzers," p. 521 in *Clinical Biochemistry - Principles and Methods*, Walter de Gruyter, Berlin, West Germany, 1974.
14. N. G. Anderson, C. A. Burtis, and T. O. Tiffany, "Enzymology, Clinical Chemistry, and the Development of Fast Analyzers," p. 155 in *Enzymology in Medicine*, ed. by P. Blume, Academic Press, New York, 1974.
15. T. O. Tiffany, C. A. Burtis, and N. G. Anderson, "Fast Analyzers for Biochemical Analysis," in *Methods in Enzymology*, vol. 31, Academic Press, New York, 1974.
16. T. O. Tiffany, "Centrifugal Fast Analyzers in Clinical Laboratory Analysis," p. 129 in *CRC Critical Reviews in Clinical Laboratory Sciences*, The Chemical Rubber Company, Cleveland, Ohio, 1974.

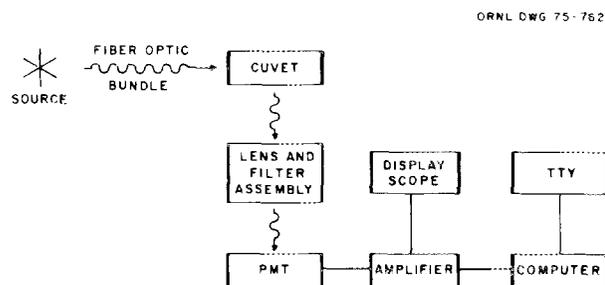


Fig. 9.7. Schematic of the multipurpose optical system developed for use with a Centrifugal Fast Analyzer.

transmission, fluorescence, chemiluminescence, or light-scattering measurements. This is achieved by combining different light sources, fiber optics (Fig. 9.8), and rotors of various designs constructed from appropriate window materials (Fig. 9.9), and by using a relative geometrical location to a photomultiplier tube.¹⁷⁻¹⁹

In addition to the miniature analyzer, a portable version is under development.²⁰ It is anticipated that the portable CFA will ultimately be a small unit that will contain both the analyzer and data system in a single cabinet. The evaluation of the second prototype of portable CFA was completed during the past year. Based on this evaluation, a third prototype was designed and is being fabricated. The new prototype (Fig. 9.10) features an improved mechanical drive and braking system to facilitate the efficiency of transfer and mixing, and a new temperature control system that utilizes a thermoelectric heat pump. The analytical module along with a microprocessor data system will be incorporated into a single cabinet.

A dedicated microprocessor data system was designed and fabricated (Fig. 9.11). The heart of the system is an Intel-8080 microprocessor chip. This chip, with about 30 additional integrated circuit chips, will make up the microcomputer that can control the analyzer unit and the data acquisition and manipulation, and can print the data and identifying information on an alphanumeric printer.

Rotors of various designs were fabricated and tested^{21,22} in a continuing effort to develop one that contains preloaded reagents and is capable of accepting, processing, and analyzing a whole-blood sample. In regard to the prepackaging of reagents, studies are

continuing in which reagents are lyophilized within the cuvettes of the rotor, followed by dynamic reconstitution at the time of analysis.²³ Stability studies indicate that some reagents are lost during the lyophilization process, after which the remaining reagents are stable for at least ten weeks. A collaborative program with one or more of the commercial reagent manufacturers was initiated in order to couple the in-house reagent technology of commercial firms with the ORNL Fast Analyzer technology.

Analytical Applications

Work continued on automating the various techniques utilized in blood banking. To date, this includes blood grouping analysis and the measurement of prothrombin times. In addition to the hematology applications, an effort was initiated to develop analytical procedures in the general area of environmental water analysis. Work also continued on the use of CFAs for genetic monitoring.

Blood grouping analysis. In the initial feasibility studies,^{1,8} the technique of blood grouping analysis using a CFA was demonstrated on an early prototype coupled to the old GeMSAEC computer system. The loading of aliquots of blood samples and antisera was performed manually. This technique has now been adapted for use with the miniature analytical system routinely operated in the clinical laboratory of the Health Division.

The use of an automated loading system²¹ to put the aliquots of whole-blood samples and antisera into their respective chambers in the rotor was a major improvement in the blood grouping procedure. Since the automatic pipettes in the loading system are used primarily to measure and dispense liquids, their use with aliquots of whole blood was a concern. Studies indicated, however, that aliquots of whole-blood samples could be measured and dispensed without encountering plugging or carry-over problems. Saline was used as the diluent instead of distilled water, which is normally used in the routine operation of the loader. No problems were encountered in the loading of the aliquots of antisera. In addition, improvements and refinements were made of the basic technique to provide better discrimination between the antigenic reactions of the weaker hemagglutinating antibodies such as anti-C(rh'), anti-D (Rh₀), and anti-E (rh''). A

17. T. O. Tiffany, J. M. Parella, W. F. Johnson, and C. A. Burtis, "Specific Protein Analysis by Light Scatter Measurement with a Miniature Centrifugal Fast Analyzer," *Clin. Chem.* **20**, 1055 (1974).

18. T. O. Tiffany, J. M. Parella, C. A. Burtis, W. F. Johnson, and C. D. Scott, "Blood Grouping with a Miniature Centrifugal Fast Analyzer," *Clin. Chem.* **20**, 1043 (1974).

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

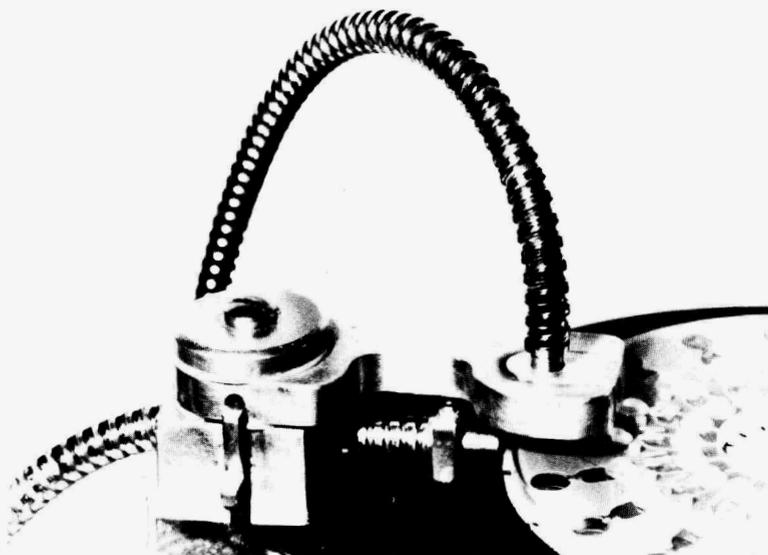
20. C. D. Scott, W. F. Johnson, L. H. Thacker, and C. A. Burtis, "A Small Battery Operated Centrifugal Fast Analyzer," *Clin. Chem.* **20**, 1003 (1974).

21. C. A. Burtis, W. F. Johnson, and J. B. Overton, "Automated Loading of Discrete, Microliter Volumes of Liquids into a Miniature Fast Analyzer," *Anal. Chem.* **46**, 786 (1974).

22. C. A. Burtis, W. F. Johnson, and T. O. Tiffany, "The Development of Rotors Having Separate Sample and Reagent Transfer Channels for Use with Centrifugal Fast Analyzers," *Anal. Lett.* **7**, 591 (1974).

23. C. A. Burtis, W. F. Johnson, J. B. Overton, T. O. Tiffany, and J. C. Mailen, "Optimization and Analytical Applications of the Technique of Dynamic Introduction of Liquids into Centrifugal Analyzers," *Clin. Chem.* **20**, 932 (1974).

A



B

ORNL PHOTO 2917-74 A

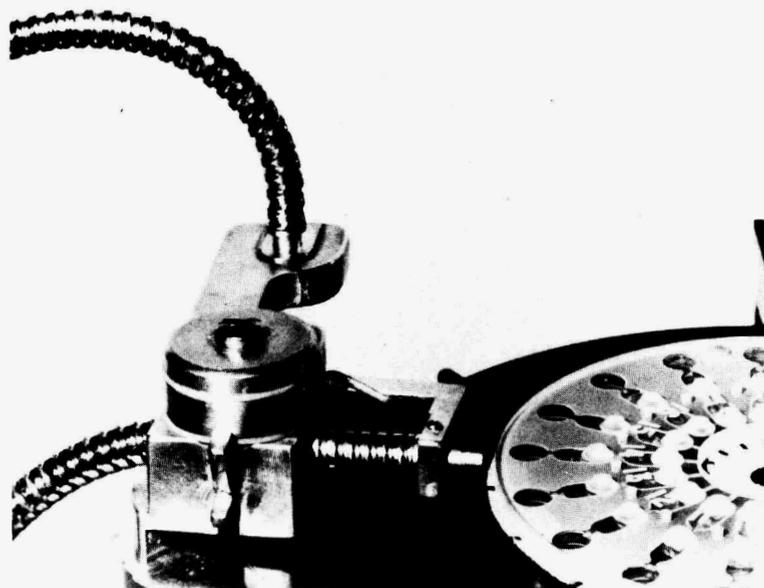


Fig. 9.8. Modification of the optical head of the Centrifugal Fast Analyzer which allows for either of two fiber optic configurations. (A) 180° orientation; (B) 90° orientation.

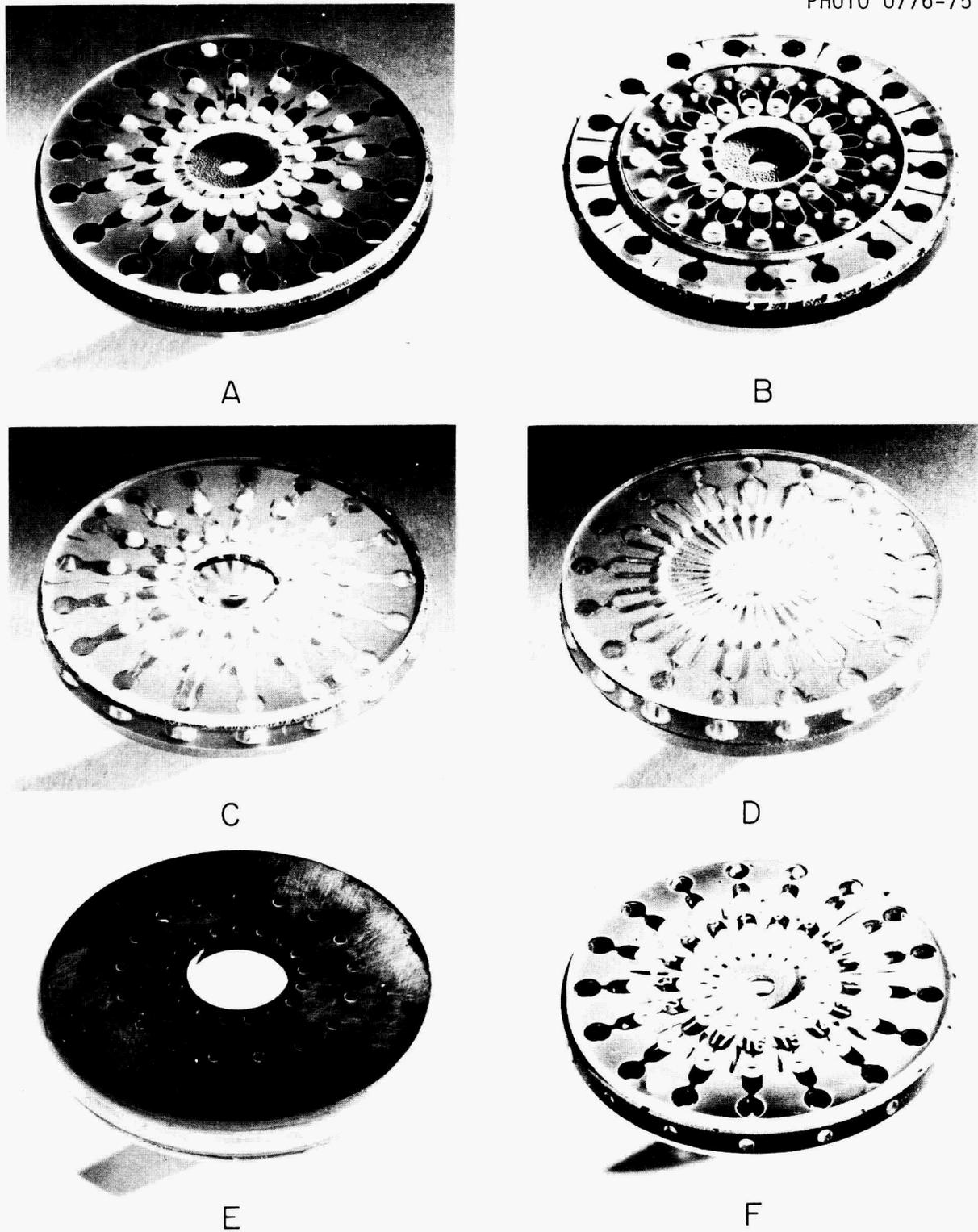


Fig. 9.9. Family of rotors designed and fabricated for use with the miniature Centrifugal Fast Analyzer. (A) General-purpose transmission rotor, body fabricated of 0.5-cm black acrylic plastic (chambers in serial array), windows fabricated of ultraviolet-transmitting (UVT) acrylic plastic; (B) general transmission rotor having quartz windows; (C) clear-body rotor, body fabricated from 0.5-cm UVT acrylic plastic, chambers in serial array, UVT windows; (D) clear-body rotor, chambers in parallel array, UVT windows; (E) clear-body rotor, black acrylic top window, UVT bottom window; (F) black-body rotor with quartz cylinders sealed into the peripheral wall of each cuvet, UVT windows.

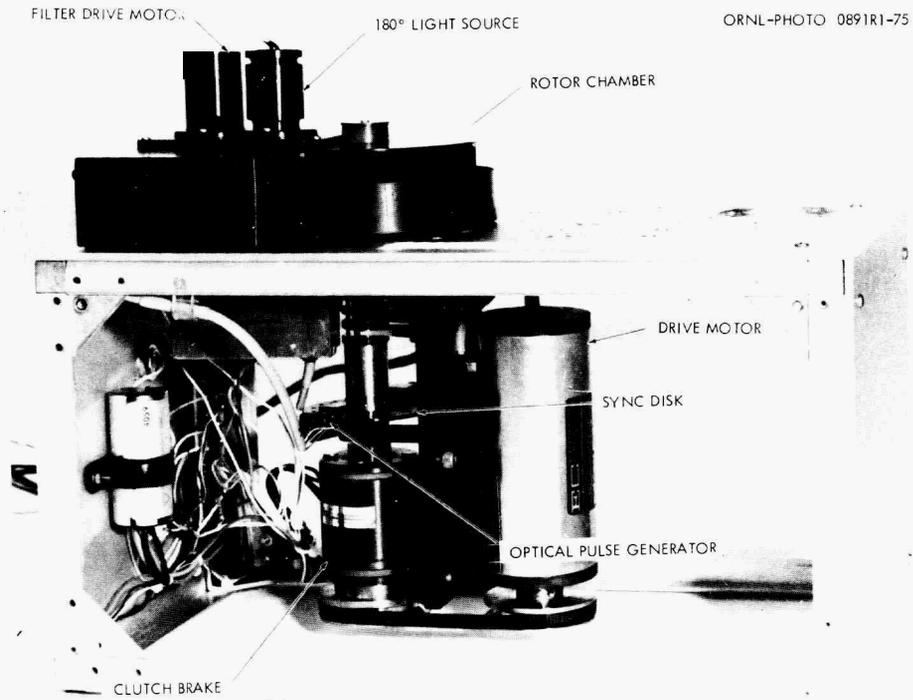


Fig. 9.10. Side view of the advanced prototype of the portable Centrifugal Fast Analyzer.

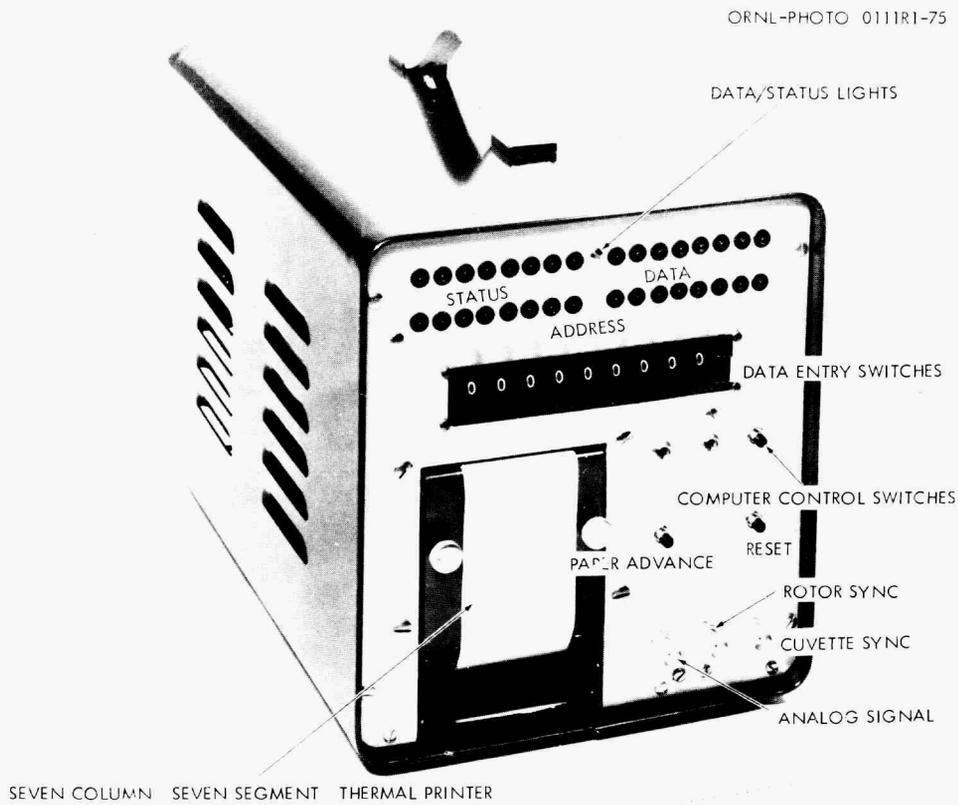


Fig. 9.11. Microprocessor data system.

study was made in which the modified procedure was compared with the manual protocols used by the medical technologists of the ORNL clinical laboratory. Equivalent results were obtained for all but three of the more than 100 samples analyzed in the study. Two of the discrepancies were due to transcription errors, while the third was a sample problem.

Protocol development. After the improved blood grouping procedure was adapted for use with the miniature analytical system, a protocol and instruction manual was written. The manual describes (1) reagent (antibodies) requirements, (2) antibody titering, (3) setup procedure, (4) operating procedure, and (5) computer programs. A copy of the manual was supplied to NIH and will accompany the analytical system that will be evaluated by an external laboratory.

Prothrombin time determination. The principle of the CFA was applied to the field of coagulation testing.²⁴ The multisample parallel-monitoring capabilities of the analyzer give it several distinct advantages over instrumentation conventionally used for clot detection. An on-board normal control plasma can be monitored simultaneously with up to 16 test plasmas. Thus the control and all test samples can be treated identically with respect to temperature, agitation, surface activation, and reagents by minimizing many of the extraneous factors that have plagued the proper control of coagulation testing. Another highly significant advantage is the small volume requirements of the analyzer; for example, less than 50 μl of plasma and 100 μl of reagent are required for the prothrombin time (PT) test.

We are evaluating the performance of the miniature CFA, the available data acquisition system, and current computer program revisions for the determination of the PT test end point. The coagulation process may be monitored either nephelometrically or turbidimetrically (Fig. 9.12) as the fibrin polymer clot forms. The modest centrifugal field generated in the small rotor ($<16 \times g$) appears to have no deleterious effect on clot formation. The precision of locating the end point is better than $\pm 5\%$, even for samples with prolonged clotting times (>60 sec). For a limited number of therapeutic samples, preliminary correlations vs a fibrin switch instrument have been satisfactory ($r > 0.9$), although CFA times are consistently longer than those

of the reference technique due to the lower operating temperature (30 vs 37°C) currently employed.

Environmental analysis. Specific environmental analyses must be adapted or developed to utilize the portable CFA. Consequently, a program was initiated to adapt or develop chemical reagents and specific methods for water analysis using the CFA. These developments include: (1) analytical procedures for phosphate, zinc, iodine, lead, and sulfate; (2) methods for other water analyses, especially for nitrite and potassium; (3) determination of arsenate in solution; and (4) determination of the catalytic effect of Tween 80 on complex formation.

Genetic monitoring. In a program funded by ERDA and conducted in collaboration with the Department of Human Genetics of the University of Michigan, Ann Arbor, we investigated kinetic spectrophotometric procedures that can be adapted to a miniature CFA for genetic monitoring of enzymes. To demonstrate the feasibility of this approach, we studied the kinetics of several glucose-6-phosphate dehydrogenase (G-6-PD) variants.

The results of the initial feasibility studies demonstrated that the A and B variants of G-6-PD can be differentiated kinetically by thermal and chemical perturbation. From such information, a simple procedure can be set up for assaying the enzymes at 40 to 45°C under two or three different reaction conditions. In this manner, changes in enzyme structure due to amino acid substitution as reflected by activity changes and aggregation could be used in a multiparameter approach to determine enzyme variants.

Transfer of Technology

One of the basic objectives of a national laboratory is to transfer developed technology into industrial, governmental, and academic sectors. Consequently, we made a concerted effort to provide the technology developed in the CFA program to interested parties. In the past year, representatives from at least 13 industrial firms, 6 governmental agencies, and 4 universities visited ORNL to discuss various aspects of our program. In addition, members of our staff presented papers at several national meetings, gave seminars at several institutions and companies, participated in workshops such as the American Society for Clinical Pathologists (ASCP), and published results in the open literature for the purpose of transferring technology. Consequently, the miniature analyzer is now under commercial development, and indications are that a prototype will be shown at the International Symposium on Clinical Chemistry to be held this summer in Toronto, Canada.

24. W. D. Bostick, M. L. Bauer, J. M. Morton, and C. A. Burtis, "Coagulation Time Determination with Automatic Multiparametric Analysis Using a Miniature Centrifugal Fast Analyzer," *Clin. Chem.* 21 (in press).

ORNL DWG 75-5219

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SAMPLES/CUVET=5 SECONDS=1

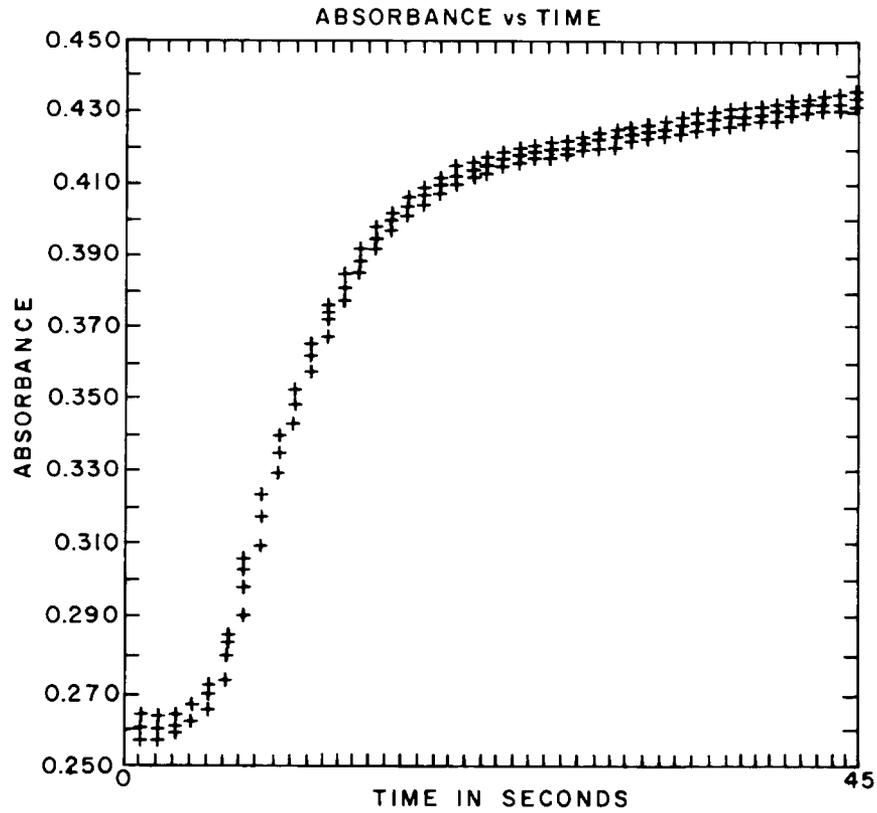


Fig. 9.12. Four replicate prothrombin time determinations as monitored by the miniature Centrifugal Fast Analyzer in the turbidimetric mode.

10. Environmental Studies

10.1 AUTOMATED ANALYSIS OF POLLUTANTS

Surface waters are becoming increasingly important in this nation as the source of water for potable and industrial water systems. Characterization of the organic constituents in surface waters assumes importance in direct proportion to the use of these waters for human consumption. Relatively little is known about the health significance of the very low concentrations (ppb) of stable organic and chloro-organic compounds found in water, although some chlorine-containing constituents have been found to be carcinogenic, mutagenic, or teratogenic.¹⁻³ Regardless of the source, whether domestic, industrial, or agricultural effluents, atmospheric washout, runoff, or by-products of natural biogeochemical systems, it is imperative that identities, quantities, and toxicological effects of the individual organic constituents and pollutants be established. Quantitative information concerning these trace compounds and the effects of treatment processes such as chlorination is essential for assessment of aquatic ecosystem effects and the ultimate effect on mankind.

High-resolution anion exchange chromatography is used as the basic separations method for analysis of trace organics in various polluted waters because of its sensitivity and capability for analyzing many low-molecular-weight refractory organics in aqueous samples.⁴⁻⁸ A routine multicomponent analytical scheme utilizing additional ion exchange chromatography, uv spectrometry, gas chromatography, and mass spectrometry is used for determination of the chemical structure of the separated unknown organic constituents.⁹

Effluents from Sewage Treatment Plants

A 98-page final report⁸ was prepared for and published by the Office of Research and Development, U.S. Environmental Protection Agency, in August 1974. As a result of this study, the following conclusions were made:

1. Over 100 refractory-organic compounds can be present in effluents from municipal sewage treatment plants at ppb levels; some of these refractory compounds are chlorinated under conditions that exist when effluents from sewage treatment plants are chlorinated.
2. High-resolution anion exchange chromatography provides a reliable and useful tool for determining

1. T. F. X. Collins and C. H. Williams, "Teratogenic Studies with 2,4,5-T and 2,4-D in the Hamster," *Bull. Environ. Contam. Toxicol.* **6**, 559 (1971).

2. C. L. Litterst and E. P. Lichtenstein, "Effects and Interactions of Environmental Chemicals on Human Cells in Tissue Culture," *Arch. Environ. Health* **22**, 454 (1971).

3. R. S. Pardini, "Polychlorinated Biphenyls (PCB): Effect on Mitochondrial Enzyme Systems," *Bull. Environ. Contam. Toxicol.* **6**, 539 (1971).

4. S. Katz, W. W. Pitt, Jr., C. D. Scott, and A. A. Rosen, "The Determination of Stable Organic Compounds in Waste Effluents at Microgram per Liter Levels by Automatic High-Resolution Ion Exchange Chromatography," *Water Res.* **6**, 1029 (1972).

5. R. L. Jolley, W. W. Pitt, Jr., and C. D. Scott, "High-Resolution Analyses of Refractory Organic Constituents in Aqueous Waste Effluents," pp. 247-52 in *Realism in Environmental Testing and Control (Proceedings of the 19th Annual Technical Meeting, Institute of Environmental Sciences, Anaheim, California, April 2-5, 1973)*.

6. R. L. Jolley, *Chlorination Effects on Organic Constituents in Effluents from Domestic Sanitary Sewage Treatment Plants*, ORNL-TM-4290 (October 1973).

7. R. L. Jolley, W. W. Pitt, Jr., C. D. Scott, and M. D. McBride, "Determination of Trace Organic Contaminants in Natural Waters by High-Resolution Liquid Chromatography," pp. 397-412 in *Proceedings of the First Annual NSF Trace Contaminants Conference, Oak Ridge National Laboratory, Oak Ridge, August 8-10, 1973*.

8. W. W. Pitt, R. L. Jolley, and S. Katz, *Automated Analysis of Individual Refractory Organics in Polluted Water*, EPA 660/2-74-076, Office of Research and Development, U.S. Environmental Protection Agency (August 1974).

9. R. L. Jolley, S. Katz, J. E. Mrochek, W. W. Pitt, and W. T. Rainey, "A Multicomponent Analytical Procedure for Organics in Complex, Dilute Aqueous Solutions," *Chem. Technol.*, p. 312 (May 1975).

refractory organic compounds present at low levels in sewage effluents and other polluted waters.

3. In addition to uv-absorbing compounds, numerous other compounds can be detected by sulfatoceric acid oxidimetry.
4. The detection of sources of pollution, the testing of the effectiveness of sewage treatment steps including possible tertiary steps, and the determination of the ultimate disposition of pollutants are obvious end uses of the high-resolution anion exchange chromatographic systems.

This research program was limited to the adaptation of existing analytical systems for use in the determination of refractory-organic compounds in polluted waters with a minimum of instrumental development. The scope of the program did not include exploiting the capabilities of the analyzers for detecting sources of pollution, testing the effectiveness of sewage treatment plants, determining the ultimate fate of pollutants, or identifying positively all of the separated organic constituents.

Significant expansion is recommended of the use of high-resolution liquid chromatographs with uv photometers and cerate-oxidative monitors for determining refractory-organic compounds in industrial and other polluted waters. This can be accomplished either by fabricating additional UV-Analyzers developed at ORNL or by modifying commercially available high-pressure chromatographs. A vigorous effort should be continued to determine the identities of the residual, stable organic compounds being discharged into surface waters. Also, potential hazards of these compounds, particularly those that are chlorinated, should be evaluated. High-resolution analyzers have been developed to the point where they could be used by appropriate agencies to determine the sources of pollution, the effectiveness of sewage treatments, and the fate of organic pollutants — all on a molecular level. This effort should be closely coordinated with the analytical development program to take advantage of improvements as they are made and of “feedback” information relating to problem areas that would lead to necessary modifications of the instruments.

A total of 56 organic compounds were identified in primary sewage treatment plant effluents (Table 10.1), and 13 organic compounds were identified in secondary effluents (Table 10.2). Forty-six of the constituents identified in primary effluents and five in secondary effluents were quantified based on a flame ionization detector (FID) response. Many of the constituents do not absorb uv light, which was the previous mode of

quantitation. In addition to the identified compounds, more than 100 mass spectra and gas chromatography retention values were obtained of unknown compounds found in chromatographic fractions of both primary and secondary sewage treatment plant effluents.

Natural Waters

The identification and quantitation of trace organics in various natural waters are being studied by using high-resolution anion exchange chromatography. Water samples from five of the six sites chosen for this study¹⁰ were examined. The concentrations of the identified constituents in the original water samples have been estimated and are given in Table 10.3. Nineteen additional unknowns were characterized with respect to gas chromatographic and mass spectral properties.

Effluents from Coal-Processing Plants

Because of the high probability of coal becoming the major energy source in the near future and the consequent utilization of coal for production of gaseous and liquid fuels, two coal-liquefaction plant effluents of possible environmental concern were examined. These aqueous samples were from: (1) the product separator, sample 12131 [dissolved organic carbon (DOC), av 10,500 $\mu\text{g/ml}$; pH, 9.0]; (2) the dryer-stage first off-gas scrubber, sample 12132 (DOC, av 140 $\mu\text{g/ml}$; pH, 2.8). Both samples were extracted with methylene chloride, and the extracts were examined by gas chromatography—mass spectrometry. The extract of the product-separator sample contained a complex mixture of a large number of compounds. Mass spectra were obtained for 15 constituents, of which phenol, three cresols, three dimethylphenols, and xylene were identified. In the less complex extract of the off-gas scrubber sample, two major and several minor constituents were detected by gas chromatography; one was identified as dioctyl phthalate by mass spectrometry.

Analytical-scale high-resolution chromatography of both samples revealed numerous uv-absorbing constituents and cerate oxidizable compounds. Over 80 uv-absorbing constituents were separated from the product separator sample in a preparative-scale chromatographic run (Fig. 10.1). Six of the separated compounds have been identified by gas chromatographic and mass spectral properties of the trimethylsilyl derivatives of the compounds and were quantified based on FID response (Table 10.4). Several unknown constituents

10. Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1974, ORNL-4966.

Table 10.1. Soluble organic constituents in primary domestic sewage

Constituent ^a	Identification method ^b	Concentration ^c (ppb)
Carbohydrates		
Galactose ^d	AC, GC	
Glucose ^d	AC, GC	
Maltose	AC, GC	0.5
Polyols		
Erythritol	AC, GC, MS	5
Ethylene glycol	AC, GC, MS	3
Galacitol	AC, GC, MS	2
Glycerine ^e	AC, GC, MS	15--19
Aliphatic organic acids		
3-Deoxyarabinohehexonic acid	MS	7
3-Deoxyerythropentonic acid	MS	4
2-Deoxyglyceric acid	MS	7
2,5-Dideoxypentonic acid ^f	MS	6
3,4-Dideoxypentonic acid	MS	13
2-Deoxytetronic acid	MS	6
4-Deoxytetronic acid	MS	6
Glyceric acid	MS	5
4-Hydroxybutyric acid	GC, MS	6
2-Hydroxyisobutyric acid	GC, MS	4
Oxalic acid	AC, GC, MS	2
Quinic acid ^f	MS	50
Ribonic acid	MS	4
Succinic acid	AC, GC, MS	24
Aromatic organic acids		
Benzoic acid ^e	AC, GC, MS	3
2-Hydroxybenzoic acid ^e	AC, GC, MS	2, 7
3-Hydroxybenzoic acid ^d	AC, GC, MS	7, 40
4-Hydroxybenzoic acid ^d	AC, GC	1
4-Hydroxyphenylacetic acid ^e	AC, UV, GC, MS	16--52, 190
3-Hydroxyphenylhydraacrylic acid	AC, UV, GC, MS	10--22
3-Hydroxyphenylpropionic acid ^d	AC, GC, MS	6, 20
Phenylacetic acid	AC, GC	10
<i>o</i> -Phthalic acid ^g	AC, UV, MS	200
Fatty acids		
Palmitic acid	GC, MS	6, 12
Amino acids		
Phenylalanine	AC, GC, MS	50, 90
Tyrosine	AC, GC, MS	34
Amides		
Urea	AC, GC, MS	16--34
Phenolic compounds		
<i>p</i> -Cresol	AC, GC, MS	20, 29
Phenol	AC, GC, MS	6, 12
Indoles		
3-Hydroxyindole	MS	2
Indican	AC, GC, F	1, 2
Pyridine derivatives		
<i>N</i> ¹ -Methyl-2-pyridone-5-carboxamide ^e	AC, CC, UV, GC	20, 25
<i>N</i> ¹ -Methyl-4-pyridone-3-carboxamide ^d	AC, UV, GC	10, 14
Purine derivatives		
Adenosine	AC, CC, UV, GC, MS	13
Caffeine ^e	AC, CC, GC, MS	10, 29--46
1,7-Dimethylxanthine ^d	AC, CC	

Table 10.1. (continued)

Constituent ^a	Identification method ^b	Concentration ^c (ppb)
Guanosine ^e	AC, CC, UV, GC, MS	4–28, <i>50</i>
Hypoxanthine ^e	AC, GC, MS	12–42, <i>25</i>
Inosine ^e	AC, CC, UV, GC, MS	11–23, <i>50</i>
1-Methylxanthine ^d	AC, CC, UV	<i>70</i>
3-Methylxanthine ^d	AC, CC	
7-Methylxanthine ^e	AC, CC, GC	2, <i>90</i>
Theobromine ^d	AC, CC	
Uric acid ^d	AC, GC, MS	<i>20</i>
Xanthine ^e	AC, CC, UV, GC, MS	2–7, <i>70</i>
Pyrimidine derivatives		
5-Acetylamino-6-amino-3-methyluracil ^d	AC, CC, UV, GC	<i>140</i>
Orotic acid ^e	AC, UV, GC, MS	2, <i>5</i>
Thymine ^e	AC, CC, GC, MS	7, 9–28
Uracil ^e	AC, CC, UV, GC, MS	16–58, <i>40</i>

^aAll constituents were identified in chlorinated effluents except those designated otherwise.

^bAC – anion exchange chromatography; CC – cation exchange chromatography; UV – ultraviolet spectroscopy; GC – gas chromatography on two columns; MS – mass spectrometry; F – fluorometry.

^cBased on ultraviolet absorbance during AC (i.e., values in italics), or on flame ionization detector response during GC.

^dIdentified in unchlorinated effluent.

^eIdentified in both unchlorinated and chlorinated effluents.

^fNo reference spectra available. Structure deduced from mass spectra analysis.

^gIdentified in Mill Creek Sewage Plant effluent.

Table 10.2. Soluble organic constituents in secondary domestic sewage

Constituent ^a	Identification method ^b	Concentration ^c (ppb)
Polyols		
Glycerine	AC, GC, UV	4
Aliphatic organic acids		
Succinic acid	AC, MS	4
Phenolic compounds		
Catechol	MS	1
<i>p</i> -Cresol	AC, GC, MS	20, <i>90</i>
Indols		
3-Hydroxyindole	MS	2
Indole-3-acetic acid	MS	13
Purine derivatives		
1,7-Dimethylxanthine	AC, CC, UV	<i>6</i>
Inosine	AC, CC, UV	<i>20</i>
1-Methylinosine	AC, CC, UV	<i>80</i>
1-Methylxanthine	AC, GC	<i>6</i>
7-Methylxanthine	AC, CC, UV	<i>5</i>
Pyrimidine derivatives		
5-Acetylamino-6-amino-3-methyluracil	AC, CC, UV	<i>30</i>
Uracil	AC, CC, UV, MS	16, <i>30</i>

^aAll constituents were identified in unchlorinated effluent.

^bAC – anion exchange chromatography; CC – cation exchange chromatography; GC – gas chromatography; UV – ultraviolet spectroscopy; MS – mass spectrometry.

^cBased on ultraviolet absorbance during AC (i.e., values in italics), or on flame ionization detector response during GC.

Table 10.3. Soluble organic constituents in natural waters

Constituent ^a	Identification method ^b	Concentration (ppb)
Polyol derivatives		
Diethylene glycol (1)	AC, MS	1
Ethylene glycol (1)	AC, MS	20
Glycerine (1, 2, 3, 4, 5)	AC, GC, MS	1–20
Inositol (1, 2, 3, 4, 5)	GC, MS	0.4–1.5
Mannitol (5)	AC, GC, MS	2
Methyl- α -D-glucopyranoside (4)	AC, GC, MS	30
Methyl- β -D-glucopyranoside (4)	AC, GC, MS	3
O-Methylinositol (1, 2, 3, 4, 5)	GC, MS	0.3–10
Xylitol (5)	AC, GC, MS	1
Carbohydrates		
Sucrose (1, 5)	AC, GC, MS	2
Fatty acids		
Linoleic acid (1, 5)	GC, MS	0.7–1.2
Oleic acid (1, 5)	GC, MS	0.7–1.6
Palmitic acid (1, 5)	GC, MS	0.3–0.4
Stearic acid (1)	GC, MS	0.5
Amino acids		
Glycine (1)	AC, GC, MS	2
Phenolic compounds		
<i>p</i> -Cresol (3)	AC, GC, MS	7
Nitrogenous compounds		
α, α' -Dipyridyl (4)	MS	4
Urea (1, 2)	AC, GC, MS	>4

^aConstituents were identified in samples taken from sites designated by the numbers in parentheses: (1) Lake Marion, (2) Fort Loudoun Lake, (3) Holston River, (4) Mississippi River, (5) Watts Bar Lake.

^bAC – anion exchange chromatography; CC – cation exchange chromatography; UV – ultraviolet spectroscopy; GC – gas chromatography; MS – mass spectrometry.

Table 10.4. Soluble organic constituents in the aqueous product separator sample from a coal–char oil conversion plant

Constituent	Concentration (mg/liter)			
	FID ^a	Enzyme ^b	Preparative AC ^c	Analytical AC ^d
Catechol	660	560	3600	2000
3-Methylcatechol	170			
4-Methylcatechol	110			
Orcinol	120		380	500
Resorcinol	220		790	1000
2-Methylresorcinol	14		100	10–15

^aBased on flame ionization detector response during gas chromatography.

^bAnalyzed by B. Z. Egan using a catechol specific enzyme technique.

^cBased on the uv absorbance of the preparative-scale chromatographic peak.

^dBased on the uv absorbance of the analytical-scale chromatographic peak.

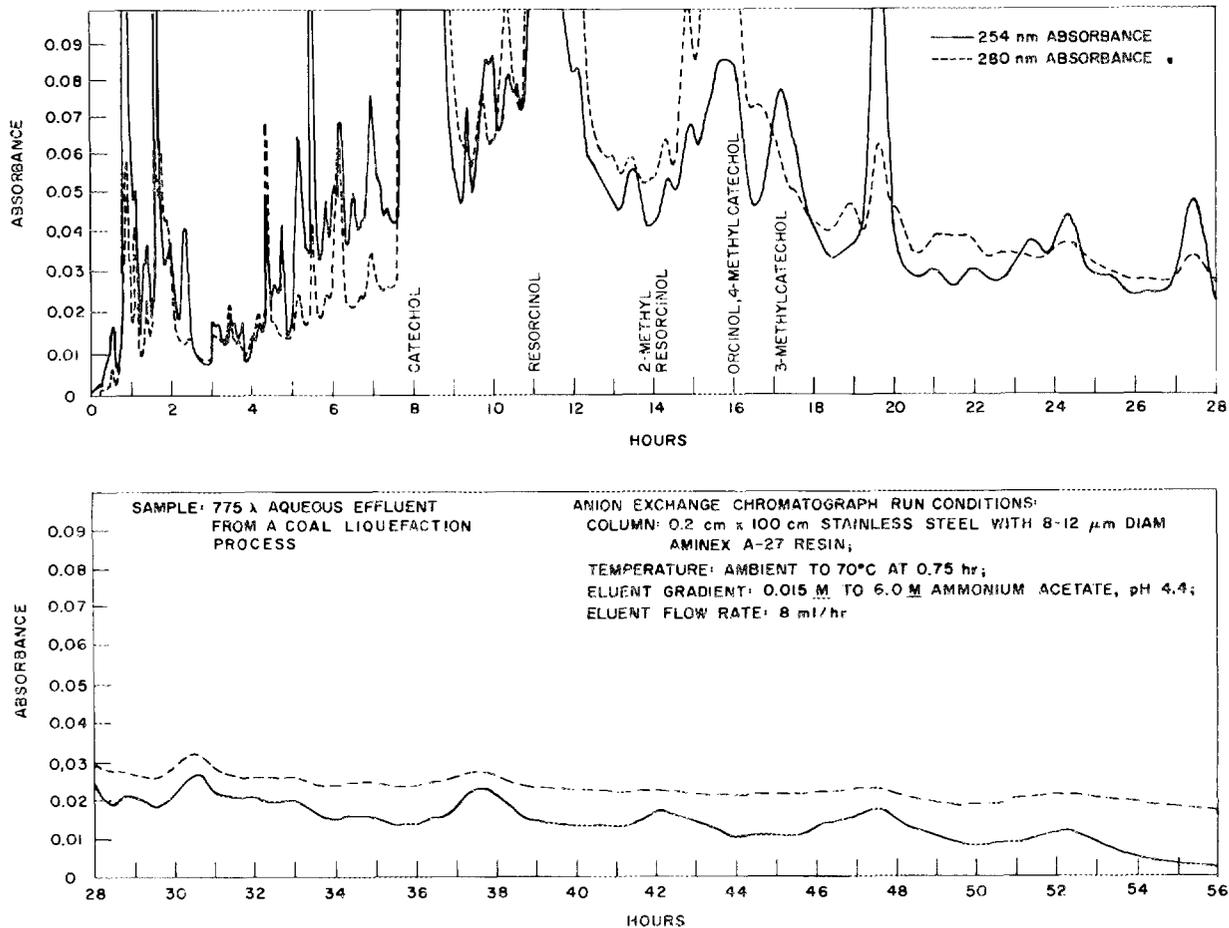


Fig. 10.1. Chromatogram of uv-absorbing constituents in the product separator sample (sample 12131) of a coal-char oil processing plant.

were also characterized with respect to molecular weight, mass spectra, and gas and liquid chromatographic elution characteristics.

10.2 ENVIRONMENTAL EFFECTS OF ANTIFOULANTS

In contemporary technology, chlorine is the principal biocide for removal of biological surface films in the cooling systems of electrical power-producing plants.¹¹ Removal of films is required to maintain a high production efficiency. Chlorination of waters containing low concentrations of organics with ppm chlorine concentrations may result in the formation of chlorine-containing organic compounds.^{6,12} Consequently, the practice of chlorinating cooling waters is being evaluated with respect to the possible formation of chlorinated organics. The methodology developed with proc-

ess effluents for identification of chlorinated organic compounds and for determination of biotoxicity is being applied in this investigation.¹³⁻¹⁵

11. J. E. Draley, *The Treatment of Cooling Waters with Chlorine*, ANL/ES-12 (February 1972).

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

13. C. D. Scott et al., *Experimental Engineering Sect. Semiannu. Progr. Rep. Mar. 1 to Aug. 31, 1974*, ORNL-TM-4777 (July 1975).

14. C. W. Gehrs, L. D. Eyman, R. L. Jolley, and J. F. Thompson, "Effects of Stable Chlorine-Containing Organics on Aquatic Environments," *Nature* **249**, 675 (1974).

15. C. W. Gehrs and R. L. Jolley, "Chlorine Containing Stable Organics: New Compounds of Environmental Concern," *Proceedings of the 19th Congress of the International Association of Limnology, Winnipeg, Manitoba, August 22-29, 1974* (in press).

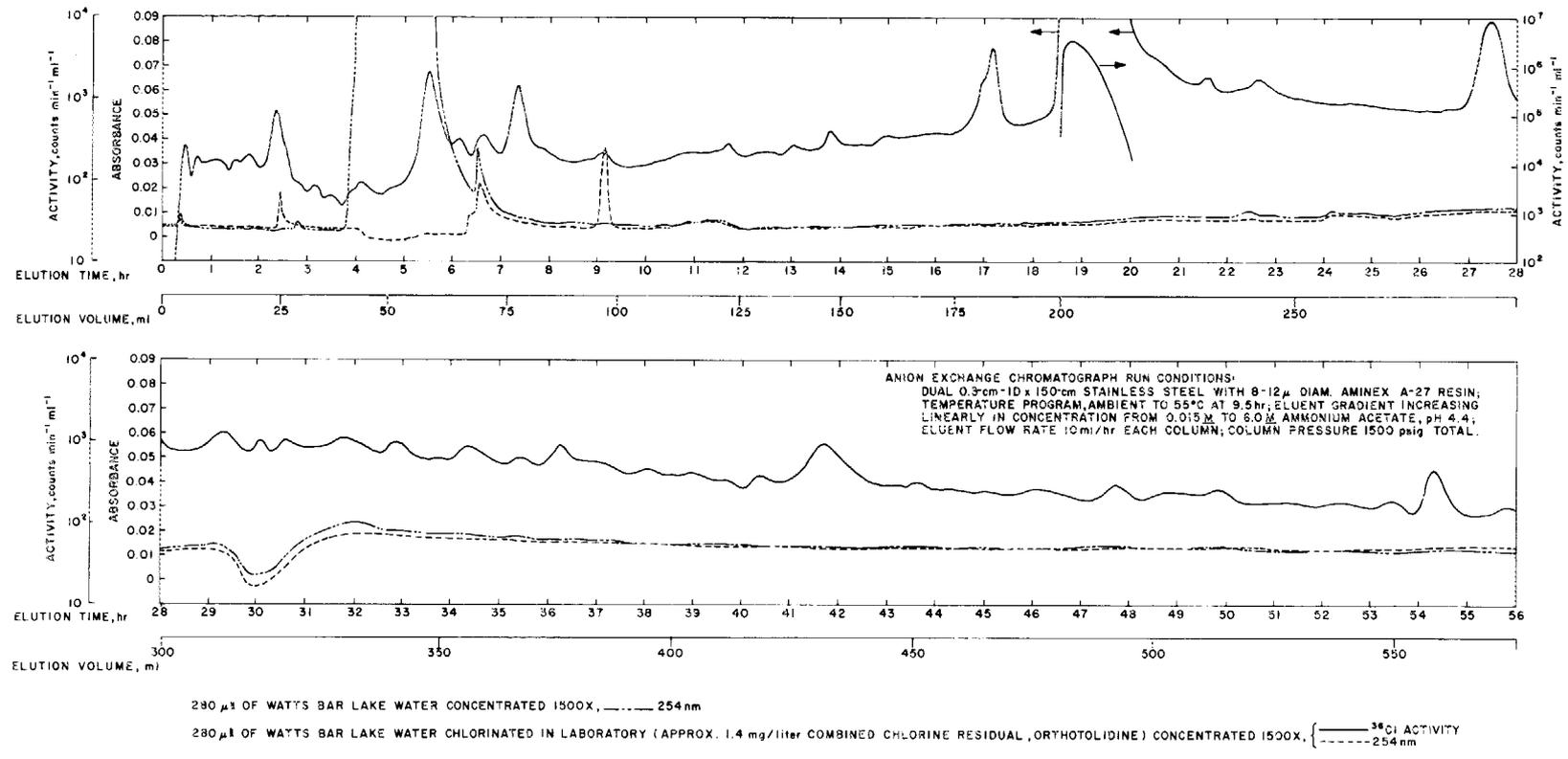


Fig. 10.2. Chromatogram showing both ³⁶Cl-tagged chlorine-containing and uv-absorbing constituents in a sample of Kingston Steam Plant cooling water chlorinated in the laboratory. A chromatogram of the uv-absorbing constituents in unchlorinated cooling water is included for comparison.

Over 50 chlorine-containing organic constituents were separated from a sample of Watts Bar Lake water that had been chlorinated to a 0.5-ppm chlorine residual. The constituents were separated and detected using the coupled ^{36}Cl tracer--high-resolution chromatographic procedure.^{6,16} The radioactivity chromatogram was quite similar to that obtained for effluents from a

secondary sewage treatment plant which had been chlorinated in a like manner (Fig. 10.2).

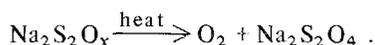
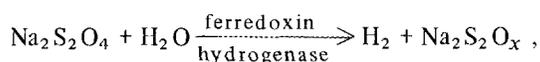
After a detailed examination of the experimental results, the major conclusion was that the yield of chlorination associated with chloro-organics is about 0.5% of the chlorine dosage for reaction conditions similar to those at the Kingston Steam Plant. With an estimated 50,000 to 100,000 tons of chlorine being used annually in cooling waters, several hundred tons of chlorinated organics are produced annually by chlorination antifoulant treatment of cooling systems, even at the low-reaction yield determined in this study. As the national production of electric power increases, this quantity can be expected to increase proportionately.

16. R. L. Jolley, "Determination of Chlorine-Containing Organics in Chlorinated Sewage Effluents by Coupled ^{36}Cl Trace--High-Resolution Chromatography," *Environ. Lett.* 7, 321 (1974).

11. Biochemical Engineering

11.1 ENZYME-CATALYZED PRODUCTION OF HYDROGEN

A previous report¹ discussed a cyclic process for producing hydrogen (and oxygen) from water, using sodium dithionite as a reducing agent and ferredoxin and hydrogenase as catalysts. This process involves two reactions:



However, a problem has been encountered in the thermal regeneration of the dithionite, namely, that heating the higher oxides, such as $\text{Na}_2\text{S}_2\text{O}_5$ and $\text{Na}_2\text{S}_2\text{O}_6$, produces SO_2 . Of several possible alternative reductants tried, sodium pyruvate appeared to be the most promising. Therefore, the rate of hydrogen production was measured as a function of pyruvate concentration, solution pH, and temperature, and the results were compared with those obtained with sodium dithionite substrate.

As with sodium dithionite substrate, hydrogen production is inhibited at higher pyruvate concentrations.² The optimum pH for hydrogen production rate is 6.5 to 6.7, which is similar to that observed with sodium dithionite substrate (Fig. 11.1).

The initial hydrogen production rate increased with increasing temperature over the range 25 to 50°C; however, after about 1 hr at 50°C, the rate decreased considerably. Similar behavior was observed for dithionite, indicating possible enzyme degradation at 50°C. However, the data obtained from initial rates can be

correlated in a plot of hydrogen production rate vs $1/T$ (Fig. 11.2). The apparent activation energy (11.5 to 12.5 kcal/mole) obtained from such a plot is similar for both dithionite and pyruvate substrates.

Under optimum conditions with a fixed amount of enzyme, the initial rate of hydrogen production with dithionite was greater than that with pyruvate. However, the maximum amount of hydrogen obtainable from dithionite was reached after about 2 hr; the yield was 0.21 mole of H_2 per mole of dithionite. The pyruvate, on the other hand, continued to produce

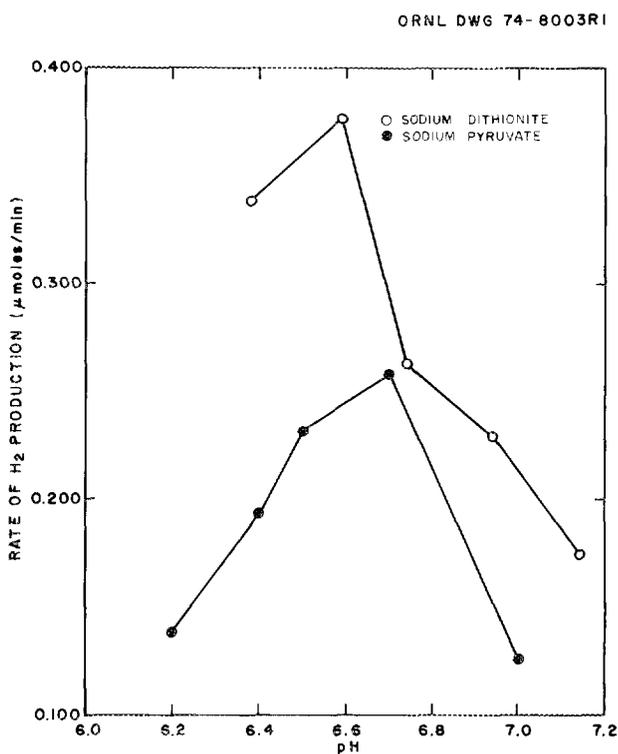


Fig. 11.1. Optimum pH for hydrogen production compared for sodium dithionite and sodium pyruvate.

1. Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1974, ORNL-4966, pp. 47-48.

2. C. D. Scott et al., Experimental Engineering Sect. Semi-annu. Progr. Rep. Mar. 1, 1974, to Aug. 31, 1974, ORNL-TM-4777 (July 1975).

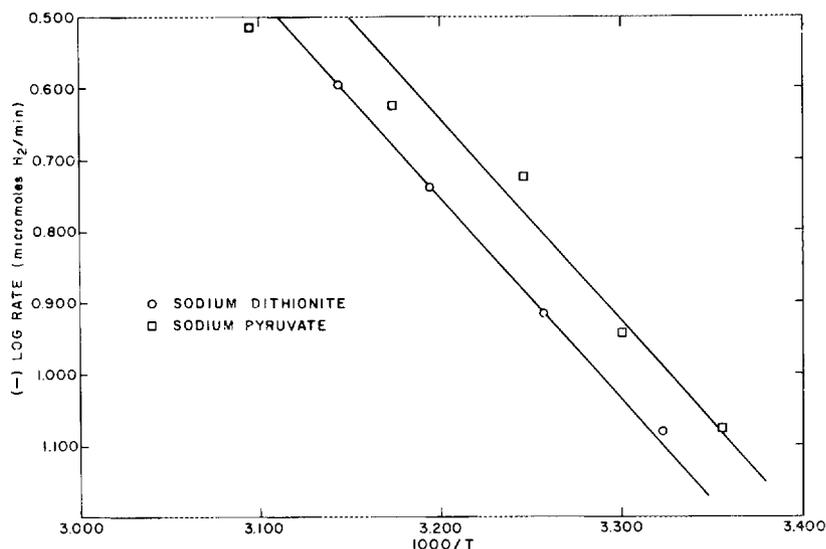


Fig. 11.2. Effect of temperature on hydrogen production rate.

hydrogen even after 5 hr, reaching a final yield near 0.91 mole of H_2 per mole of pyruvate (Fig. 11.3). In either case, the initial rate of hydrogen production can be increased considerably by increasing the enzyme concentration.

During this report period we investigated the possibility of immobilizing the ferredoxin-hydrogenase enzyme system,³ using a cell extract containing both ferredoxin and hydrogenase without further separation or purification. In various experiments we succeeded in trapping the enzymes in polyacrylamide gels by inducing polymerization of the monomer in the presence of the enzyme extract. Quantitative comparison of the activity of the gel-entrapped enzymes with that of the free enzymes is complicated by the difficulty of measuring the enzyme concentration in the gel. Nevertheless, none of the gels we prepared appeared to give more than 1% of the hydrogen production rate observed for the free enzyme. However, the immobilized enzymes remained active for several days; the hydrogen production rates obtained by addition of fresh dithionite after several days compared favorably with those obtained initially with the freshly prepared gels.

3. C. D. Scott et al., *Experimental Engineering Sect. Semi-annu. Progr. Rep. Sept. 1, 1974, to Mar. 31, 1975*, ORNL-TM-4961 (in press).

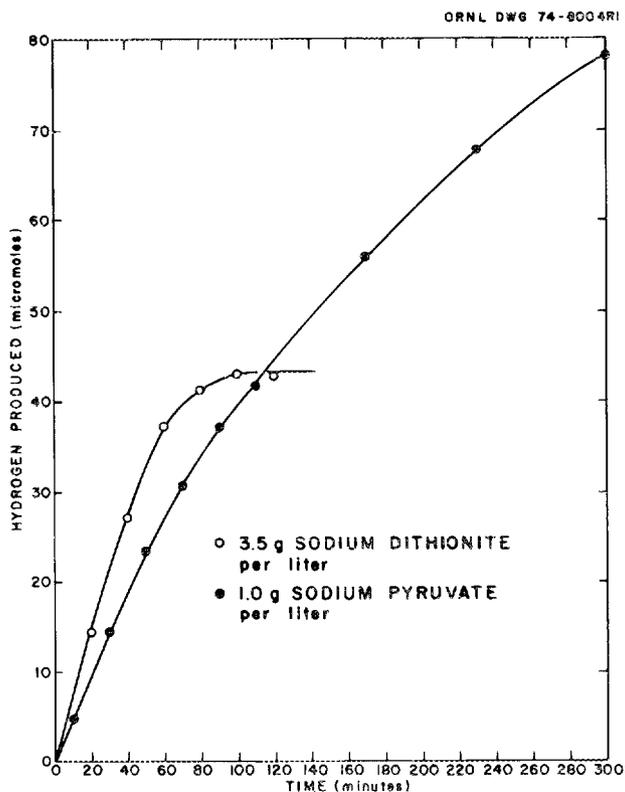


Fig. 11.3. Comparison of hydrogen production by sodium dithionite and sodium pyruvate. Solution, 0.05 M phosphate; pH, 6.6; temperature, 40°C.

11.2 BIOREACTOR DEVELOPMENT

Three types of reactors are being studied as potential bioreactors: (1) continuous stirred-tank reactor (CSTR), (2) packed-bed reactor (PBR), and (3) tapered fluidized-bed reactor (TFBR).

Continuous Stirred-Tank Reactor

Since an activated sludge unit, a CSTR, is the system most commonly used today to process polluted waters, it was chosen as our baseline processing scheme for the investigation of phenol removal from waste streams. A small, activated sludge unit with a capacity of approximately 3 liters was assembled with a Lucite reactor and a standard Imhoff cone as the settling tank (1-liter volume). In this system, an air lift recycles settled sludge from the bottom of the settling cone to the reactor, and excess sludge is removed manually. The air diffuser is a stainless steel pipe, with several small holes in line longitudinally, which is inserted through the wall of the reactor so that it extends across the entire width of the reactor. The air bubbling from this pipe aerates and mixes the fluid in the reactor.

A typical growth and pH-vs-time curve for *Trichosporon cutaneum* is shown in Fig. 11.4. The pH was recorded continuously and adjusted manually. Note that the slope of the pH-vs-time curves increases as the cell concentration increases. To date, the maximum phenol utilization has been 0.1 millimole of phenol per liter of reactor volume per minute.

As indicated by the curves in Fig. 11.4, a significant variation in pH occurs during active growth of the

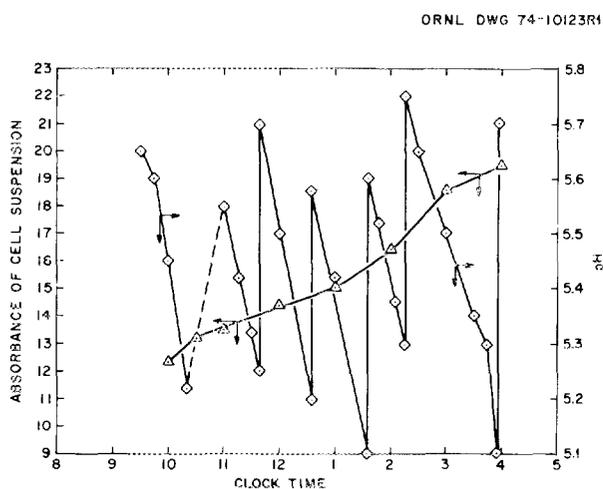


Fig. 11.4. Typical growth curve and pH cycling of CSTR without an automatic pH controller.

yeast, making pH control difficult. To alleviate this situation, a pH controller was added to the activated sludge unit. This unit worked satisfactorily, eliminating the need for manual pH adjustment. Because the mixture became acid during growth, ammonium hydroxide was used to adjust the pH via the controller.

The CSTR operates on a continuous feed basis. For our preliminary work, growth medium (minus thiamine) plus phenol at a concentration of 0.05 M was used as the feed solution. The volumetric flow rate of the feed was adjusted so that the phenol concentration in the reactor did not exceed 0.005 M. With a reactor volume of 2.25 liters, we were able to maintain flow rates of 75 ml/hr. Unfortunately, the yeast did not form a good settleable sludge, and even with the settling cone, much was lost in the effluent. With a flow rate of 50 ml/hr, all phenol was removed from the feed, and the yeast growth was sufficiently rapid to maintain an essentially constant biomass in the reactor.

Packed-Bed Reactor Studies

As an adjunct to the CSTR studies, a PBR was set up as a test reactor for phenol removal. The 1-in.-ID by 3-ft tubular reactor was packed with 1/4-in. Berl saddles and seeded by filling it with a suspension of yeast in nutrient solution. Air and feed solution containing 500 ppm of phenol passed upward through the column. The feed pump was initially adjusted to deliver approximately 45 ml/hr, while the phenol concentration in the effluent was monitored intermittently to check for phenol breakthrough. The feed rate was increased daily until breakthrough occurred. As the biomass increased, the maximum feed rate increased until, ultimately, a feed rate of 240 ml/hr could be maintained without breakthrough. The air flow rate was maintained at 440 ml/min.

Start-up and routine operation of this reactor have been trouble-free. Start-up proceeded smoothly, with growth plus attachment exceeding washout. Thus, a visible, stable biomass quickly formed at the lower end of the reactor and slowly increased in height until it filled the reactor. Yet, significant occlusion of packing voids or general biomass fouling did not occur. The shear developed by the high flow rate of air through the reactor should help to minimize the occlusion by excessive biomass.

Air distribution throughout the reactor is fairly good. A cylindrical glass frit is used to sparge air into the bottom of the column; however, the packing appears to augment the rapid coalescence of the small bubbles. The problems involving air-liquid contact and dissolved-

oxygen availability obviously demand considerable attention. An oxygen probe will be used to aid in this investigation.

Tapered Fluidized-Bed Reactor

A TFBR is a special adaptation of fluidized-bed technology which appears to be especially suited for bioreactor operation. A TFBR can be used as a bioreactor for viable bacteria or yeast systems where the host is either self-attached, chemically bonded, or entrapped, and also for any type of immobilized enzymatic system. The use of a TFBR as a bioreactor for denitrification of nitrate in waste streams was investigated. Using anthracite coal as the bed material, we obtained a maximum removal rate of 5 moles of NO_3^- per hour per liter (volume as settled packing volume), based on a feed stream concentration of approximately 9 moles of NO_3^- per hour and a residence time of 1.2 hr.

The use of contained microorganisms for chemical conversion of a feed stream to produce useful products or to eliminate pollutants can be accomplished by the use of a TFBR as a bioreactor. A TFBR has an included angle of 1 to 4°; this degree of taper provides a decreasing linear velocity with increasing column height. Such an arrangement gives a stabilizing effect because the top of the bed is more dense, thereby eliminating any tendency for the bed to spout, even at high flow rates, where the bed is very dilute (90% void volume). Thus, the TFBR has desirable hydraulic characteristics that allow it to operate over a wide range of flow rates in a stable fluid-bed mode.

The TFBR also has a number of attractive biological characteristics. The micromovement of the stable fluid will grind off layers of bound bacteria which, under normal fixed-bed operation, would bridge from particle to particle, thereby filling the void, decreasing the available flow area (50 to 80% void volume at typical fluidization flow rates), and restricting the availability of all of the bound bacteria to the feed stream chemicals. Many fluidizable materials can be found that are compatible with microorganisms. Bacterial compatibility is linked to a number of physical and chemical properties, such as size, porosity, surface texture, chemical positioning, and solubility. The TFBR is a completely closed system; thus, air can be easily excluded for strictly anaerobic operation. Seeding the bed with a bacterial suspension by recycle is easily accomplished.

The TFBR equipment (Fig. 11.5) consists of (1) a tapered glass column 42 in. long, 1 in. in diameter at

the bottom end, and 3 in. in diameter at the top end; (2) a feed tank and feed pump; and (3) a top gas-liquid separator followed by a solid-liquid separator. A tapered fluidized-bed section was fabricated from a 3-in. section of glass pipe by forming on a tapered carbon mandrel. The total length of the reactor is 42 in.; its capacity is 2349 ml. The angle of the taper is 0.68° from the pipe center (i.e., an included angle of 1.36°). The gas at the top of the fluid bed is water sealed and is vented through a wet-test meter for volumetric measurement. Solids that overflow from the fluid bed are recovered in settling chambers which can be drained when necessary.

Design Equations for Biological Reactions

For an ideal plug flow reactor, the design equation is

$$t = S_0 \int_0^X \frac{dX}{(-r)}, \quad (1)$$

where X is the percent conversion, S_0 is the substrate concentration in the feed, and t is the residence time. For Michaelis-Menten (M-M) kinetics, the reaction rate is

$$(-r) = \frac{V_m S_0 (1 - X)}{K_m + S_0 (1 - X)}. \quad (2)$$

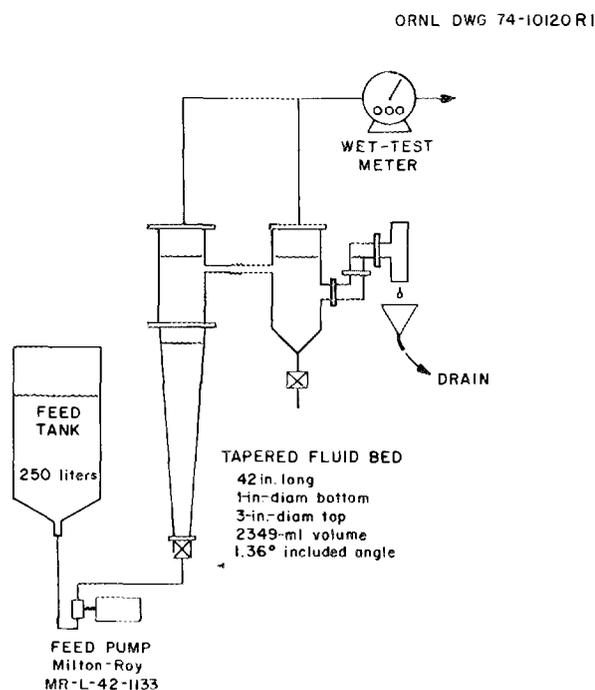


Fig. 11.5. Tapered fluidized-bed bioreactor.

Thus when M-M kinetics are applicable, the design equation becomes

$$\frac{t}{X} = \frac{S_0}{V_m} - \frac{K_m}{V_m} \cdot \frac{\ln(1-X)}{X} \quad (3)$$

For a product-inhibited reaction, the rate equation is

$$(-r) = \frac{V_m S_0 (1-X)}{K_m + S_0(1-X) + (K_m/K_i)S_0 X} \quad (4)$$

and the design equation becomes

$$\frac{t}{X} = \frac{S_0}{V_m} \left[1 - \frac{K_m}{K_i} \right] - \frac{K_m}{V_m} \left[1 + \frac{S_0}{K_i} \right] \frac{\ln(1-X)}{X} \quad (5)$$

In either case, plotting t/X vs $\ln(1-X)/X$ should give a straight line.

For a substrate-inhibited reaction, the rate expression is

$$(-r) = \frac{V_m S_0 (1-X)}{[S_0(1-X) + K_m + S_0^2(1-X)^2/K_i]} \quad (6)$$

and the design equation becomes

$$\frac{t}{X} = \frac{S_0}{V_m} - \frac{K_m}{V_m} \cdot \frac{\ln(1-X)}{X} + \frac{S_0^2}{K_i V_m} (2-X) \quad (7)$$

which is not very amenable to a linear analysis.

11.3 BIOPROCESS DEVELOPMENT

Phenol Removal

The CSTR was used to determine the maximum conversion rate of phenol for a given feed concentration and to investigate the stability of reactor operation at maximum conversion. With the reagent concentrations in use, the limit of detectability of the phenol assay is about 10 ppm of phenol; thus the maximum rate of removal is determined for a phenol concentration of approximately 10 ppm in the reactor. Microbial concentration and phenol removal rates from a feed stream containing 2500 ppm of phenol are shown in Figs. 11.6 and 11.7. Significant drops in microbial concentration at the middle and end of October 1974 were due to cell washout resulting from excessively high flow rates. We found that residence times of less than 20 hr would lead to a net cell loss from the reactor; that is, cells were being washed out of the reactor at a greater rate than they were being generated. Since the biomass never formed a good settleable sludge, sludge recycle was not effective in maintaining a constant concentration of biomass as the residence time decreased. Although some biomass recycle was effected via the clarifier, the microbial concentration in the effluent from the clarifier rarely decreased to less than half that in the reactor.

When washout commenced, the pumping rate was decreased until the microbial concentration stabilized, then slowly increased until phenol was detected in the reactor. Washout occurred twice during October 1974; in each case, the residence time decreased below 20 hr.

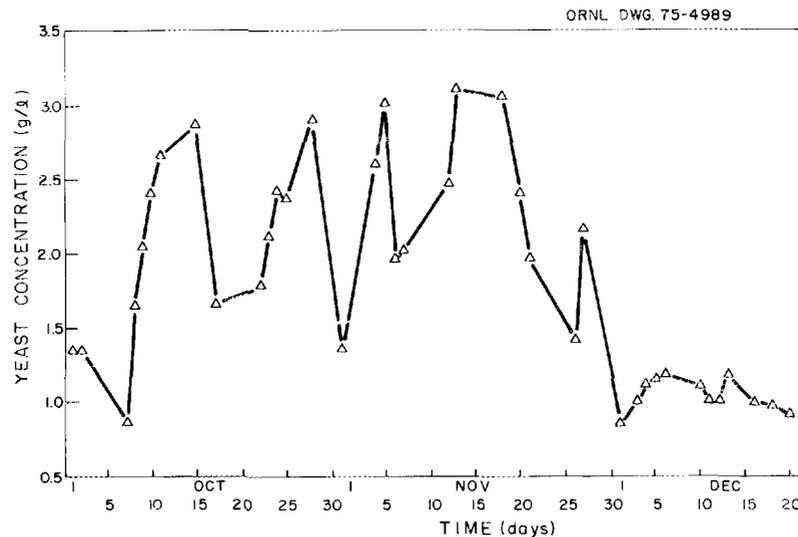


Fig. 11.6. Operating history for the continuous stirred-tank reactor relative to microbial concentration.

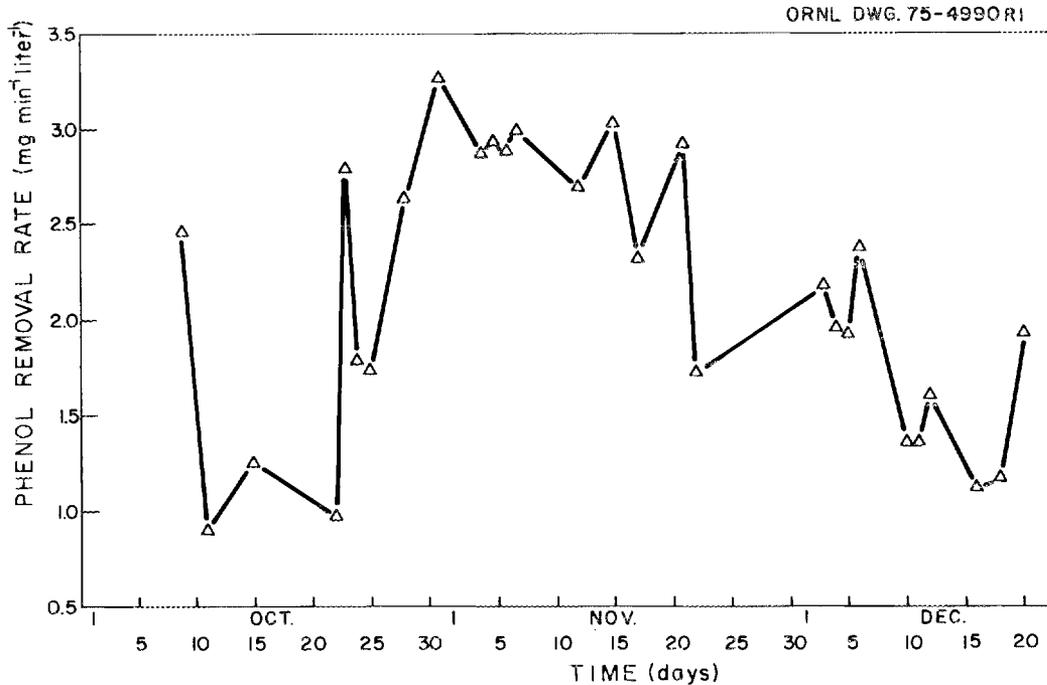


Fig. 11.7. Operating history for the packed-bed reactor relative to phenol removal rate.

The maximum flow rate the reactor could accommodate was 127 ml/hr.

Toward the end of November a malfunction occurred that caused the reactor to be without feed for one to two days. The performance of the reactor decreased noticeably after this period. Microscopic examination of the reactor biomass showed that the yeast population diminished to undetectable levels within a week after the malfunction. The bacterial population that had established itself in the reactor continued to degrade phenol; however, neither the biomass concentration nor the rate of removal of phenol could be increased to their former levels. Thus, during December, the reactor was shut down, cleaned, and reseeded with fresh *Trichosporon cutaneum*.

This work illustrates that, for biological oxidation of phenolic wastes in a stirred-tank reactor, the reactor can be operated quite well near the residence time at which cell washout begins. Table 11.1 compares the performance of our reactor with that of Bethlehem Steel's pilot-plant system for phenolic waste treatment.

As described in the previous section, a packed-bed reactor was investigated for use as a bioreactor for removing phenol. Its performance with respect to phenol removal for the first 1.5 months of operation is shown in Fig. 11.8. At the end of this report period, the

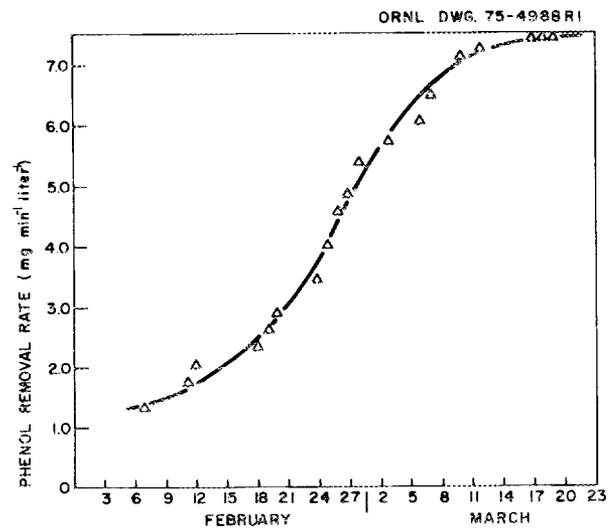


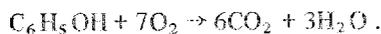
Fig. 11.8. Performance of the packed-bed reactor with respect to phenol removal for the first 1.5 months of operation.

reactor was being operated with a residence time of 1.12 hr. Phenol was not detectable in the effluent; however, since phenol breakthrough had occurred a few days previously at this same residence time, we assumed that the maximum throughput of the reactor was being approached.

Table 11.1. Comparison of ORNL phenol degradation studies with those made by Bethlehem Steel

Parameter	Results of studies made by	
	Bethlehem Steel	ORNL
Phenol concentration	3500 ppm	2500 ppm
Reactor volume	1062 gal	2.25 liters
Flow rate of phenol solution	61.2 gal/hr	118 ml/hr
Flow rate of dilution water	330 gal/hr	0
Phenol removal rate	4.8 g liter ⁻¹ day ⁻¹	4.2 g liter ⁻¹ day ⁻¹
Residence time	Total flow = 2.7 hr; phenol flow = 17 hr	20 hr
Effluent concentration	0.4--0.7 mg/liter	~10 mg/liter

Oxygen requirements for the biological oxidation of phenolic wastes. In developing a fluidized-bed bioreactor for aerobic microorganisms, allowances must be made for the oxygen requirements of the biological reactions occurring in the reactor during routine operation. Complete biological oxidation of phenol to carbon dioxide and water is characterized by the following equation:



Thus the theoretical oxygen requirement is 2.38 mg of oxygen per milligram of phenol. For a feed solution containing 500 ppm of phenol, the oxygen requirement would be 1190 mg of oxygen per liter, which is equivalent to 4.45 liters of air per liter of solution. In practice, the actual delivery rate would be significantly in excess of the stoichiometric requirements. This high air-flow rate is expected to disrupt plug flow characteristics in the reactor, contributing to a significant loss in stagewise efficiency. This loss will be studied experimentally.

Denitrification Tests

Low-level aqueous nitrate waste streams (500 to 5000 ppm of NO_3^- after acid recovery) that may contain small concentrations of alpha emitters are generated at ERDA installations where large volumes of nitric acid are used during the processing of uranium. Various regulations prevent this waste from being discharged directly into the environment because nitrate contributes significantly to high rates of eutrophication, and alpha emitters are undesirable contaminants. We are interested in the removal of nitrate from such streams via biological processes. Since there are microorganisms that can remove nitrate under anaerobic conditions, we are attempting to utilize controlled bacterial denitrifi-

cation in a bioreactor to eliminate nitrate from test solutions.

Two series of tests were performed in the TFBR described, using about 530 ml (~400 g) of settled coal per test. The size of the coal used in the first series was -65 +80 mesh, while that used in the second series was -200 +375 mesh. The surface areas of the two sizes of coal are 3.2 m²/g and 58.6 m²/g respectively. After fines had been removed from the TFBR by flushing with water at maximum anticipated operating flow rates, the feed solution containing nitrate (Table 11.2) and seed bacteria was introduced into the system. Methanol was added to supply the necessary carbon for bacterial growth; however, cheaper sources of carbon could be substituted. Nitrate served as the terminal electron acceptor for the bacteria in the anaerobic reactor environment; its presence in the feed stream resulted in the evolution of nitrogen gas and a very small amount of CO₂ gas by the bacteria. The effluent was recycled for two to four days, at which time the bed started to discharge nitrogen gas.

The nitrate ion was assayed successfully with the use of a nitrate ion specific electrode. One variable not measured was the amount of bacteria attached to the coal (reactor biomass); no satisfactory method has been

Table 11.2. Composition of feed solution for the denitrification bioreactor

Component	Concentration	Composition
NH ₄ NO ₃	2.85 g/liter	
KH ₂ PO ₄	0.002 g/liter	
MgSO ₄ ·7H ₂ O	0.01 g/liter	
Methanol	0.65 ml/liter	
Iron solution	0.65 ml/liter	6 g FeCl ₃ /liter
Molybdenum solution	0.001 ml/liter	1 g Na ₂ MoO ₄ ·2H ₂ O/liter

found that will measure the total weight or volume of biomass in the reactor. However, we expected that the amount of biomass would remain fairly constant once steady-state operation was achieved. If the layer of microorganisms on the coal becomes too thick, the abrasive action of the fluidized bed will remove it. The loose biomass will wash out of the column under the appropriate hydraulic conditions.

Test with 65-mesh coal. The fluidized-bed test with 65-mesh coal was operated continuously for 40 days. The outlet flow rate to the drain was 12 to 90 ml/min (90 ml/min = residence time of 24 min). An internal (recycle) flow rate up to 180 ml/min was used to attain fluidization velocity. The maximum velocity at the 3-in. section was 0.0022 fps.

During the test, a few particles that appeared to be clumps of bacteria were flushed from the column. No signs of bed material agglomeration were evident during the testing period.

The nitrate input varied from 4 to 36 g-moles of NO_3^- per hour. The nitrate removal varied from 1 to 4

g-moles of NO_3^- per hour; during the major portion of the test, the removal rate was approximately 2 g-moles of NO_3^- per hour. The off-gas composition was found to be greater than 99% N_2 by gas chromatography; the remainder was probably CO_2 .

Test with 200-mesh coal. The fluidized-bed test with 200-mesh coal extended over a period of about 38 days. The fluidization flow rate before bacteria were added to the column was about 23 ml/min or 0.00028 fps; the calculated fluidization velocity was 0.00034 fps. The height of the fluidized bed decreased with time, indicating that the bacteria caused the effective size of particles to increase. The agglomeration of particles was confirmed by microscopic examination.

The average use rate was about 3 g-moles of NO_3^- per hour (1 to 5 g-moles/hr). The volumetric gas rates, when converted to moles of NO_3^- , agreed well with the denitrification rates. On the basis of this run, we conclude that small amounts of the bed should be withdrawn and cleaned periodically to minimize particle agglomeration and maintain steady-state operation.

12. Coal Technology Program

12.1 HYDROCARBONIZATION RESEARCH

Hydrocarbonization is an important type of coal liquefaction process that combines low-temperature, high-pressure, and fluidized-bed operation using hydrogen-rich gas for fluidization. The hydrocarbonization process can produce liquid fuels, desulfurized char, 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 1500°F and pressures up to 150 atm, but optimum conditions may be significantly milder.

A thorough review and evaluation of existing information in the literature on hydrocarbonization and carbonization (low hydrogen pressure) processes have

1. 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).

been completed, and a summary report¹ has been prepared and submitted for approval by ERDA – Fossil Energy.

The experimental development effort progressed significantly in two areas. Lucite models of a recirculating fluidized-bed concept were tested over a range of conditions. These results contributed to the design of a bench-scale hydrocarbonization reactor. A high-temperature experimental system was designed and built, and operations were started. This system permits relatively rapid and inexpensive testing of various components of the bench-scale hydrocarbonizer at atmospheric pressure.

The bench-scale hydrocarbonizer is in the design phase. The conceptual design includes the following objectives: (1) coal feed rate of about 10 lb/hr, (2) pressure vessel design for 350 psig and 1250°F, and (3) gas superficial velocities of up to 2 fps in the reactor. The 4-in. nominal pipe size reactor shown in Fig. 12.1 was designed to permit demonstration of the recirculating fluidized-bed concept on the smallest practical engineering scale.

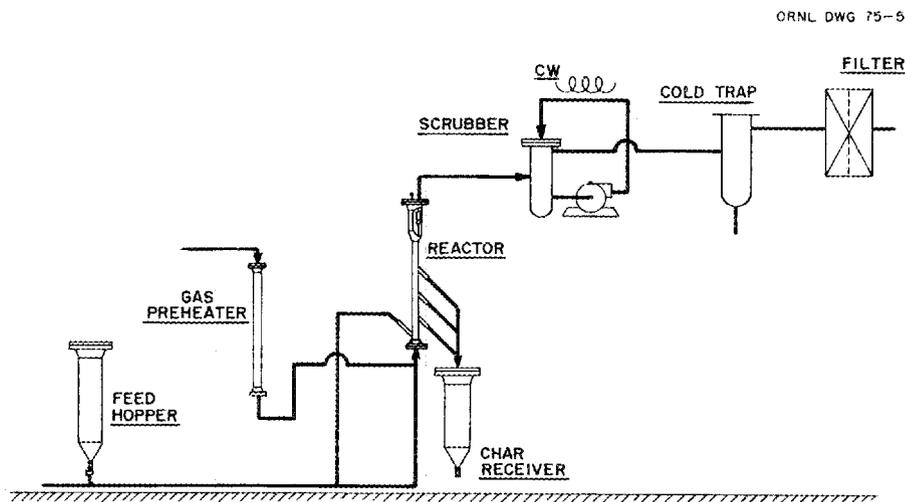


Fig. 12.1. Pressurized hydrocarbonizer flowsheet.

12.2 SEPARATIONS TECHNOLOGY

Examination of the overall solids-liquid separation problem involves consideration of four basic steps: pretreatment, solids concentrations, solids separation, and posttreatment. The number of steps required for a given separation depends on the characteristics of the stream to be processed and the specifications for the effluent from the separations section. Large variations exist, both in the coal liquefaction process streams and in the degree of separation required. Thus the solids-liquid separation scheme must be tailored to specific processes. However, a number of conditions are common to all conversion processes: high pressure, high temperature, high viscosity, small (colloidal) particles, and liquid phase as the more valuable product. These properties were used in choosing separation schemes for more-detailed study from the many properties available in the broad field of solids-liquid separations.

The initial experiments, which began January 15, 1975, were limited to pretreatment techniques — principally agglomeration and solvent extraction. Studies of methods for concentration (hydroclones) and solids separation (precoat filtration, centrifugation) are planned for the coming year.

Solvent Extraction of COED Unfiltered Raw Oil

The Char Oil Energy Development (COED) process has been developed through the pilot-plant stage by the FMC Corporation. There is a need for an improved solids-liquid separation scheme for the COED unfiltered raw oil (UFO). The relative abilities of several solvents to extract solid material from COED UFO are presented in Table 12.1. Results are listed in decreasing order of ability to dissolve the oil phase and to reduce the solids content.

The agglomerating tendencies of the solids in the presence of solvents were particularly noted. Figure

Table 12.1. Solvent extraction of an unfiltered oil from the COED process

Solvent	Rank	Heavy phase/UFO (weight ratio \times 100)
Quinoline	1	3
Tetrahydrofuran	2	4
Pyridine	3	6
Acetone	4	6
Toluene	5	14
Xylene	6	19
Benzene	7	19

12.2 shows solids from UFO, and Fig. 12.3 shows the latter stages of an agglomeration produced by toluene. Unlike the UFO, nearly all particles are associated, and the area between agglomerates is relatively clear. In the initial stages of agglomeration, small "bridges" of submicron particles covered with an oil solution are lined up to facilitate the transfer of liquid and particles from one agglomerate to another.

In the two-phase system of unfiltered raw oil-tetrahydrofuran (UFO-THF), three categories of particles tended to collect at the interface: those that remained in the oil-rich phase, those that remained in the THF-rich phase, and those that collected at the interface. During dissolution by quinoline, many small particles tended to agglomerate and float to the top of the film. The larger particles remained near the bottom and were well dispersed. Both pyridine and mineral oil produced less-pronounced agglomeration; however, it was significant enough to warrant further studies at other concentrations.

Further tests of the agglomerating tendencies of solvents in *well-mixed dispersions* with UFO showed no flotation or interface effect. However, the agglomerating effect in the presence of toluene was still evident. Benzene and xylene insolubles were agglomerated similarly to the toluene insolubles. The large agglomerates in the latter cases suggested that solvent extraction followed by settling or centrifugation might be a viable separation scheme. Initial settling rate measurements were promising, but the economics would depend on the solvent recovery step and on the degree to which the inorganic sulfur accumulated in the heavy phase. Preliminary studies using the electron microscope indicated that most of the pyritic sulfur was in the heavy phase.

Particle Size Distribution of H-Coal Solids

Particle size distributions were determined on a sample of filtered solids from the H-Coal process of Hydrocarbon Research, Inc. One of the objectives in the initial particle size determination was to evaluate available techniques for sizing colloidal particles from coal liquefaction streams. H-Coal streams have proved to be among the most difficult to filter; thus they provided a severe test. The sizes of the particles, which were too small to be measured by either an optical microscope or a Coulter counter, could be determined only by using the electron microscope. One-half of the total number of particles had sizes of less than 0.11 μ , while one-half of the total sample solids volume was

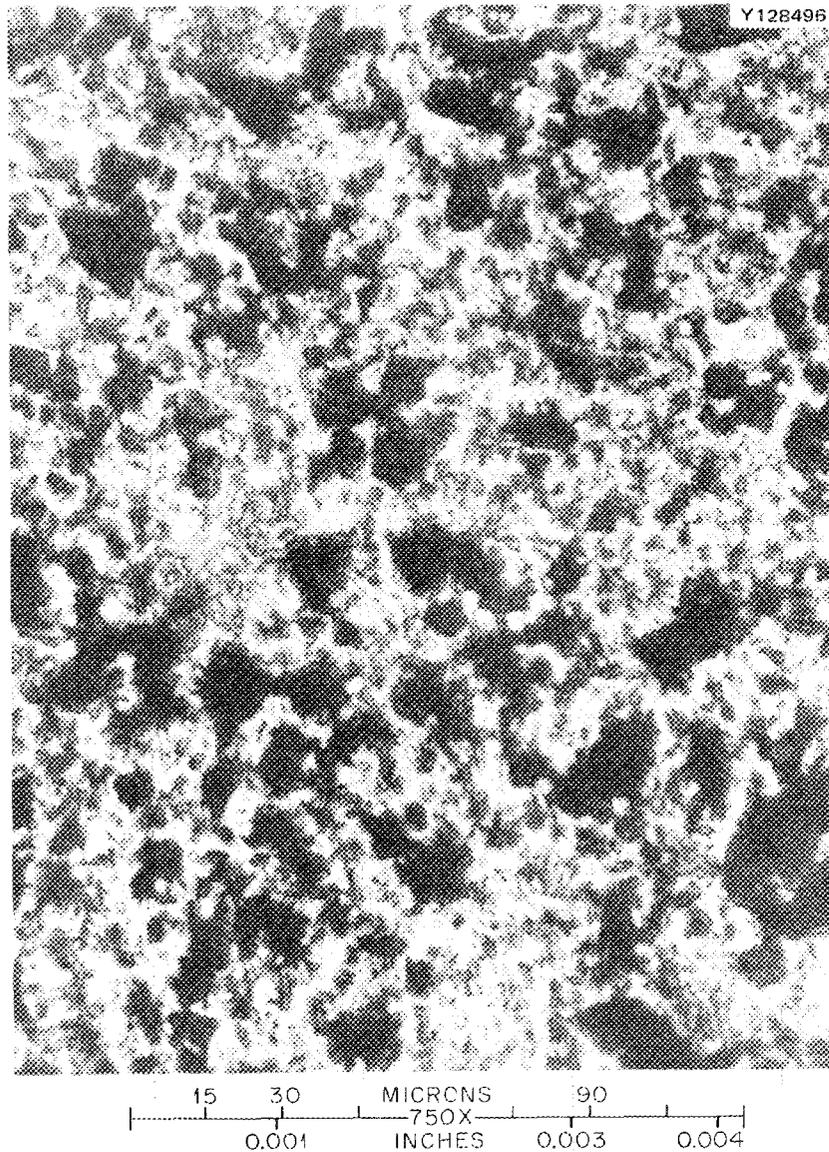


Fig. 12.2. UFO from the COED process. Magnification, 1000X.

composed of particles smaller than 0.98μ . Unfiltered material from the COED process or from the Solvent Refined Coal process, developed by Spencer Chemicals, is not expected to contain as many small particles. Optical microscope results show a much broader particle size distribution for the COED material; the sizes of a significant portion of the particles are above 10μ .

Identification of Pyritic Sulfur in COED Unfiltered Oil

The size range of particles containing sulfur is important. Different methods of separation would be

indicated, depending on whether the sulfur was present principally in the larger particles or in the smaller particles. It is also important to determine whether the mineral matter goes to the heavy phase of a solvent fractionation. A qualitative evaluation using an optical microscope with polarized light indicated that most of the pyritic sulfur was associated with the smaller particles.

Characterization of COED Process Materials

Chemical analyses were made of UFO and filtered oil from the COED process. Significant observations were as follows:

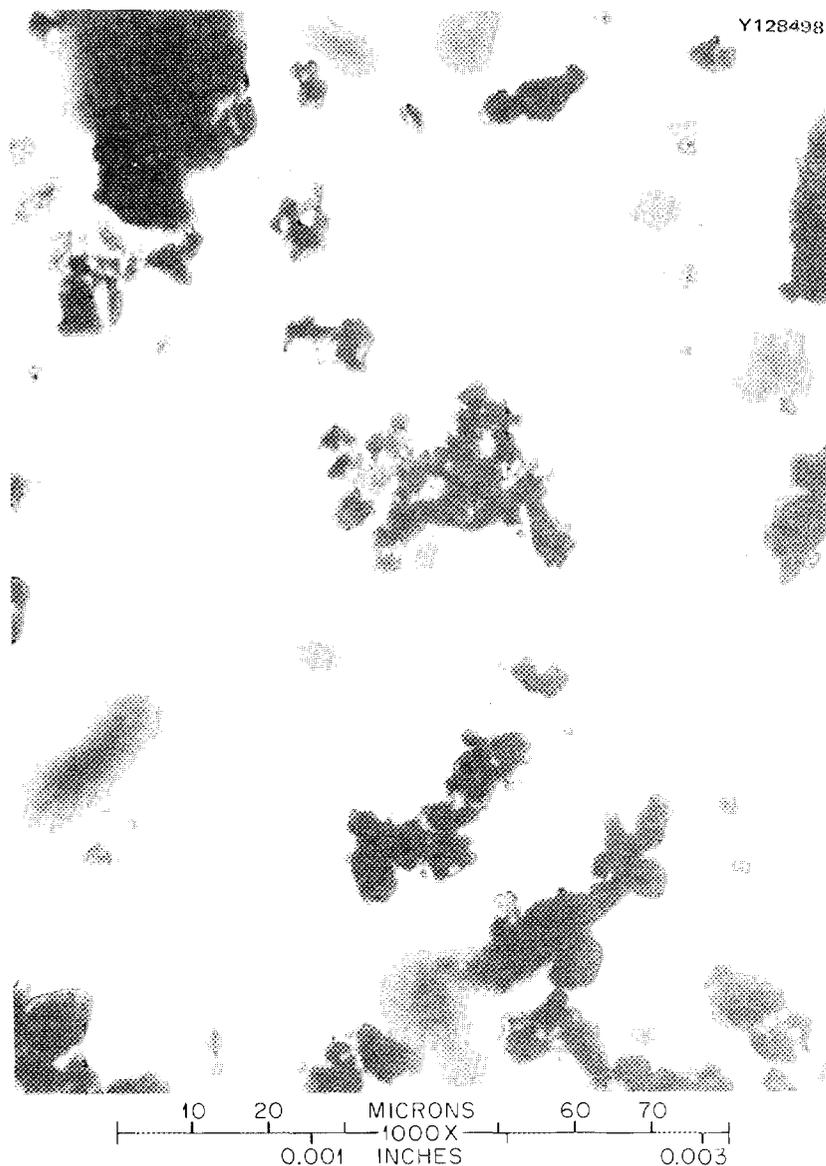


Fig. 12.3. UFO from the COD process with toluene added. Magnification, 1000X.

1. The carbon/hydrogen ratio decreased slightly with filtration, indicating that highly unsaturated hydrocarbons were removed with the solids.
2. Much of the ash (inorganics) was removed by filtration.
3. The amounts of the following elements were significantly reduced by filtration: aluminum, boron, calcium, chlorine, potassium, manganese, sodium, and nickel.
4. The amounts of the following elements were significantly increased by filtration: iron, magnesium, silicon, strontium, and vanadium.

12.3 EXPERIMENTAL ENGINEERING SUPPORT OF AN IN SITU GASIFICATION PROCESS

Experimental engineering support of the Lawrence Livermore Laboratory (LLL) in-situ gasification project was initiated by the USAEC Division of Applied Technology (USAEC-DAT). Early efforts were directed toward high-temperature desulfurization of the gasification product stream using molten-salt techniques. Subsequent meetings with LLL and USAEC-DAT representatives, however, revealed significant information gaps associated with the chemical reactions and fluid-flow patterns which will be

encountered underground. Therefore, the work, now funded by ERDA — Fossil Energy, has been redirected to include more urgent studies of pyrolysis of large coal blocks and pyrolysis in large-diameter beds.

The LLL in situ gasification concept requires that deep, thick coal seams be fractured by using chemical high explosives. After fracturing, oxygen and steam will be piped to the top of the seam to feed a flame front that will move slowly down through the bed. Within a narrow band, which includes the flame front, coal will be combusted and gasified. Ahead of this reaction zone, coal will be slowly pyrolyzed. Product gases will then penetrate the fractured coal seam and be recovered from the bottom.

Most pyrolysis studies have been confined to the heating of small, finely ground samples of bituminous coals. Explosive fracturing, however, is likely to produce large blocks of coal that will not necessarily behave as powders during pyrolysis. A block pyrolyzer was constructed for initial experiments that utilize 6-by 6-in. right circular cylinders machined from large blocks of subbituminous coal and instrumented with thermocouples. Figure 12.4 is a schematic representation of the block pyrolyzer.

One objective of early experiments on instrumented coal blocks was to determine bulk-heat transfer properties during pyrolysis. The effects of an adherent ash and

of the nonisotropic nature of the material will be examined in later tests.

Experiments in a deep-bed pyrolyzer with a moving furnace will more closely simulate in situ pyrolysis. A reactor 8 in. in diameter by 8 ft long will be half-filled with coarsely ground coal; a porous, ceramic packing material will be used to fill the remainder of the reactor. As the furnace moves down the length of the reactor, nitrogen will be used to sweep gaseous products into the treatment and analysis unit built for the block pyrolyzer. Both axial and radial temperature profiles will be measured. Tars are produced, condensed downstream of the furnace, and revaporized; therefore, gas yields may be higher as a result of tar cracking. Construction of the reactor was completed in early January 1975, but installation in the laboratory has been delayed.

Health hazards posed by carcinogenic components of coal-derived liquids were evaluated, and a formalized description of both the underlying safety philosophy and the operational procedures governing the conduct of work in the Experimental Engineering Section was prepared. This preliminary document was issued as an internal memorandum, pending formulation of Laboratory-wide safety procedures. Comprehensive area and personnel monitoring programs are being implemented in cooperation with the Health Division.

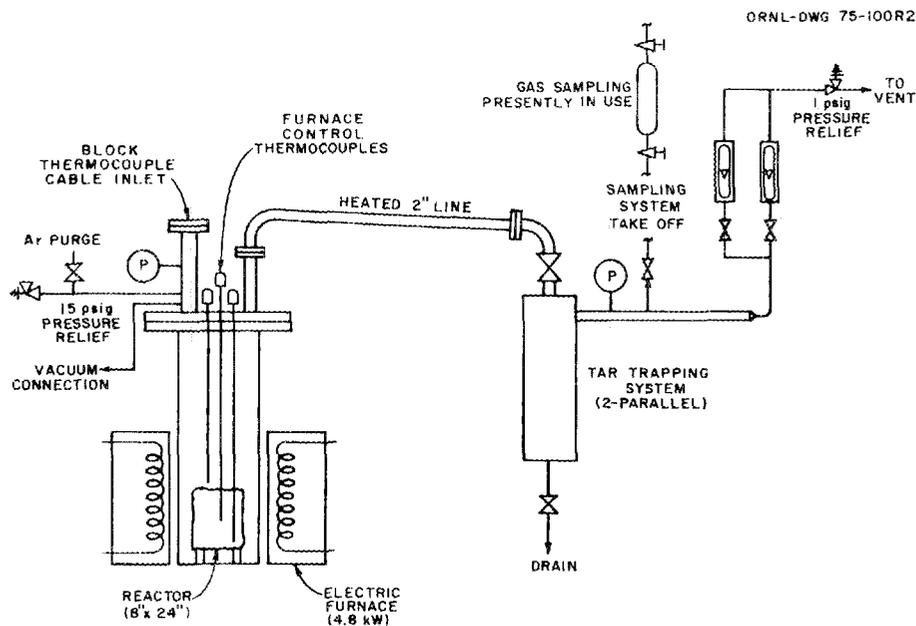


Fig. 12.4. Block pyrolyzer.

13. Actinide Oxides, Nitrides, and Carbides

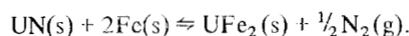
13.1 ESTIMATION OF THERMODYNAMIC DATA

A method was developed to estimate Gibbs free energy functions (fef) from 289 to 2000°K for many types of crystalline compounds. This method was developed because molar heat capacities for many actinide and lanthanide carbides and nitrides of interest to nuclear technology have not been measured; thus it is not possible to calculate the fef values from experimental data. A paper describing the method was prepared for submission to the *Journal of the American Ceramic Society*. The abstract follows;

“Estimation of Gibbs Free Energy Functions,” by T. B. Lindemer. *Abstract*: A computational method has been derived for the estimation of the molar heat capacity contribution to the Gibbs free energy function (fef) from 298 to 2000°K. The method is based on the observed temperature invariance of certain ratios of the integrals of these molar heat capacity contributions. This method has been applied to the analysis of fef data for metal carbides, nitrides, fluorides, borides, and silicides in the crystalline state. The estimated fef for a given compound is more accurate than that obtainable by other known estimation techniques and permits a more accurate calculation of ΔG_T^0 , than is possible from the commonly used approximation $\Delta G_T^0 = \Delta H_{298}^0 - T \Delta S_{298}^0$.

13.2 NITRIDE PHASE EQUILIBRIA

Compatibility studies of uranium nitride with chromium, iron, and nickel indicate that compounds of the AB₂ type, such as UFe₂, may form according to the reaction



These AB₂ compounds adopt one of three closely related crystal structures called Laves phases. In general, Laves phases form the numerically largest group of intermetallic compounds.

In our compatibility studies, we have been interested in the possibility of forming Laves-phase compounds with uranium (A component) and combinations of

chromium with iron or nickel (B component). Chromium alone does not form intermetallic compounds with uranium,¹ but chromium with iron or nickel could combine with uranium to form Laves-phase compounds.

We used Pauling's valence bond theory of metals^{2,3} as a basis for calculating bond numbers in uranium-transition metal and transition metal-transition metal Laves-phase compounds. Relationships given by Pauling enabled us to determine the *d* orbital participation in bond formation of the transition metals. We found that the inability of chromium alone to form Laves-phase compounds with uranium is due to the inability of the chromium *d* orbitals to take part in bonding to the extent necessary for compound formation. These calculations also indicated, however, that chromium would combine with iron and, possibly, with nickel to form Laves-phase compounds of the type U(M_xCr_{1-x})₂, where M = Fe or Ni.

Based on these calculations, alloys of uranium, iron, and chromium were prepared by arc-melting mixtures

1. G. B. Brook, G. I. Williams, and F. M. Smith, *J. Inst. Metals* **83**, 271 (1954).

2. L. Pauling, p. 220 in *Theory of Alloy Phases*, American Society for Metals, Cleveland, Ohio, 1956.

3. L. Pauling, *The Nature of the Chemical Bond*, 3d ed., Cornell University Press, Ithaca, N.Y., 1960.

Table 13.1. Uranium-chromium-iron C15 cubic Laves phases

Alloy composition, 33.3 at. % U plus:		Lattice constant (Å)
at. % Cr	at. % Fe	
11.3	55.4	7.0905 ± 0.001
22.2	44.5	7.1098 ± 0.001
33.3	33.3	7.1452 ± 0.002
44.5	22.2	7.1660 ± 0.0065
55.4	11.3	(7.1580 ± 0.0091) ^d

^dCr and Fe lines also present.

of the respective elements and annealing in flowing argon for 66 hr at 800°C. The compounds thus formed were brittle in nature and were ground into powder for examination by x-ray diffraction. The results of the x-ray analysis are presented in Table 13.1. These results confirm that compounds of the type $U(Fe_xCr_{1-x})_2$ do exist and that they have the C15 Laves-phase structure. The lattice constant increased with additional chromium up to a value of 7.1660 ± 0.0065 Å. The alloy with

the greatest chromium content (55.4 at. %) had chromium or iron peaks present in the x-ray spectrum in addition to peaks caused by the Laves-phase compound. The values of the lattice constants are consistent with our analysis of Laves phases in terms of Pauling's metal bonding theory.

A report entitled *Laves Phases of Uranium and Transition Metals* was prepared and is being published as ORNL-TM-4915.

14. Studies in Chemical Engineering Science

14.1 MASS TRANSFER RATES IN OPEN BUBBLE COLUMNS

Measurements of mass transfer rates in 1.5- and 3-in.-diam open bubble columns were continued during this report period.¹⁻³ Results were extended to include the effects of liquid viscosity as well as the effects of liquid and gas flow rates on mass transfer rates of CO₂ into aqueous solutions. These data, along with selected previous data,^{4,5} were combined to produce correlations for estimating the effects of gas velocity, liquid viscosity, and column diameter on liquid-film mass transfer coefficients.

The overall volumetric mass transfer coefficient was correlated with gas velocity and liquid viscosity over both the "bubbly" and "slugging" flow regimes⁶ as follows:

$$K_L a = 0.0049 U_G^{0.843} \mu_L^{-0.519}, \quad (1)$$

where

$K_L a$ = volumetric overall mass transfer coefficient, corrected for axial dispersion and end effects, sec⁻¹,

U_G = superficial gas velocity, cm/sec,

μ_L = liquid viscosity, cP.

The mass transfer coefficient was also correlated using dimensionless groups as follows:

$$N_{Sh} = 1.11 \times 10^{-11} \cdot N_{Re}^{0.849} \cdot N_{Sc}^{1.80} \cdot N_{Su}^{1.15}, \quad (2)$$

where

N_{Sh} = modified Sherwood number = $(K_L a) D_c^2 / D_{12}$,

N_{Re} = Reynolds number = $D_c U_G \rho_L / \mu_L$,

N_{Sc} = Schmidt number = $\mu_L / \rho_L D_{12}$,

N_{Su} = Suratman number = $D_c \rho_L \sigma_L / \mu_L^2$,

D_c = column diameter,

D_{12} = diffusivity,

ρ_L = liquid density,

σ_L = interfacial tension.

However, these groups include other properties, such as liquid density and interfacial tension, that were not significantly varied in this study. The dimensionless correlation is recommended for estimating mass transfer rates for liquid-film-controlled systems other than the carbon dioxide–aqueous glycerol system, but caution should be used when extrapolating to physical properties widely different from those used in this study.

14.2 PERMEATION-OXIDATION STUDIES

The escape of tritium from fusion power reactors by permeation through external piping or heat exchange surfaces can result in unacceptable tritium release rates to the environment or severely affect process requirements for tritium blanket recovery systems. A secondary containment system will be more effective if the tritium is oxidized to a nonpermeating and recoverable form, T₂O. Oxidation has also been proposed as the principal process for recovering the bulk of the tritium produced in a controlled thermonuclear reactor blanket. Tritium would be allowed to permeate from the blanket into a helium

1. A. Grauer et al., *Axial Mixing in an Open Bubble Column, Part VIII: Mass Transfer Effects*, ORNL-MIT-193 (1974).

2. S. G. Dawson et al., *The Effects of Viscosity on Mass Transfer in an Open Bubble Column*, ORNL-MIT-199 (1974).

3. S. A. Reber et al., *The Effects of Liquid Flow Rate and Viscosity on Mass Transfer in Open Bubble Columns*, ORNL-MIT-201 (1974).

4. J. J. Toman et al., *Axial Mixing in an Open Bubble Column, Part VI: Mass Transfer Effects*, ORNL-MIT-175 (1973).

5. A. S. Y. Ho et al., *Axial Mixing in an Open Bubble Column, Part VII: Mass Transfer Effects*, ORNL-MIT-183 (1974).

6. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1974*, ORNL-4966, pp. 55–57.

coolant and would then be continuously oxidized to nonpermeable T_2O and recovered on molecular sieves. Hence an efficient oxidation technique could be used both for containment of tritium permeating external piping and for recovery of tritium from a blanket system. The effectiveness of the oxidation step is crucial to either application.

The phenomenon to be investigated in this study is the oxidation of tritium as it permeates through the first containment or heat exchange surface. An important consideration is the chemical form of the tritium as it leaves the permeated surface. Low concentrations of oxygen are likely to be present in either the helium coolant or reactor containment atmosphere (and higher concentrations of oxygen could be added). Atomic tritium, permeating a metal barrier, should react rapidly with oxygen in the gas phase. However, the effectiveness of certain metals (i.e., those being considered for fusion reactor piping and heat

exchangers) for catalyzing the oxidation reaction is unknown.

A schematic equipment diagram of the apparatus used to examine hydrogen isotope permeation-oxidation phenomena is shown in Fig. 14.1. Basically, the system consists of a type 304 stainless steel permeation tube surrounded by a $1\frac{1}{2}$ -in.-diam tubular vacuum chamber and furnace, a VacSorb roughing pump, a 20-liter/sec VacIon pump, and a variable leak valve. A UTI model 100 C Precision mass analyzer and two nude ion gages (millitorr and ultrahigh vacuum) are attached to the $1\frac{1}{2}$ -in.-diam vacuum chamber. The $\frac{1}{4}$ -in.-diam permeation tube has a 32-mil wall thickness and a heated length of approximately 12 in. The tube can be easily replaced to permit testing of other materials. Prior to assembly, the surface of the permeation tube was cleaned by electropolishing.

Six runs were made in the permeation-oxidation system; in each run, 99.75 vol % deuterium was fed to

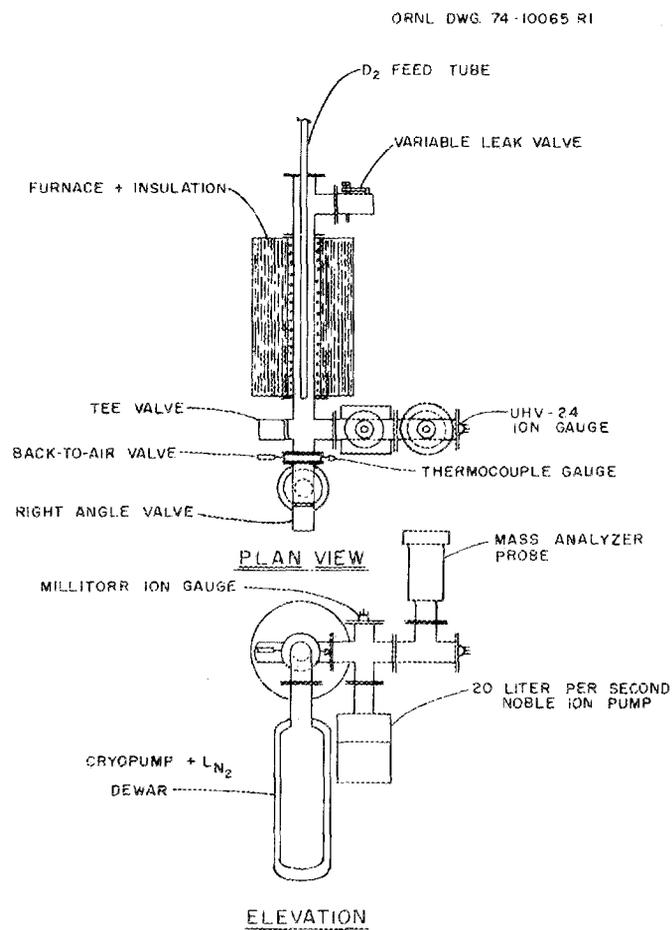


Fig. 14.1. Schematic equipment diagram for permeation-oxidation studies.

the inside of the stainless steel permeation tube at a pressure of 2.0 psig. The temperature of the permeation tube was maintained at 300, 350, or 400°C. Partial-pressure data were measured for residual gases until the system approached steady-state conditions (up to two weeks for each system perturbation). The objectives of the first four runs were to test the system for leaks and to determine the concentration of residual gases in the original vacuum chamber as a function of temperature before oxygen was added to the system. In run 5, which was made at 300°C, the variable leak valve was opened two and one-half turns to permit the inleakage of 99.5 vol % oxygen. Within 24 hr the electron multiplier current from the analyzer was fluctuating for all mass numbers. Therefore, with oxygen partial pressure this high (or higher), the existing tungsten filaments in the analyzer probe must be replaced with thoriated-iridium filaments. In run 6 the temperature was maintained at 300°C, and the variable leak valve was closed to shut off the supply of oxygen. Within 24 hr the electron multiplier current was restabilized. After oxygen had been admitted to the vacuum chamber, the partial pressure of deuterium decreased by a factor of 30. Apparently, the permeation rate through the tube was reduced because of the oxide film produced on the type 304 stainless steel surface during run 5.

Deuterium permeation data will be obtained at 400°C, and possibly 500°C, using the existing oxidized stainless steel surface with little or no further addition of oxygen. Then an orifice will be installed between the vacuum chamber and the ion pump—mass spectrometer probe to permit a relatively high oxygen concentration in the test chamber while still limiting the flow of oxygen to the ion pump and mass spectrometer probe. Oxygen partial pressures as high as 0.001 torr in the volume surrounding the permeation tube are desired. In the immediate future, permeation-oxidation studies will be made with an existing palladium tube and perhaps with nickel or a nickel alloy.

14.3 FLOODING STUDIES IN COLUMNS FILLED WITH GOODLOE PACKING

The Krypton Absorption in Liquid CO₂ (KALC) development facility uses Goodloe packing^{7,8} in a 3-in.-diam column, but earlier tests indicated that the capacity (flooding rate) of this column was significantly less than that predicted by the packing manufacturer.⁹

Therefore, an experimental study was made of flooding rates with Goodloe packing in an air-water system to assist in evaluating this material for use in KALC or other gas-liquid sorption processes.

Figure 14.2 presents flooding curves in the form suggested by the manufacturer. The air flow at which flooding occurs, G_{max} , is plotted against the ratio of water flow rate to maximum air flow rate, L/G_{max} . The upper curve represents data collected for a similar system at the ORGDP.¹⁰ The three lower curves represent experimental data obtained in our study. The first results we obtained, which are shown on the bottom curve, were considerably lower than those predicted by the Goodloe correlation. This implied that there was a constriction in the column; therefore, the entire column was inverted 180° and retested. The experimental data from the inverted column were higher and, for L/G_{max} ratios greater than 10, agreed well with the correlation; however, at lower L/G_{max} ratios, the experimental curve dropped below the correlation.

The column was then completely repacked with new Goodloe packing. In replacing the column, extra care was exercised to ensure that axial compression of the packing was minimized, in accordance with the manufacturer's instructions. The results from this new packing were essentially the same as those obtained for the inverted column.

These results indicate that the flooding behavior of Goodloe packing can be difficult to predict, and that considerable care should be taken in preparing the column. In designing systems with this type of packing, we recommend that the "new packing" flooding curve of Fig. 14.2 be used. At low values of L/G_{max} , this curve is lower and more conservative than the manufacturer's curve. Since it is unlikely that exact packing properties can be reproduced, a further allowance for 30% scatter from the most probable curve is recommended.

7. "Goodloe Column Packing," Bulletin No. G-702, Packed Column Co., Edison, N.J.

8. C. D. Scott et al., *Experimental Engineering Semiannual Progr. Rep. Mar. 1, 1974, to Aug. 31, 1974*, ORNL-TM-4777 (July 1975).

9. "Packed Column Information Bulletin," Packed Column Co., Edison, N.J.

10. M. J. Stephenson, ORGDP, personal communication, 1974.

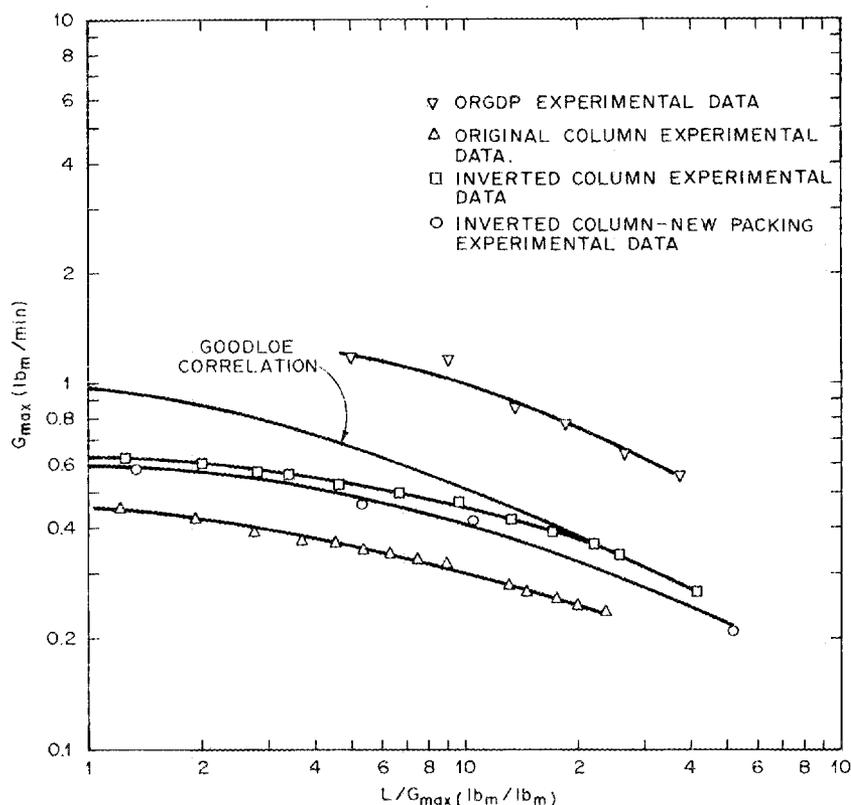
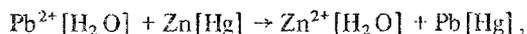


Fig. 14.2. Comparison of experimental data and manufacturer's flooding correlation.

14.4 SALT-METAL CONTACTOR DEVELOPMENT: EXPERIMENTS WITH A MECHANICALLY AGITATED NONDISPERSING CONTACTOR USING WATER AND MERCURY

Mass transfer rates between water and mercury were measured in a mechanically agitated contactor using the reaction



which was assumed to be instantaneous, irreversible, and occurring entirely at the water-mercury interface.

Data from a series of five experiments performed in the water-mercury contactor were reanalyzed in an attempt to determine whether an apparent change in mass transfer coefficient during the operation of a run was due to a change in the controlling resistance to mass transfer from one phase to the other. Several inconsistencies were found between the model and the experimental data.

Runs were made in the water-mercury contactor at an elevated temperature ($\sim 40^\circ\text{C}$) to test the validity of the

assumption that the interfacial reaction is instantaneous. Results from these tests were inconclusive.

An investigation was initiated to determine whether polarography is a viable alternative method for measuring mass transfer rates in a stirred-interface contactor using mercury and an aqueous electrolyte solution. Although several electrolyte solutions were investigated, none was found to be entirely inert to mercury. Information in the literature¹¹ suggested that an Fe^{2+} - Fe^{3+} redox couple (using iron complexed with oxalate ions) may be suitable as an electrolyte for our application. Further tests will be performed to determine whether the iron oxalate electrolyte will produce suitable polarograms.

14.5 PREPARATION OF SMALL-PARTICLE SORBENTS

Numerous industrial processes involve interaction and mass transfer between solid particles in fixed beds and

11. I. M. Kolthoff and J. J. Lingane, *Polarography*, 1st ed., Interscience, New York, 1946.

gas or liquid streams. Generally, the limiting factor on the efficiency or effectiveness of the process is the resistance to mass transfer, both between the stationary and mobile phases and within the stationary or solid phases. These resistances can be reduced by decreasing the size of the particles in the fixed beds. However, smaller particles require a higher pressure to force the fluid through the bed. The pressure losses for particles of a given size can be minimized by using uniformly sized spheres as the bed material.

Sol-gel processes for preparing uniformly sized metal oxide spheres in the range of several hundred microns in diameter have been developed and successfully demonstrated at ORNL.^{12,13} The goal of this research is to extend the capability of these processes to particle sizes less than $10\ \mu$.

Nozzle design. Although there is apparently no inherent lower limit to the diameter of spheres that can be formed by the sol-gel processes, several considerations impose practical lower limits on such diameters. The most constraining ones are: (1) nozzle fabrication, (2) sphere production rate, and (3) nozzle plugging. Discussions with both glassblowers and metallurgists indicated that the practical lower limit for the inside diameter of the nozzle is approximately 10 to $15\ \mu$. Glass nozzles approximately $20\ \mu$ in diameter and

stainless steel nozzles about $25\ \mu$ in diameter were fabricated and tested. The results indicate that nozzles of this size present insurmountable difficulties (i.e., plugging). The sphere-forming process that produces the most uniformly sized drops involves the use of a two-fluid nozzle with laminar flow and an imposed vibration in the drive fluid.¹⁴ For $10\text{-}\mu$ -diam drops, the maximum production rate using this technique is about 5,000,000 drops per minute, or about $0.003\ \text{cm}^3/\text{min}$. Thus, for a satisfactory total production rate, some multiple-nozzle arrangement is necessary. Two designs were fabricated and tested, but equal flow through each nozzle could not be attained. The difficulties encountered indicated that sufficient throughput and small, uniform product cannot be obtained by using the two-fluid nozzle and laminar flow.

12. S. D. Clinton, P. A. Haas, and L. J. Hirth, "Process for Preparing Oxide Gel Microspheres from Sols," U.S. Patent 3,290,122 (July 28, 1964).

13. P. A. Haas and S. D. Clinton, "Preparation of Thorium and Mixed Oxide Microspheres," *Ind. Eng. Chem., Product Res. Develop.* 5(3), 236-44 (1966).

14. P. A. Haas and W. J. Lackey, *Improved Size Uniformity of Sol-Gel Spheres by Imposing a Vibration on the Sol in Dispersion Nozzles*, ORNL-TM-4094 (May 1973).

ORNL DWG 75-874 R1

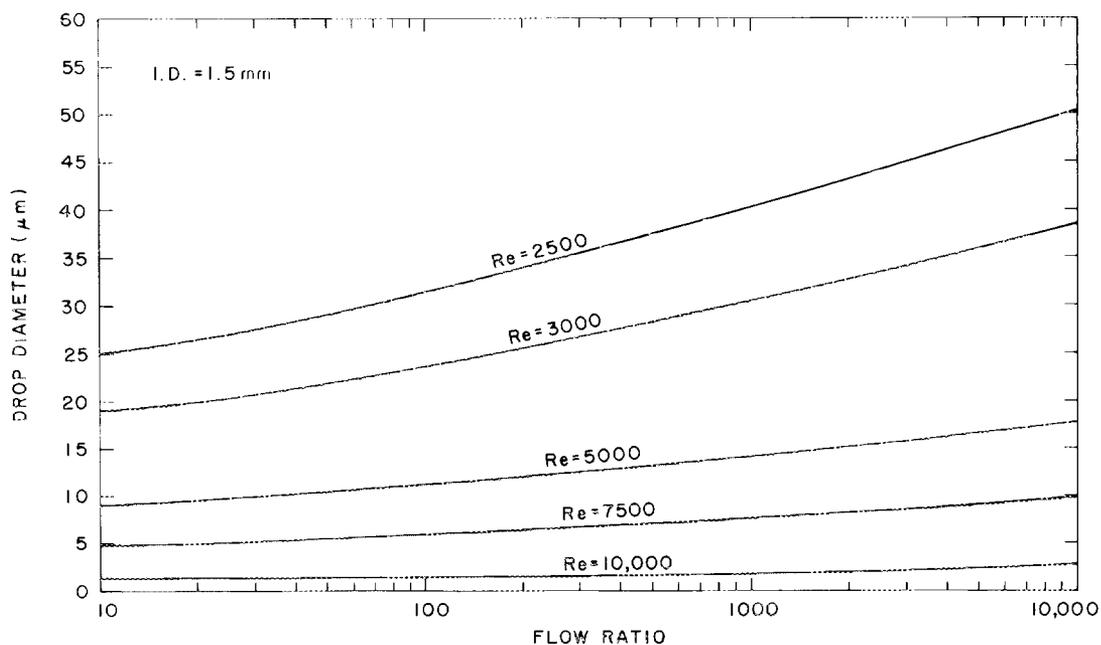


Fig. 14.3. Effect of drive fluid/sol volumetric flow-rate ratio and drive fluid Reynolds number on sol drop diameter.

solid graphite rods 1 to 1½ in. in diameter and 24 in. long. The burner will be adiabatic; all heat will be removed by the flowing gases. The oxygen inlet rate will be fixed, whereas the recycle rate will be varied by an automatic control system to maintain a preset exit temperature for the flue gas. The flue gas will be

cooled, pressurized, and recycled to the burner entrance. The graphite temperature will be measured at several locations, and the off-gas will be continuously analyzed for O₂, CO, and CO₂. A computer program, which was written to simulate the system, will analyze results as they become available.

15. Controlled Thermonuclear Program

The controlled thermonuclear reactor (CTR) studies in the Chemical Technology Division are concerned with tritium and deuterium handling, processing, and containment. Fusion reactors will be required to recycle and purify large quantities of tritium and deuterium unburned in the plasma and to recover, for future use, tritium bred in the blanket system. These operations must be performed with minimal release of tritium into the environment under either normal or emergency operating conditions. This relatively new program for support of CTR development is concerned with process problems of future fusion power reactors as well as problems of near-term experimental and demonstration devices that will be required during the next few decades. In many cases, the handling and processing techniques needed for fusion experiments are the same as those to be used in reactor systems; sometimes, however, simpler techniques can be used in experimental systems. Often the differences associated with the scale of needed systems are such that practical experimental equipment can be designed with more confidence than can equipment for full-scale power systems.

At present, recovery of tritium from the blanket system appears to be the most difficult processing operation. The maximum permeated concentration of tritium in the blanket is very low and is set either by limits on environmental release rates or by economic limits imposed by tritium inventory costs. The unburned plasma recycle system will be required within the next decade. Although it is less difficult than the blanket recovery system, many of the plasma recycle processing steps must be investigated immediately.

The scope of the Chemical Technology Division CTR effort includes conceptual evaluation of tritium systems for fusion power reactors and near-term test reactors, as well as experimental studies of tritium handling techniques. The conceptual studies are especially useful for identifying the most urgent needs of the CTR program and directing the experimental efforts into the most profitable studies. The program also benefits consider-

ably by interaction with related programs within the Thermonuclear, the Chemistry, and the Metals and Ceramics Divisions; significant cooperative efforts have been made with each of these divisions during the past year. Funding for the studies comes from the Division of Controlled Thermonuclear Research (DCTR) and the Division of Physical Research (DPR). Conceptual evaluations and more strictly applied studies are funded by DCTR, while the more fundamental work is supported by DPR. A related study is also discussed in Sect. 14.2.

15.1 SCOPING STUDIES OF A TRITIUM HANDLING SYSTEM FOR AN EXPERIMENTAL FUSION POWER REACTOR

ORNL has initiated scoping studies for an experimental fusion power reactor (EPR) which is expected to begin operation in 1985. These studies are being made to better define the purpose and size of the EPR, the experiments needed, and the relationships between the EPR, the test reactor to be built at Princeton by 1980, and the demonstration reactor tentatively scheduled for operation by 1995.

Tritium Process Requirements

The first step in scoping the tritium systems for an EPR is to estimate the rates of consumption and throughput. Assuming 20 MeV/fusion, the consumption rate is 0.135 g of tritium (or 1300 Ci of tritium per MWd). If the EPR operates at an average thermal power of 150 MW and 1% burn rate, the tritium consumption rate will be about 20 g/day (200,000 Ci/day), and the throughput will be roughly 2 kg/day (20 mCi/day).

An obvious question is whether the projected consumption of tritium in the EPR can be supplied from the then-existing ERDA production channels or whether the EPR will be required to breed its own tritium supply. Unclassified information now indicates that tritium for two years of operation could be provided to the DCTR program from normal ERDA

production channels, assuming that ample notification is given and barring unforeseen higher-priority demands.¹ Therefore, tritium breeding in the EPR is not expected to be an essential part of the plant operation, and preliminary conceptual designs should not be constrained to provide breeding capability. It will, however, be desirable to carry out breeding and recovery experiments in one or more of the several replaceable blanket modules.

One purpose of tritium production experiments in the EPR would be to provide verification in integral experiments of calculational procedures and fundamental neutronic data used to predict breeding in fusion reactors. Another purpose would be to demonstrate tritium confinement and recovery techniques by the small-scale operation of a system with future applicability. Choices for the experimental modules need not be made until several years after the design is selected for the basic EPR machine, and the EPR conceptual design should include a strong emphasis on the primary tritium system.

Process Requirements for Primary Tritium System

The high throughput rate of tritium in the EPR makes recycling within the plant a practical necessity. Assuming that the burn rate is 1% of the throughput rate and that process losses² should be less than 10% of the burn rate, the recovery fraction must be at least 99.9%. Logistics, economics, and safety considerations dictate that the inventory in the process system be as low as is practical. If cryosorption pumps are used, they would have to be regenerated frequently, perhaps daily, and would contain about one day's throughput of tritium (2 kg). Assuming that the inventory in the other process equipment was approximately 2 kg, the total process inventory would be about 4 kg.

The principal tritium handling equipment for the EPR will be vacuum system components. The systems for the EPR could be similar to the cryosorption systems in the ORMAK F/BX conceptual design. Before firm decisions are made on the EPR, however, other storage

systems (e.g., regenerable getters) and process systems (e.g., mercury diffusion pumps) will be examined. Pumping speed and hydrogen isotope storage requirements will affect these considerations. A 1% burn rate and the daily regeneration of vacuum pumps imply a storage capacity on the vacuum pumps of 10,000 liters of hydrogen isotopes. Typical cryosorption pumps associated with this storage capacity would have a total pumping speed of 10,000,000 liters/sec. If this speed is much greater than the EPR Tokamak operation requires, then either special cryosorption pump designs (containing more sieve per unit volume) or lower-speed mercury diffusion pumps will be considered. If cryosorption pumps are used, rapid low-temperature regeneration will be necessary; experiments are under way at ORNL to confirm this point and to evaluate proposed regeneration procedures. Removal of helium from uranium beds will have to be accomplished efficiently in the EPR to avoid loss of tritium to the helium vent. The required percent recovery will be considerably higher in the EPR than in the ORMAK F/BX. Larger quantities of gas could, on the other hand, make a few operations simpler in the EPR. Removal of tritium and deuterium from uranium beds may be possible at higher pressures, perhaps at pressures sufficiently high to permit recycling directly to the feed system.

Isotope separation capability will definitely be required at the EPR site. However, the throughput and separation needed cannot be specified at present because they depend largely upon the still-undefined characteristics of the systems for injection heating and fueling of the plasma. The technology of hydrogen isotope separation is well established, and only a limited amount of development appears to be required for the EPR.

Considerations of other details in tritium handling equipment design will be studied as decisions are made and as information is generated in other parts of the EPR design effort. Items of particular interest to the tritium system design are as follows:

1. primary and secondary vacuum pumping speed requirements,
2. pulse schedule,
3. feed methods (gas fill, injector, and solid fuel),
4. number of feed points,
5. injector capacities and efficiencies,
6. injection ion composition (D-T mixtures or separate injections),
7. purity requirements for feed and injected material.

1. Under USAEC policy, charges to the DCTR program would have been essentially shipping and handling costs; current ERDA policy is presumably the same. Since EPR operation is more than ten years in the future, this policy could change, especially if research and production functions in differing agencies are relocated.

2. Process losses must occur predominantly via discard or waste material rather than by leakage to the secondary containment.

15.2 PREPARATION FOR TESTS OF CRYOSORPTION PUMPING FOR FUSION REACTORS

Cryosorption pumping appears to be the most promising method for achieving the low operating pressures required by fusion reactors and for efficiently recovering tritium and deuterium. After each heating cycle, Tokamaks require large pumps for evacuation of the plasma liner so that unburned hydrogen isotopes may be recovered and recycled.

The cryosorption pumping technique utilizes the condensation of gases on molecular sieves that have been cooled to liquid-helium temperatures (4.5°K). Because such pumps need no lubricants or operating fluids within the vacuum chamber, they are clean, vibration free, and unaffected by magnetic fields. The objectives of this program will be to investigate the operating characteristics of such devices. Investigations will determine pumping speeds and capacities of selected gases at specified pressures and desorptive regeneration requirements. Pumped gases are expected to include the isotopes of hydrogen and hydrogen-helium mixtures.

Basically, the pumping system includes a cryosorption pump, a 6-in.-diam vacuum chamber, millitorr and ultrahigh-vacuum gages, a roughing pump, and a 20-liter/sec noble-ion pump. A mass analyzer probe and constant-leak valve are also attached to the vacuum chamber.

Pumping tests will be preceded by a bakeout period during which the outgassed materials are removed by the roughing system. The cryosorption pump will then be cooled to liquid-helium temperatures, and subsequent experiments will involve the injection of hydrogen into the vacuum chamber at a measured rate to determine pumping speeds. Since this type of pump has a finite capacity, the effects of loading will be observed along with desorptive regeneration characteristics of the cryogenic molecular sieve bed. A residual-gas analyser will be used for periodic testing of the composition of the gas within the vacuum chamber.

15.3 TRITIUM SORPTION STUDIES

The sorption of tritium from the potassium coolant or the lithium blanket by using hydrogen-gettering

metal sorbents appears to be a promising method for recovering tritium bred in fusion reactor blankets. A study of tritium sorption is continuing with experiments that involve batch contacting of tritiated liquid potassium and potential metal sorbents. The metals tested to date have been yttrium, zirconium, uranium, and titanium. As reported previously, none of the metals sorbed any detectable quantities of tritium from molten potassium during contact times of up to four days. An impenetrable oxide barrier apparently forms on the surface of the metal and closes the interior to hydrogen permeation. Coating different zirconium sorbents with nickel, vanadium, and iron did not improve the transport of tritium.

The batch contact of possible sorbent materials with tritiated potassium will continue; however, preparations are also being made to test the effectiveness of potential sorbent materials in tritiated lithium. The relative ineffectiveness of some materials as sorbents or sorbent coatings may improve in lithium, where surface oxides can be more effectively reduced.

15.4 TRITIUM SORPTION IN LITHIUM-ALUMINUM AND LITHIUM-BISMUTH ALLOYS

Lithium-aluminum alloys were proposed for low-tritium-inventory CTR blankets, and lithium-bismuth alloys have been suggested as solvents for extracting tritium from molten-salt blankets. However, insufficient information was available to evaluate the usefulness of either system. An experimental effort was made to obtain some of the necessary data relative to tritium uptake throughout the temperature and pressure range of interest. Neither system showed significant tritium uptake, which made accurate measurements difficult. The results, however, were sufficiently reliable to demonstrate that Li-Bi alloys will not be useful as tritium extractants. Although bulk tritium sorption in Li-Al alloys was desirably low, several observations were made that indicate that additional data will be required before Li-Al is used in CTR blankets. Tritium uptake was highest in samples with large surface areas, and partial dissolution of bulk samples showed higher tritium concentrations near the surfaces. These results can indicate significant surface sorption and/or low bulk diffusion rates. Either could affect the application of Li-Al in CTR blankets.

16. Iodine Studies

16.1 IODINE SORPTION ON CHARCOAL IGNITION AND DESORPTION

Nuclear reactor installations use large quantities of especially impregnated charcoal for cleanup of radioactive iodine during normal operation. A remote possibility exists that charcoal adsorbers would be required to retain larger quantities of radioactive iodine than normally adsorbed if certain postulated accidents occurred for some reactors. Our experimental program is being conducted to determine the effects that such loading (as simulated in the laboratory) would have on the retention of iodine and whether the resulting decay heat would ultimately lead to ignition of the charcoal.

Our experimental method is to load highly radioactive $^{130}\text{I}_2$ on a well-insulated charcoal bed 1 in. in diameter and 2 in. deep. Air is flowed at 33 fpm and 70°C to provide adequate cooling for 2 to 6 hr, while sequentially operated collection traps measure radioactive iodine desorbed from the end of the bed. The air coolant velocity is then reduced to 3.8 fpm (25°C reference) for 3 hr and further reduced to 0.7 fpm (25°C) unless ignition has already occurred.

Previous experiments with nearly dry air showed that the heat from decaying iodine can result in ignition of charcoal and that the amount of iodine desorbed before ignition is usually insignificant. Details of these experiments have been reported.¹

Our test parameters were extended to include higher-moisture-content air as well as charcoal that has been in service and accumulated quantities of adsorbed atmospheric contaminants. The principal results of the recent experiments are summarized in Table 16.1.

The attainment of ignition in our experiments depends upon the simple heat balance of heat input (radioactive decay plus oxidation of charcoal and

organic constituents) vs heat output (air flow and conduction losses). In our apparatus, ignition occurs when the heat input is approximately $15 \text{ cal min}^{-1} (\text{g charcoal})^{-1}$. Since the decay heat in recent experiments is only $1 \text{ cal min}^{-1} (\text{g charcoal})^{-1}$, the importance of oxidation heat is apparent. The presence of moisture reduces slightly the oxidation rate, partly by diluting the oxygen in the air. The experiments with MSA-85851 charcoal show a large reduction in oxidation heat release with moist air, but much of the reduction should probably be attributed to the burnoff of active sites in the charcoal during the longer time required to raise the charcoal bed to the ignition temperature with the lower radioactivity level used in run 8. In contrast to the experiments conducted at 3.8-fpm air velocity, the maximum temperature during each of the experiments that ignited at 0.7-fpm velocity reached a maximum followed by a slow decrease. The calculated oxidation heat release rate decreased during this period, indicating a burnoff of active sites or a combustion poisoning effect. The CHART computer program as modified to include oxidation heat was shown to correctly calculate charcoal bed temperatures.¹

The rate of oxidation heat release varied widely among the charcoals, with the impregnants causing much of the difference. The relatively high potassium content of MSA-85851 and of GX-176 tends to promote oxidation; triethylenediamine (TEDA) in GX-176 oxidizes at temperatures above 150°C . Run 10 used Witco grade 42 charcoal which was removed from the HFIR air cleaning system after four years of service and which contained approximately 130 mg of adsorbed atmospheric contaminants per gram of charcoal. Apparently this material oxidized readily, raising the charcoal bed temperature sufficiently to cause ignition of the base charcoal. Unused charcoal from the same purchase lot did not release measurable oxidation heat in run 9, and the temperature reached a plateau of 186°C .

The movement of radioactive iodine within the test beds was monitored by an ion chamber with a

1. R. A. Lorenzo, W. J. Martin, and H. Nagao, "The Behavior of Highly Radioactive Iodine on Charcoal," *Proceedings of the 13th AEC Air Cleaning Conference Held in San Francisco, August 11-15, 1974*.

Table 16.1. Summary of recent experiments with highly radioactive ^{130}I adsorbed on charcoal

	MSA-85851 ^a		Witco Grade 42 ^d			GX-176 ^a Run 7
	Run 4	Run 8	Run 6	Run 9	Run 10 (from HFIR)	
^{130}I , Ci ^b	1130-970	465-240	650-450	535-270	485-260	810-590
Lowest air velocity, fpm at 25°C	3.8	0.7	0.7	0.7	0.7	3.8
Ignition temperature, °C	300	Not measured	368	Not reached	283	292
Maximum temperature at lowest velocity, °C	575	387	431	186	473	530
Water vapor partial pressure, torr	4	100	3	95	110	4
Oxidation heat release rate, ^c cal min ⁻¹ (g charcoal) ⁻¹						
At 200°C	0.36	0.1	~0.02	Not measured	8	1.2
At 300°C	15	5	1.3	Not measured	40	18
Adsorption coefficient, ^c g I (g charcoal) ⁻¹ atm I ₂ ⁻¹						
At 100°C	4.0×10^5	1.1×10^5	1.0×10^5	1.0×10^5	0.33×10^5	1.0×10^5
At 200°C	2.3×10^3	2.5×10^3	1.5×10^3	1.2×10^3	0.4×10^3	1.5×10^3
Fraction desorbed, ppm						
Elemental iodine	~2	1.6	~10,000	0.5	1600	3.4
Particulate iodine	17	1.2	15	0.5	2.5	10.2
Penetrating iodine	≥3.4	68	≥6.4	63	94 + 1280 ^d	≥5.6
Total	>22	71	~10,000	64	2950	≥19

^aMSA-85851 is a coconut-base charcoal impregnated with approximately 4% (KI + I₂). Witco Grade 42 is a petroleum-base charcoal impregnated with approximately 4% KI. GX-176 is a coconut-base charcoal impregnated with 1% KI, 1% triethylenediamine (TEDA), and a proprietary flame retardant.

^bOne curie of ^{130}I produces a maximum beta radiation intensity of $\sim 5 \times 10^5$ rads/hr in the first $\frac{1}{8}$ -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 $1/T$ (°K) correlation. Some of the listed values are extrapolated beyond the range of experimental data for comparison.

^dThe 94-ppm release was a highly penetrating form of iodine. The 1280-ppm release was a moderately penetrating form similar to CH₃I in adsorption behavior.

collimator that scanned the depth of the bed in $\frac{1}{8}$ -in. increments. From the observed movement within the bed, we calculated the iodine partial pressure and the corresponding linear adsorption coefficient as shown in Table 16.1. The observed differences among charcoals were small; the greatest difference was between runs 9 and 10, which illustrated the deleterious effect of extended service life.

Of great interest in this program is the release of radioactive iodine from the end of the test bed (Table 16.1). The large releases of elemental iodine occurred when beds were operated at high temperature for long periods of time. The amount of particulate iodine released was small, even during ignition. The amount of penetrating iodine (chemical forms such as CH₃I that are not as easily adsorbed as I₂) was small in the low-moisture runs. With a higher moisture content in runs 8 and 9, we discovered that the iodine released during these runs was very poorly adsorbed and was released continuously at a fractional rate of approximately 7×10^{-6} hr⁻¹. This highly penetrating iodine was not detected during the low-moisture runs because of shorter operating times, smaller collection traps, and

concealment by ^{131m}Xe , an ^{131}I daughter that accumulates in the recirculating system. Reexamination of available data from these runs indicates that highly penetrating iodine was present but to a lesser extent. During run 10, which was made with the charcoal from the HFIR, the release rate of highly penetrating iodine was practically the same; however, a much larger amount of CH₃I-like material was released at a continuous fractional rate of 90×10^{-6} hr⁻¹.

Attempts to identify the chemical forms of the highly penetrating iodine have not yet been successful, but various significant characteristics have been observed. The partition coefficient in water (condensate) at 0°C is ≤ 10 g I cm⁻³ of water/g I cm⁻³ of air, and the material did not cold-trap from air at dry-ice temperature or from helium at liquid-nitrogen temperature. A silver-exchanged type 13X molecular sieve collects the material much more efficiently than any of the common types of KI, KI₃, and TEDA-impregnated charcoals. The high-temperature collection on a silver-exchanged molecular sieve shows promise for efficient collection, especially when preceded by an oxidizing catalyst.

16.2 REACTION OF ORGANIC IODIDES WITH HYPERAZEOTROPIC NITRIC ACID

The purpose of this study is to determine the ultimate fate of organic materials in nitric acid systems. Complete recycling of all processing streams involves the possibility of recycling traces of organics that can cause subsequent difficulties in separating fission products, particularly radioiodine. The study is oriented toward the planned LMFBR processing scheme, which includes the removal of iodine by 20 M HNO₃ (Iodox process).²⁻⁵

The effects of solvent and diluent degradation on solvent extraction systems have been widely investigated.⁶ The deleterious effect of traces of organics on iodine separation has been less widely studied, but is well authenticated.^{7,8}

We studied the reaction of hyperazeotropic nitric acid with short-chain aliphatic iodides, nitrates, and acids; these were added to nitric acid, saturated with iodic acid, and refluxed with air sparging to remove volatile products. The off-gas was passed through cold traps and a gas analysis train. Contents of the traps and the reaction vessel were analyzed for organic materials by gas-liquid chromatography and for total carbon. The analyses allowed us to identify compounds and to close the material balance for carbon.

Strong nitric acid converts aliphatic iodides to the corresponding nitrates.⁹ With methyl iodide in 20 M HNO₃, the conversion was 100% within the limits of analytical accuracy. Only traces of CO₂ and CO were found. Except for the acids, longer-chain aliphatic compounds suffered considerable attack. Ethyl nitrate was converted into CO₂ to the extent of 70 to 80%, with acetic acid accounting for most of the remainder;

n-butyl nitrate was converted into CO₂ (40 to 45%), into butyric acid (40%), and the remainder into unidentified species. When the butyl nitrate was added in aliquots to the boiling pot, about 9% was oxidized to butyric acid, 11% to acetic acid, and 30% to propionic acid (Table 16.2). Most oxidation occurred within the first few minutes. Aliphatic acids were rather stable; acetic acid was unattacked by boiling in 20 M HNO₃ for 4 hr, and only 20% of the *n*-butyric acid was attacked. (The carbon from that 20% remained in the reaction vessel in some as-yet unidentified species.)

The factor for separating methyl nitrate from nitric acid solutions by fractional distillation was found to be about 15. Distillation is not practical for separating longer-chain organic nitrates from the acid. We have approached 100% removal of 0.1 M acetic acid, the most refractory of the known short-chain compounds,

2. Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1972, ORNL-4794; *ibid.*, ORNL-4682, pp. 61-62 (1971).

3. Staffs of the Chemical Technology and the Metals and Ceramics Divisions, LMFBR Fuel Cycle Studies Progress Report No. 37, ORNL-TM-3807, p. 11-18 (April 1972).

4. J. C. Mailen and T. O. Tiffany, *J. Inorg. Nucl. Chem.* 37, 127-32 (1975).

5. R. H. Rainey and J. C. Mailen, *J. Chem. Eng. Data* 19, 262-63 (1974).

6. "Symposium on Solvent Extraction Chemistry, Gatlinburg, Tenn., Oct. 23-26, 1962," *Nucl. Sci. Eng.* 16, 381-455 (1963); 17, 234-308, 557-650 (1963).

7. Health Physics and Medical Division, UKAEA Research Group, Harwell, UK, AERE-M-1211 (May 1963).

8. W. A. Rodger and S. L. Reese, *Reactor and Fuel Processing Technol.* 12(2), 173 (1969).

9. N. V. Svetlakov et al., *J. Org. Chem. (USSR)* 4, 1829-33 (1968).

Table 16.2. Oxidation products of organics in 20 M HNO₃

Starting compound	Compounds found in products (% of total C added)					% carbon accounted for
	Unchanged	CO ₂	CO	Organic acids	Other	
Methyl nitrate	~100	Trace	Trace			~100
Ethyl nitrate		73		17, acetic		90.8
<i>n</i> -Butyl nitrate (added in aliquots)	0	41	0	11, acetic; 30, propionic; 9, butyric	<1, methyl nitrate	91.2
<i>n</i> -Butyl nitrate (added before heating)	0	40-45	0	40, butyric		
Acetic acid	100	0	0	0	0	100
<i>n</i> -Butyric acid	80	~2		Trace acetic	~18, unidentified; trace methyl nitrate	~100

from 5 and 8 *M* HNO₃ by wet air oxidation at or above 230°C.

Our work showed that the methyl group is almost unattacked and that other aliphatic groups are oxidized

to carbon dioxide and aliphatic acids by 20 *M* nitric acid. The oxidation-degradation in nitric acid does not destroy the organics completely; special oxidation techniques must be used for this purpose.

17. Reactor Safety Research

17.1 FISSION PRODUCT RELEASE FROM LWR FUEL

This program was initiated in FY 1975 to provide a more detailed understanding of fission product behavior under LWR accident conditions. Safety analyses have emphasized the need for improved information in order to evaluate more accurately the consequences of radioactivity release and to ensure conformance with established guidelines concerning radiological dose to individuals near a power reactor. Determination of the chemical and physical forms of the released fission products will be given particular attention.

Two types of accidents — both involving steam atmospheres — are of interest in this study; spent-fuel transportation accidents might result in rod failures in the 500–700°C temperature range, and in-reactor loss-of-coolant accidents might cause rod failures (and fission product release) at higher temperatures (up to 1500°C). At these temperatures, the source of released fission products is almost entirely that inventory accumulated in the pellet-clad gap region of the fuel rod

during long periods of normal reactor operation. While additional information at even higher temperatures (1500 to 2500°C) is of interest, no experiments at this level are currently planned.

The initial effort in this program included a literature survey of existing data, previously used experimental techniques, and available methods for characterizing the chemical and physical forms of the fission products under test conditions. A work plan summarizing the state of the art and outlining the proposed experimental program was prepared and submitted to the Nuclear Regulatory Commission (NRC) in draft form for review. The revised work plan, incorporating comments made during the review, was transmitted to the Office of Nuclear Regulatory Research (ONRR)-NRC on March 7, 1975.

In preparation for the experimental studies, a contaminated hot cell was cleaned and repainted, and the necessary equipment was installed. A schematic diagram of the apparatus is shown in Fig. 17.1. All components of the experimental system were checked for proper operation and found to be satisfactory. A series of

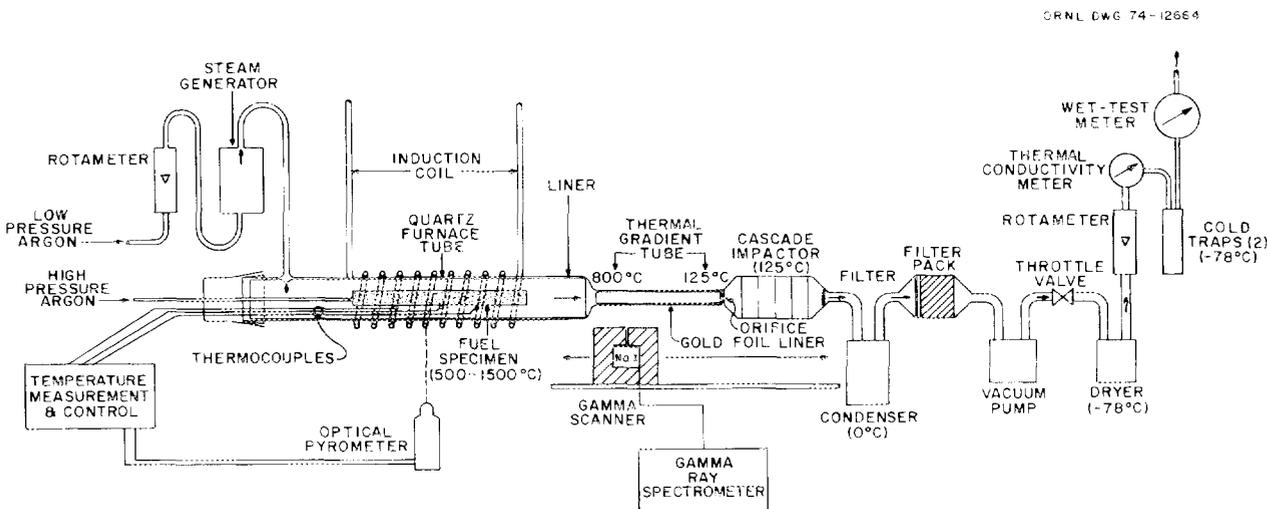


Fig. 17.1. Apparatus for studying fission product release from irradiated LWR fuel rods.

control tests will be conducted to ensure accurate calibration and interpretation of the characterization techniques, such as deposition in a thermal gradient, particle size classification in a cascade impactor, chemical analysis of the steam condensate, and gamma-ray spectrometry of all samples. Electron spectroscopy and x-ray diffraction will be utilized for compound identification where appropriate. Both irradiated and unirradiated (with fission products implanted) fuel specimens will be ruptured by internal gas pressure at elevated temperatures in later tests.

Irradiated fuel specimens currently available for testing are limited in utility because of low burnup (~1000 MWd/metric ton) or low linear thermal power (<160 W/cm) during irradiation. Therefore, in order to better simulate prototypical conditions, we requested two fuel rods from the fully irradiated H. B. Robinson No. 2 fuel assembly being acquired by ONRR-NRC. Detailed specifications for the examination, sectioning into short lengths, and resealing for testing of these rods were prepared and submitted to three different hot-cell facilities for cost estimates; based on their estimates, a subcontract is being negotiated to conduct this work in FY 1976. Thus, a supply of PWR-irradiated fuel specimens spanning the burnup range 10,000 to 30,000 MWd/metric ton will be available for testing.

A limited, parallel set of experiments to investigate the chemical forms of fission products released from UO_2 is being pursued using a Knudsen cell-mass spectrometer technique. Identification of the cesium species evolving from mixtures of UO_2 powder and elemental cesium, Cs_2O , and CsI over the temperature range 700 to 1300°C is the primary objective of this program. These tests will necessarily be performed in vacuum.

17.2 TRANSIENT RELEASE FROM LMFBR FUEL

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

It is desired to experimentally produce an energy deposition in LMFBR fuel that is characteristic of a severe hypothetical reactor transient by applying direct electrical current to mixed oxide fuels in the presence of sodium. The program includes tests with and without sodium, investigations of alternative methods for generating fuel and sodium aerosols, the use of UO_2 as a fuel

stimulant, and parallel underwater and undersodium efforts to study the behavior of, and possible attenuation effects within, the vapor bubble itself.

The release experiments will make use of several different vessels of various sizes. The primary fuel aerosol vessel, which has been designated as CRI-III, is being fabricated. Because fuel aerosols must be secondarily contained and the tests must be conducted in a hot cell, CRI-III is necessarily relatively small (i.e., <1 m³ in volume). A larger vessel, CRI-II, which has a volume of several cubic meters, will be used for ex-hot-cell comparative-size-effect aerosol studies in which U_3O_8 aerosols will be generated from metallic uranium reacting with oxygen.

Experimental Program

Cold proof tests. Cold proof tests of UO_2 aerosol behavior are being performed to determine the operational reliability and precision of our aerosol characterization equipment and techniques. Additionally, the results of these tests provide a basis for evaluating some of the input terms in the HAA-3B code.¹ Examples of the type of information used as computer input, and of the sensitivity to the effective particle density, are shown in Fig. 17.2.

In the initial tests, U_3O_8 aerosols were used at concentrations of about 3 g/m³ in a 70-liter auxiliary vessel. The objectives of these tests are to check out and calibrate some of our aerosol instrumentation. Very encouraging performance was indicated for a split-fiber optic device to be utilized for measuring particle concentrations. The measurements compared favorably with HAA-3B calculations. Comparison with actual concentrations will be made when analytical results for the samples taken during the tests become available.

The full-size aerosol test chamber in the present series of tests is a 1200-gal stainless steel vessel, designated as CRI-II. The aerosol is generated by inductively heating 1-cm cubes of metallic uranium under vacuum conditions to incipient melting and then vigorously oxidizing the sample by admitting oxygen gas; the oxygen also serves to transport the airborne fraction of the oxides into the vessel.

Scoping tests made at the Arnold Engineering Development Center. A key item in the program is development of the capacitive discharge vaporization (CDV) technique to produce amounts and rates of energy depositions in fuel samples characteristic of an HCDA.

1. T. D. Hubner, E. V. Vaughan, and L. Baumash, *HAA-3 User Report*. AI-AEC-13038 (Mar. 30, 1973).

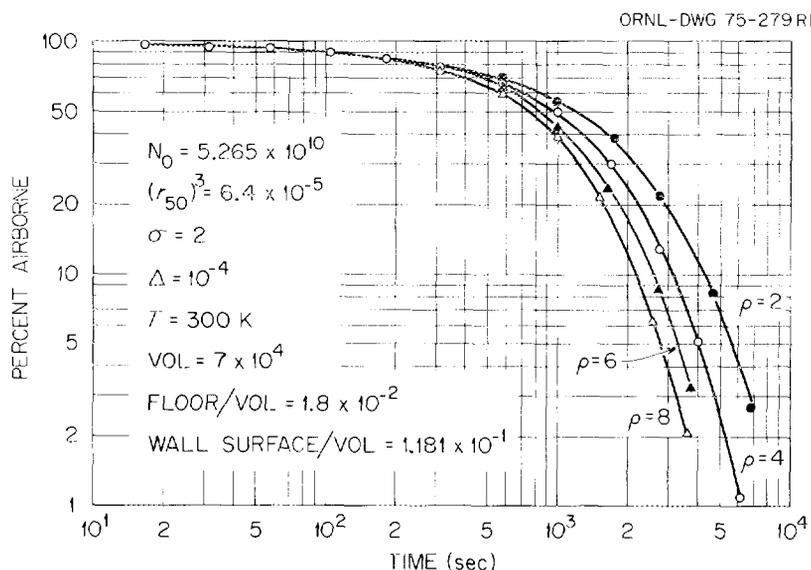


Fig. 17.2. Effect of U_3O_8 aerosol density on deposition behavior predicted by HAA-3B.

Toward this end, arrangements were made to use existing equipment at the Arnold Engineering Development Center (AEDC) for scoping tests on fuel vaporization. Their von Karman facility was reactivated, and the required changes were made to adapt the capacitor banks for our project.

The first three of a planned series of four groups of tests were completed. These tests were designed to study the effects of preheat temperature, capacitor power and voltage, and system resistance to rupture by pressure buildup. While not all of the tests were successful with regard to vaporizing a significant amount of fuel, sufficient information was obtained to give reasonable assurance of the viability of the CDV technique for energy deposition and subsequent fuel vaporization.

The three series of tests were expected to emphasize, successively, the effects of (1) UO_2 preheat temperature, (2) capacitor energy and voltage, and (3) sleeve resistance to rupture by pressure generation. With somewhat surprising case, the first series performed gave encouraging results; and a significant yield ($\sim 2\%$ of the fuel pellet weight) of submicron UO_2 particles was obtained, although the energy deposition in the fuel was relatively inefficient.

In the second series, the initial tests gave highly efficient energy deposition (75 to 80%) but, disappointingly, no disassembly or aerosol. After some consideration we concluded that, in addition to enhanced thermal conductivity due to the type of fuel, the samples were probably too massive, being about twice

the weight of the first successful shot. Therefore, additional energy was scheduled for the final trial, which was made with a different fuel loading. This test, No. 6, was much more successful, since about 10% of the pellet stack was vaporized. During this test, some rather significant observations concerning aerosol behavior were made, including the measurement of both agglomerated and primary particle sizes.

Five additional fuel vaporization tests were conducted at AEDC. Descriptions of fuel assemblies used for all of the AEDC tests of interest, along with the data collected for each test, are given in Table 17.1. (Note that all conclusions reported here are preliminary and subject to change after further assessment.)

Test 6 was housed in a quartz containment sleeve of 2-mm wall thickness. The setup gave a good aerosol yield which we hoped to increase in tests 7 and 8 by using quartz containment of 4-mm wall thickness. These tests differed from one another only in that test 7 employed 40 wt % UO_2 pellets along with microspheres, whereas test 8 utilized only UO_2 microspheres as fuel simulant. In each case, disassembly was observed within about the same time and energy input range as in test 6, but the new tests appeared to yield less aerosol.

The AEDC series included preliminary tests to determine what effect(s) the cladding material might have during fuel vaporization. For this purpose, we added stainless steel to the UO_2 microspheres in test 9. In this case, the energy input before disassembly was more than twice the highest input experience previously, and the aerosol yield appeared to exceed that obtained in

Table 17.1. Test conditions and preliminary results for AEDC fuel vaporization experiments

Shot number	Capacitor bank		Sieve		UO ₂ mass (g)	Deposited energy (kJ)	Disassembly time (msec)	Results	
	Energy (kJ)	Voltage (kV)	Material	ID (mm)					OD (mm)
2	42	2	Al ₂ O ₃	9	12	22	9.1	~1.1	About 200 mg of UO ₂ vaporized
5A	42	2	Quartz	14	18	46	29.6	No disassembly	Center melted; 30% void
5B	42	2	Quartz	14	18	46	29.6	No disassembly	Center melted; some liquid expelled
6	84	2.8	Quartz	11	15	38	~9.7 + (18) ^a	~0.7	~1 to 2 g vaporized
7	71	2.6	Quartz	10	18	15.2	9.2	0.65	~0.5 g vaporized
8	71	2.6	Quartz	10	18	24.6	10.7	0.8	~0.5 g vaporized
9	71	2.6	Quartz	10	18	16.5	22.9 ^b	1.5	~1 to 2 g vaporized
10	51	2.2	Quartz	6	10	14.6	11.7	1.8	~0.5 g vaporized
11	71	2.6	Quartz	8	37	25.3	12.3	1.5	~0.1 g vaporized

^aEfficiency of postdisassembly energy deposition is uncertain.

^bContained 2.6 g of stainless steel filings mixed with UO₂ microspheres.

test 6. The observed improvement is thought to be due to a lower resistivity-temperature coefficient resulting from the presence of the stainless steel. This would tend to flatten the radial temperature profile and significantly reduce the power density along the center line of the fuel during the electrical discharge.

Test 10 represented an attempt to reduce the heating power level without significantly decreasing the voltage and the stored energy in the capacitor bank. Hence, to increase the electrical resistance of the assembly, a longer and smaller-diameter fuel assembly was employed. Although a reduction in total power level was observed, the aerosol production appeared to be about the same as that observed during test 8.

The sample of fuel simulant used in test 11 was contained in a heavy (14-mm-thick) quartz tube along

the front 60 mm of the assembly. The thickness of the quartz containment was reduced to 1.5 mm for the last 20 mm of length at the low-voltage end of the assembly. The intent was to cause the thin-walled area to rupture first, allowing the current at the ruptured end of the assembly to be carried by a low-impedance arc. The results were disappointing in that complete disassembly apparently occurred after about the same energy input as in test 10, and with a lower aerosol yield.

Additional tests at AEDC will be conducted with various material and voltage combinations in an effort to further improve the efficiency of the CDV process. Design and construction of the comparable ORNL high-voltage facility were initiated.

18. Nuclear Regulatory Commission Programs

18.1 DEVELOPMENT OF "AS LOW AS PRACTICABLE" (ALAP) 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 ALAP guidelines for the release of radioactive materials from all segments of the nuclear fuel cycle. Three draft reports are expected to be submitted to the NRC in July and August 1975, as follows: *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing "As Low As Practicable" Guides -- Conversion of Yellow Cake to Uranium Hexafluoride; Reprocessing of High-Temperature Gas-Cooled Reactor Fuel Containing Uranium-233 and Thorium*; and *Fabrication of High-Temperature Gas-Cooled Reactor Fuel Containing Uranium-233 and Thorium*. These reports are expected to be issued to the nuclear industry, governmental agencies, and the public for comment in FY 1976 after they have been reviewed by the NRC and revised at ORNL. Four previous reports (one of which contains two volumes) in this series¹ were prepared for issue as ORNL-TM documents in May 1975. 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 typical and normal 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.

18.2 SAFETY REVIEW OF NUCLEAR FACILITIES

The Chemical Technology Division, with support from the General Engineering, Health Physics, and Instrumentation and Controls Divisions, is providing technical assistance to the NRC, Division of Materials and Fuel Cycle Facility Licensing, in assessing the safety of fuel cycle facilities and in preparing generic reports on these facilities.

During this report period, we participated in the review of safety analysis reports accompanying license applications for a construction and operating permit to

1. The previous reports in this series are: B. C. Finney, R. E. Blanco, R. C. Dahlman, F. G. Kitts, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing "As Low As Practicable" Guides -- Nuclear Fuel Reprocessing*, ORNL-TM-4901 (May 1975); W. H. Pechin, R. E. Blanco, R. C. Dahlman, B. C. Finney, R. B. Lindauer, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing "As Low As Practicable" Guides -- Fabrication of Light-Water Reactor Fuel from Enriched Uranium Dioxide*, ORNL-TM-4902 (May 1975); M. B. Seats, R. E. Blanco, R. C. Dahlman, G. S. Hill, A. D. Ryon, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing "As Low As Practicable" Guides -- Milling of Uranium Ores*, ORNL-TM-4903, vol. 1 (May 1975); A. D. Ryon and R. E. Blanco, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing "As Low As Practicable" Guides -- Appendix A. Preparation of Cost Estimates for Volume 1, Milling of Uranium Ores*, ORNL-TM-4903, vol. 2 (May 1975); W. S. Groenier, R. E. Blanco, R. C. Dahlman, B. C. Finney, A. H. Kibbey, and J. P. Witherspoon, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing "As Low As Practicable" Guides -- Fabrication of Light-Water Reactor Fuels Containing Plutonium*, ORNL-TM-4904 (May 1975).

perform major modifications at the Nuclear Fuel Services (NFS) West Valley Fuel Reprocessing Plant and to operate the modified NFS plant, and operating permits for the Allied General Nuclear Services Barnwell Fuel Reprocessing Plant and the Allied General Nuclear Services Barnwell Fuel Receiving and Storage System. Specific areas of review were: (1) ventilation and off-gas treatment, (2) radioiodine control, (3) instrumentation and controls, (4) liquid- and solid-waste treatment, (5) process, (6) radiological protection, (7) accidents, and (8) normal and emergency utility support systems.

18.3 SAFETY REVIEW OF TRANSPORT CASKS

The design of each shipping container expected to transport significant quantities of radioactive material

must be reviewed and approved by the Transportation Branch of the NRC. The NRC review covers all areas of cask design and analysis. On occasion, the Transportation Branch will request that ORNL review certain parts of these safety analysis reports for packagings and transmit the resulting evaluation to them. During this report period, we made a review of the pressure relief device on the GE IF 300 spent-fuel shipping cask. In addition, we completed a detailed computer analysis of the shielding capabilities of concrete and a Chemtree compound² for a given source of neutrons and gamma rays.

2. Shielding compound marketed by the Chemtree Corporation, Central Valley, N.Y. 10917.

19. Diffusion of Adsorbed Species in Porous Media

The long-range goal of this program is to gain an understanding of the controlling mechanisms for migration of strongly adsorbed species in porous media. Diffusion of cesium through graphite components of gas-cooled reactors is an example, since most of the cesium activity in HTGR cooling circuits¹ results from cesium isotopes that leak out of coated fuel particles^{2,3} and seep through graphites surrounding the fuel regions. In this program, cesium transport is being studied at temperatures ranging from 600 to 1000°C, wherein cesium could exist at least initially as a metallic vapor, but more likely as a mobile adsorbed species on graphite surfaces. One objective is to ascertain an approximate vapor-phase to adsorbed-phase transport ratio. Another objective concerns the development of a phenomenological model that will aid in the analysis of results from various HTGR surveillance programs. Cesium migration modes have been found to be strongly dependent on the type of graphite under study.

Some comparative results are shown in Fig. 19.1. Curve I on the figure presents data for a low-gas-permeability graphite resulting from furfuraldehyde impregnation of a base stock material (Hawker-Siddeley graphite). Curve II presents data for a high-gas-permeability graphite (Great Lakes H-327) used as a structural graphite in the Fort St. Vrain HTGR.

The transient situation utilized in a portion of our analyses derives from the differential mass balance relationship given by

$$D \frac{\partial^2 C_p}{\partial x^2} = \epsilon \frac{\partial C_p}{\partial t} \quad (1)$$

The units selected for the constants and variables in Eq. (1) are somewhat specialized, since the system is set up to allow easy inclusion of gas-phase contributions. Thus the diffusion coefficient, D , has units of pore volume per time-bulk length product. The concentration, C_p , has units of moles (gaseous and adsorbed cesium) per pore volume; the variable bulk length, x , along the diffusion path, is the position coordinate. Finally, ϵ represents the porosity or pore to bulk volume ratio, and t represents time.

Experiments are initiated by placing cesium, with about 30% of the ¹³⁷Cs isotope, on the surfaces of diffusion specimens in the form of cesium oxides derived from an aqueous solution. During heating to the diffusion anneal temperature under pure helium, the oxide converts (at about 500°C) to the metal, which produces an impulse with strength Q_0 , moles per cm² of surface area normal to x . If the diffusion anneal time is short, the solution to Eq. (1) is simply

$$C_p(x, t) = \frac{Q_0}{\sqrt{\pi D \epsilon t}} e^{-x^2 \epsilon / 4 D t} \quad (2)$$

The preexponential term is the time-variable surface concentration $C_p(0, t)$. Conversion to bulk concentrations, $C'(x, t)$, is accomplished by multiplying both sides of Eq. (2) by ϵ .

Slicing up small specimens to determine concentration profiles directly can be an extremely arduous and time-consuming task — particularly when one must contain and collect quantities of contaminated dry graphite dust. We prefer to section by grinding away portions of the specimens (using kerosene as a cutting fluid) and measuring FR , the fraction of total activity remaining, as a function of grinding distance. The subsequent equation is

$$FR = (1/Q_0) \int_x^\infty C'(x', t') dx' = \operatorname{erfc} \left(\frac{x}{2 \sqrt{\frac{\epsilon}{Dt}}} \right) \quad (3)$$

1. H. J. de Nordwall, J. O. Kolb, F. F. Dyer, and W. J. Martin, "Fission Product Behavior in the Coolant Circuit of the Peach Bottom HTGR," *GCR Programs Progr. Rep. Dec. 31, 1972*, ORNL-4911 (March 1974).

2. R. B. Evans III and M. T. Morgan, *Mathematical Description of Fission Product Transport in Coated Particles During Postirradiation Anneals*, ORNL-4969 (June 1974).

3. M. T. Morgan, H. J. de Nordwall, and R. L. Towns, *Release of Fission Products from Pyrocarbon Coated HTGR Fuel Particles During Postirradiation Anneals*, ORNL-TM-4539 (December 1974).

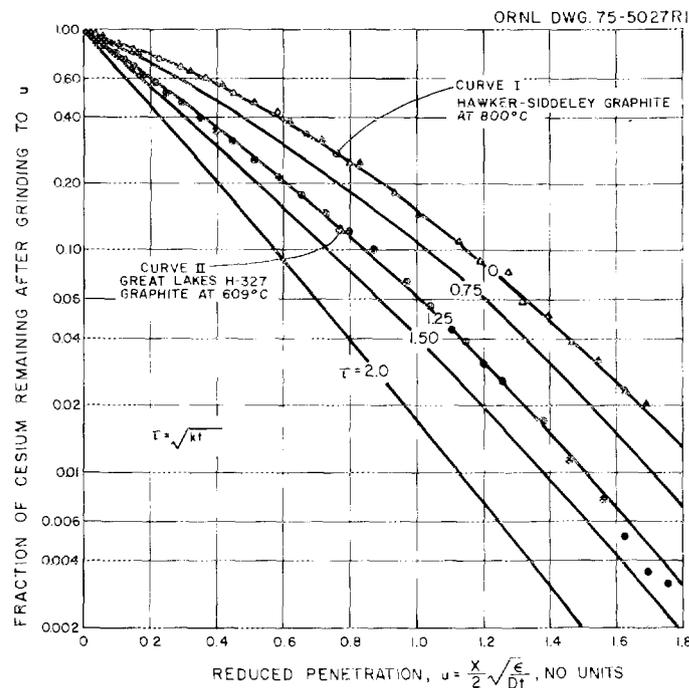


Fig. 19.1. Graphical presentation of cesium penetration data for two different nuclear-grade graphites. All solid curves represent solutions of Eq. (5) for various τ values. Data on curve I are for two diffusion specimens that exhibited idealized, $\tau = 0$, behavior. Data on curve II indicate plate-out or trapping effects.

A plot of this function appears as the $\tau = 0$ curve on Fig. 19.1 (i.e., curve I). All the Hawker-Siddeley graphite data fall on the curve for Eq. (3), and nearly all the ^{137}Cs tracer, as Q_0 , was engaged in the diffusion process. Additional information appears in Table 19.1. Note that the diffusion coefficients are based on the determination of the factor by which the experimentally determined x values must be multiplied in order to make them fall on the correct u values at appropriate FR values. This factor is $\sqrt{\epsilon/4Dt}$.

Based on considerations set forth by Rodliffe⁴ and Wichner⁵ using extrapolated gas-adsorbed phase equilibrium data for cesium-graphite systems, one must conclude that gas-phase transport is negligible in the case of data for curve I. Most of the cesium diffuses along surfaces in a highly idealized fashion.

When the same experiments are performed with H-327 graphite, notable deviations from idealized behavior are observed. First, only part of the Q_0 , placed

on the surface initially, diffused into the specimen; the residual was immobilized and remained very close to the $x = 0$ surface. Second, the profiles tended to be linear with penetration and did not exhibit the downward curvature (on semilog paper) that one would expect if Eqs. (2) and (3) were being followed. In fact, the curves are reminiscent of those obtained when one examines profiles for an immobilized daughter of a very mobile noble-gas precursor after diffusion into graphite under quasi-steady-state conditions.⁶ The conclusion is obvious; a trapping effect must have been occurring at the $x = 0$ surfaces and along internal pore surfaces as well. To account for these effects, deep profile data were extrapolated back to $x = 0$ to eliminate specimen surface trapping effects. Then possible mechanisms of internal trapping were explored. The first inclination was to add a first-order-reaction rate term like

$$r_t = \epsilon k(C_p - KC_t) \quad (4)$$

to the right-hand side of Eq. (1) and then to examine applicability of the integrated results. Here, r_t is the

4. R. S. Rodliffe, *The Effect of Flow on Mass Transport of an Absorbing Radioactive Species in a Porous Medium*, United Kingdom CEGB Report, RD/B/N2375, 27:12479 (September 1972).

5. Chem. Tech. Div. Internal Communication, R. P. Wichner to R. B. Evans III (December 1974).

6. R. B. Evans III, J. L. Rutherford, and A. P. Malinauskas, *Gas Transport in MSRE Moderator Graphite Parts II and III*, ORNL-4389, p. 32, Fig. 13 (May 1969).

Table 19.1. Cesium diffusion results for two nuclear-grade graphites as shown on Fig. 19.1

Migration parameters	Curve I Hawker-Siddeley graphite (impregnated)	Great Lakes graphite (H-327)
Diffusion time, min	1260	70
Penetration, x , at $FR = 0.5$, cm	0.093	0.096
Bulk diffusion coefficient D/ϵ , cm^2/sec	1.2×10^{-7}	7.9×10^{-6}
Amount of tracer ^a Q_0 , $\mu\text{moles}/\text{cm}^2$	3.66×10^{-3}	$(1.83 \times 10^{-3})^b$
Final surface concentration $C'_T(0, t')$, $\mu\text{moles}/\text{cm}^3$	2.10×10^{-2}	1.28×10^{-2}

^aCesium-137 isotopes plus nonradioactive species.

^bAmount engaged in diffusion process; total amount was 2.37×10^{-3} $\mu\text{mole}/\text{cm}^2$.

trapping (or plate-out) rate, and KC_T represents a "back pressure" term. Considerations of long-term results suggest that the latter might be negligible. Accordingly, the integration was carried out using only the first term. The result for C_p was merely Eq. (2) multiplied by e^{-kt} for the mobile fraction. Grinding experiments

"see" both immobile and mobile fractions; so the total bulk concentration was computed via

$$C'_T(x, t) = \epsilon C_p e^{-kt} + \epsilon k \int_0^t C_p e^{-kt'} dt', \quad (4a)$$

which yields

$$\frac{C'_T(x, t')}{C'_T(0, t')} = \frac{e^{-(u^2 + \tau^2)} + (\sqrt{\pi}/2)\tau [e^{-2u\tau} \text{erfc}(u - \tau) - e^{+2u\tau} \text{erfc}(u + \tau)]}{e^{-\tau^2} + (\sqrt{\pi})\tau [1 - \text{erfc}(\tau)]}, \quad (4b)$$

where

$$u = (x/2)(\sqrt{\epsilon/Dt}),$$

$$\tau = \sqrt{kt}.$$

The corresponding fraction-remaining expression for our sectioning procedure is

$$FR = e^{-2u\tau} + (1/2) [e^{2u\tau} \text{erfc}(\tau + u) - e^{-2u\tau} \text{erfc}(\tau - u)]. \quad (5)$$

Figure 19.1 shows that data for H-327 graphite give a good correlation when one assumes a value of $\tau = 1.25$ (curve II) for this particular experiment. This gives a positive indication that the trap model, as explained above, is an adequate representation of cesium migration behavior in the H-327 material. The same model has been used by General Atomic to correlate long-term in-pile experiments, using the same graphite but dif-

ferent boundary conditions.⁷ However, a rather poignant feature of performing long-term experiments with H-327 graphites should be noted. After a relatively short time, the value of τ overwhelms the value of u . Complementary error functions like $\text{erfc}(\tau \pm u)$ fade away at $\tau > 2.0$; diffusion information from discrete u values is lost; and the only information that can be gained in this case is a value for the grouping, $2u\tau/x$, which is obtained from the slope of the curves on Fig. 19.1 at high τ values [see also first term of Eq. (5)]. The value of this group is $\sqrt{\epsilon k/D}$. While this value may comprise adequate information for reactor analyses, it is not sufficient for mechanistic studies. It would appear that a complete picture of cesium diffusion in highly permeable graphites can only be gained through properly timed laboratory experiments.

7. C. F. Wallroth, N. L. Baldwin, C. B. Scott, and L. R. Zumwalt, *Postirradiation Examination of Peach Bottom Fuel Test Element FIE-3*, USAEC Report GA-A13004 (August 1974).

20. Miscellaneous Programs

20.1 RESOURCE STUDIES

The Chemical Technology Division continued to contribute to ORNL interdivisional efforts on resources and energy analyses. Preparation of a 400-page book, *World Energy Conference Survey of Energy Resources, 1974*, was completed in August 1974 by H. E. Goeller and W. L. Carter. This work, sponsored by the AEC Office of Planning and Analysis, included a world review of coal, oil, gas, oil shale, hydraulic, nuclear, and renewable (solar, wind, tidal, geothermal, and ocean thermal gradient) energy resources with new estimates from 70 nations that cooperated in the effort. About 5000 copies of the book were printed by McGregor and Werner, Washington, D.C.; 2500 copies were distributed to attendees from nearly 100 countries at the World Energy Conference held in Detroit in September 1974, and the remainder are on sale by the Joint Engineering Council, New York, and the World Energy Conference Central Office in London.

ORNL will in all likelihood continue in the preparation of future surveys, provided that funding can be arranged. Members of the World Energy Conference are anxious that we continue this work but are also entertaining proposals from other national committees.

The Division, represented by H. E. Goeller, also participated in the LMFBR Program Review Group at AEC Headquarters during the fall of 1974, particularly with regard to a reevaluation of U.S. and world reserves and resources of uranium and thorium and their adequacy for a nonbreeder energy industry. It was generally concluded that without the introduction of commercial breeders in the early 1990s, U.S. and world resources of nuclear fuels will be insufficient to supply a nonbreeder industry beyond the early decades of the next century. This work is summarized in ERDA-1, *Report of the Liquid-Metal Fast Breeder Reactor Program Review Group* (January 1975).

Early in 1975, H. E. Goeller became a member of the ORNL Program Planning and Analysis Office and is continuing general studies on nonrenewable resources.

The purpose of these studies is to seek out areas where there is an early need of resource conservation, improved recycling of metals and development of substitutes for those elements in jeopardy of exhaustion, and to determine where ORNL expertise and facilities may be sequestered to provide needed research and development.

H. E. Goeller is also participating in a study on the rational use of potentially scarce metals being conducted by the Scientific Affairs Division of the North Atlantic Treaty Organization (NATO). This study is examining the present world demand, production, consumption, and uses of about a dozen scarce metals and is appraising the possibilities for increased recycling and substitution, particularly for dissipative uses. A substudy on mercury has now been completed. The findings of the NATO study group will be summarized in a report scheduled to be completed by the end of the calendar year.

20.2 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 convince the public that the package behavior can be predicted with confidence. The ERDA Division of Waste Management and Transportation (WMT) has organized an advisory committee to provide guidance for the program.

In the past year, a 7000-lb cask was tested twice by dropping it from 30 ft onto an armor-plate surface of a reinforced concrete impact pad at the ORNL drop test facility. These drops provided engineering data and information on the adequacy of the instrumentation used to record dynamic data throughout the test program.

Drops of heavier casks will take place at the Tower Shielding Facility (TSF), which has a great lifting capacity but has lacked a surface upon which to drop casks. A study of the capacity of the TSF indicates that casks possibly weighing as much as 40 tons could be dropped from about 240 ft. Results of the study were submitted to an internal (ORNL) safety review committee and approved. Based on this study, a complete safety analysis was written and is being submitted to the Oak Ridge Operations Office of ERDA for approval.

A 23-ton Heavy-Water Components Test Reactor (HWCTR) cask was received from the Savannah River Operations Office. A test plan was then written and submitted to the WMT advisory committee. Based on their comments, the plan was updated and the cask was modified.

A temporary impact pad, weighing about 110,000 lb, was designed and installed at the TSF to accommodate some interim testing. We expect to make several drops of a 7000-lb cask to study the behavior of the temporary impact pad and the towers under drop conditions. The Paducah release mechanism will be used to make these drops. This mechanism was redesigned and remodeled to increase its lifting capacity to more nearly match the capability of the towers. Following these initial tests, the HWCTR cask will be dropped 30 ft at an oblique angle onto the temporary impact pad in accordance with the approved test plan. Both the cask and towers will be instrumented to monitor their behavior.

20.3 DISPOSAL OF ORNL RADIOACTIVE WASTE BY HYDRAULIC FRACTURING

A study was conducted in FY 1974 to verify that a site proposed for a new Shale Fracturing Disposal Facility at ORNL was suitable for hydrofracture operations. An injection well and four monitoring wells were drilled and cased, and a test injection was made using a grout tagged with radioisotope tracer. The results of the study indicate that the proposed site is satisfactory.

At ORNL, intermediate-level waste solution (waste with a specific activity of between 1.5×10^{-6} and 2.0 Ci/gal) is being disposed of by the shale fracturing

process. In this process, the waste solution is mixed with cement and injected into an impermeable shale formation at a depth of about 800 ft. There the waste grout sets, fixing the radionuclides in the cement matrix. Subsequent injections form new grout sheets adjacent and parallel to the earlier grout sheets.

The existing Shale Fracturing Disposal Facility has worked quite well for the disposal of intermediate-level waste but cannot handle either slurries or wastes with a specific activity higher than 2 Ci/gal. The need for a disposal system for these types of waste is imminent, and a new shale fracturing facility is being proposed. A part of the preliminary planning for the facility is verification of the suitability of the selected site by a demonstration that the strata are suitable, that injection pressures will not be excessive (>5000 psi), and that the fractures formed by the injection will conform to the bedding planes (essentially horizontal). Demonstration of these criteria requires a "site proof" injection of 50,000 to 100,000 gal of water or grout tagged with a radionuclide tracer that can be detected at observation wells several hundred feet from the injection well. The orientation of the fracture can then be verified by the comparative depths of the injection and point of detection.

Four observation wells and an injection well were drilled, cased, and cemented at the site of the proposed new disposal facility, which is about 800 ft southwest of the existing shale fracturing site. The observation wells were located 200 ft north, south, east, and west of the injection well. All of the wells deviate considerably from vertical; however, in general, the five wells form a parallel system quite suitable for determining the orientation of injected grout sheets. The overall trend of the wells is to the north-northwest (local north) updip to the southeasterly dipping rocks.

The two methods considered for making the injection were: mixing and injecting the grout at the new wellhead, or mixing the grout at the existing facility and pumping it overland to the new well. The second method was chosen because better control of the grout mixture could be achieved by making use of the instrumentation at the existing facility. In the first option, the formidable logistical problem of supplying blended solids to the mixer at a fast and constant rate could be avoided, and recently installed modifications at the existing facility could be evaluated during an injection of essentially nonradioactive grout. A flow diagram of the equipment arrangement for the injection is shown in Fig. 20.1.

The injection proceeded smoothly. A total of 65,700 gal of water was mixed with the stored solids and

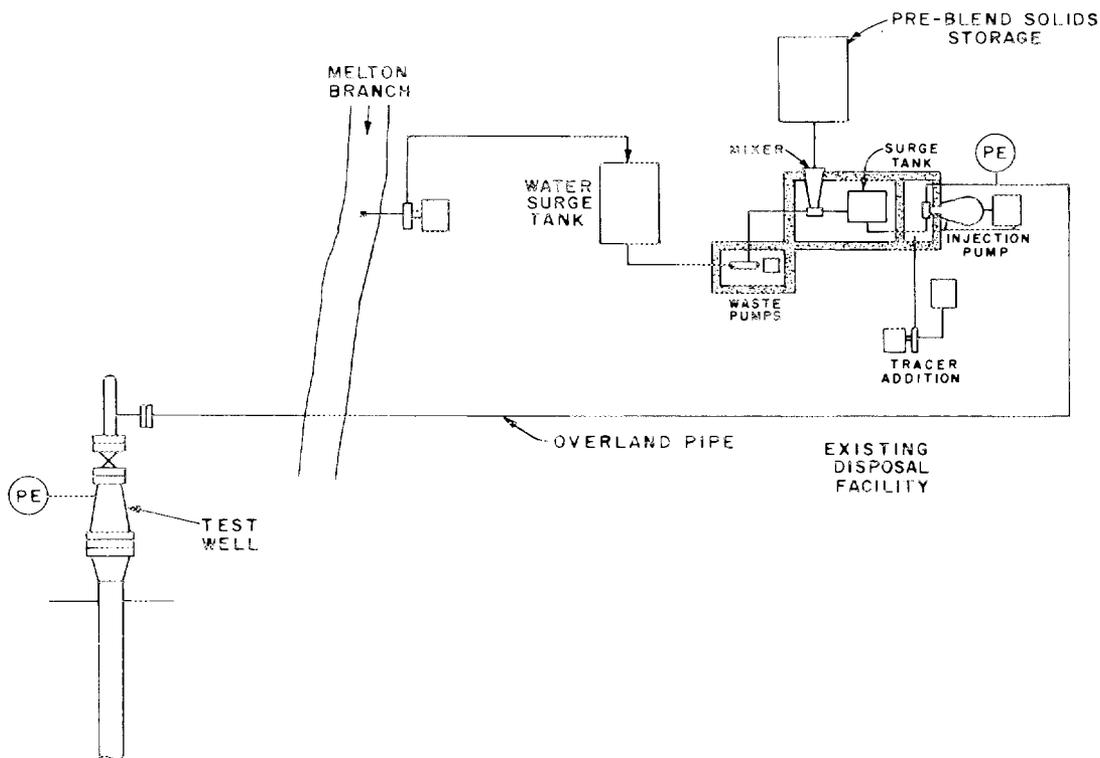


Fig. 20.1. Flow diagram of equipment arrangement for injection.

injected. The injected grout volume was 97,643 gal. The injection rate averaged 247 gpm at an average pressure at the facility of 2900 psi.

The results of the test injection were entirely favorable. The injection pressures were slightly less than had been anticipated. The fracture moved out parallel to the bedding and to the structure of the area by advancing to the three observation wells in which it was detected. This means that there can hardly be any important folding in the Pumpkin Valley shale, at least at the depth of the test. The completed investigations and tests show clearly that the proposed new site is well suited to waste disposal by hydraulic fracturing, as had been anticipated from earlier experiences in the general area.

20.4 STORAGE, PURIFICATION, AND DISTRIBUTION OF ^{233}U

Oak Ridge National Laboratory serves as a national distribution center for ^{233}U . The facility includes shielded wells for storing up to 454 kg of ^{233}U in solid

form (density = 1 g/cm^3) and tanks (containing borosilicate glass for neutron poisoning) that can store 900 kg of ^{233}U in the form of uranyl nitrate solution at ^{233}U concentrations up to 250 g/liter. The Building 3100 vault, designed for storage of unirradiated fissile materials according to the latest AEC specifications,¹ was placed in service during this report period.

The storage facility accepts ^{233}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 ^{233}U at the rate of 25 kg/week. An ion exchange and nitrate-to-oxide conversion line, with a capacity of 22 kg of ^{233}U

1. R. W. Horton and J. R. Parrott, *Criticality and Safety Analysis: Building 3100, A Storage Vault for Uranium and Plutonium*, ORNL-TM-3929 (February 1973).

per week, was placed in operation for the Light Water Breeder Reactor (LWBR) support program.²

Receipts of ^{233}U during this report period other than those involved in the LWBR program (Sect. 7.1) consisted of 1.1 kg of uranium as ^{233}U oxides, 0.6 kg of $^{233}\text{UO}_2\text{-PuO}_2$ (U/Pu \approx 5) fuel, and 0.5 kg of normal uranium metal in five shipments.

As of March 31, 1975, 859.1 kg of ^{233}U and 801.7 kg of ^{235}U were stored at the facility. Of these, 101.6 kg of ^{233}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 six years, the uranium concentration remained constant. During the past year, the soluble neutron poisons, cadmium and gadolinium, apparently decreased to about two-thirds of the required concentration; therefore, more had to be added.

In addition to the ^{233}U and ^{235}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.

20.5 CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIVES

The Chemical Technology Division has participated in the Plowshare Program for several years by studying the potential behavior of radionuclides in underground applications of nuclear explosives. Our participation in the program was terminated during the past year. Experimental studies were completed of tritium behavior during in situ recovery of oil from oil shale, and a paper describing our studies of radionuclide behavior in copper recovery from ores was submitted for publication in the *Transactions of the Society of Mining Engineers of AIME*. The abstract follows:

"Radionuclide Behavior in Copper Recovery with Nuclear Explosives," by W. D. Arnold and D. J. Crouse. *Abstract:* The potential behavior of radionuclides released in an underground nuclear detonation to fracture copper ore for subsequent in-situ leaching and copper recovery was studied with regard to contamination of the copper product and hazards to operating personnel. The laboratory test results indicate that only small fractions of the radioactive fission products would be dissolved on leaching the ore. Tritium (as tritiated water) would be the dominant radionuclide in the circulating leach liquor, assuming use of a fusion explosive. The test results showed solvent extraction to have important advantages over cementation for recovering copper from the leach liquors. While the radioactivity of the copper metal product produced by either method should be extremely low, the solvent extraction process provides a more effective separation of copper from the radioactive contaminants and entails fewer radiation protection problems. For these reasons, it is the preferred process.

A possible mechanism for tritium contamination of shale oil is penetration of tritiated water vapor into the pores and fractures of the shale, followed by incorporation of part of the tritium into the hydrocarbon structure of the oil when the kerogen breaks down during retorting. Whereas tritiated water on or near the shale surfaces can be removed before oil recovery by washing the shale with water or by injecting water into the system during retorting,³ tritiated water that penetrates into the shale is less easily removed. Tritiated water penetrated to the center of a 7-cm cube (500 g) of oil shale in a 43-day exposure to 0.25 g of water vapor containing 95 μCi of tritium, at 85°C. The tritiated water entered the shale from all directions, but slightly more along the bedding planes than across them. Analyses of core samples taken along the major axes through the center of the cube showed that tritium contamination of the shale decreased with depth, from 0.137 $\mu\text{Ci/g}$ near the surface in the two cores taken along the bedding planes and 0.115 $\mu\text{Ci/g}$ in the core taken across the planes, to 0.054 $\mu\text{Ci/g}$ at the center.

20.6 PREPARATION OF TRAINING GUIDES FOR NUCLEAR FACILITY PERSONNEL

The *Guide to the Selection, Training and Licensing or Certification of Reprocessing Plant Operators* was prepared for distribution by the ERDA Division of Operational Safety (DOS). The rough draft 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, and it appears that the final draft can be presented to DOS with very little alteration.

At present, a guide for fuel fabrication plant operators is being written and is scheduled for completion in rough draft form during the first quarter of 1976. Similar guides are planned for milling and mining, feed preparation, enrichment, fuel storage, and transportation sections of the nuclear fuel cycle.

Proposals for FY 1976 include production of video tapes and brochures for training operators in many sectors of the nuclear industry. The tapes and brochures would be produced mainly by Chemical Technology Division personnel for distribution by the DOS and would be available as an aid for training programs in use

2. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1972*, ORNL-4794, pp. 52-53.

3. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1974*, ORNL-4966, p. 71.

by commercial processors and reprocessors of nuclear fuel.

**20.7 ENVIRONMENTAL IMPACT STATEMENT
ON THE U.S. NUCLEAR POWER
EXPORT PROGRAM**

An environmental impact statement (EIS) on the U.S. nuclear power export program is being prepared by the *Division of International Programs*. The EIS will cover 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 being prepared by the Chemical Technology Division include the section that provides a general description of the nuclear fuel cycle and the sections that describe

the operation of fuel fabrication plants under normal and accident conditions. Plants fabricating fuel for light-water-cooled reactors with and without plutonium recycle and for high-temperature gas-cooled reactors are considered. The section on the nuclear fuel cycle will supply as much detail as necessary to give the lay reader a grasp of the technical nature of the cycle. The sections on fuel fabrication will describe the environmental, economic, social, and other secondary impacts of plants committed to fulfilling foreign requirements. Environmental considerations include the radionuclides released by the plants and the associated dose commitments of the general population. Nonradioactive effluents or wastes produced by the plants and their effect on the environment are also considered.

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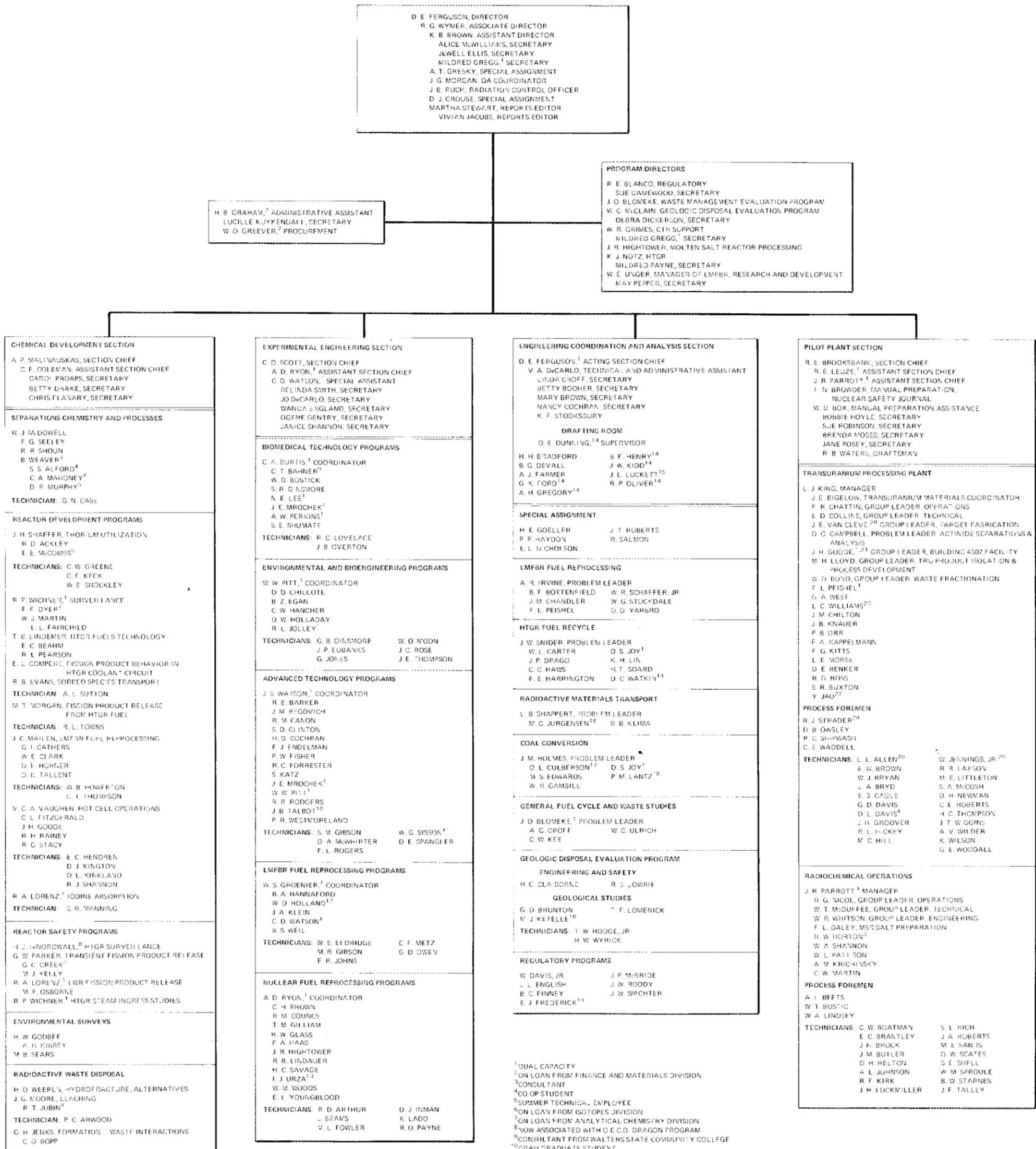
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