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Chemical Technology DIVISION

Annual Progress Report

PERIOD ENDING MARCH 31, 1974

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for Plutonium and Uranium

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CHEMICAL TECHNOLOGY DIVISION

ANNUAL PROGRESS REPORT

for Period Ending March 31, 1974

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AUGUST 1974

OAK RIDGE NATIONAL LABORATORY
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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, 1973–March 31, 1974. Further information regarding work in the various programs can be obtained from the topical reports and journal articles cited in the references.

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1. Development of Aqueous Processes for LMFBR 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 *Aqueous Fuel Reprocessing Quarterly Reports for Periods Ending: June 30, 1974; September 30, 1974; December 31, 1974;* and *March 31, 1974* (ORNL-TM-4301, -4394, -4488, and -4587). 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 on head-end reprocessing and fuel refabrication, 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. It has been reported separately in monthly GCR documents, as well as in Section 1 of the *Gas-Cooled Reactor Programs Annual Progress Report for the Period Ending December 31, 1973* (ORNL-4975).

3. Molten-Salt Reactor Program

Oak Ridge National Laboratory is developing a molten-salt breeder reactor (MSBR) which would operate on the ^{232}Th-^{233}U fuel cycle. The Molten-Salt Reactor Program was interrupted for about a year from January 1973 to January 1974; hence, there was no activity in this area during much of the current report period. Consequently, we will simply outline briefly the work which is scheduled to be undertaken in the near future in the Chemical Technology Division.

The Chemical Technology Division's efforts in the Molten-Salt Reactor Program will fall into three main categories:

1. The establishment of the basic chemical information necessary to suggest and to demonstrate methods for management and control of tritium, to assess the effects of fission product behavior on MSBR operation, and to develop coolant-salt technology using fluoroborates or alternative fluids.
2. The development of processes and associated technology to economically remove protactinium and fission products from MSBR fuel salt.
3. The preparation of purified salt to be used for experiments in all parts of the Molten-Salt Reactor Program.

3.1 MOLTEN-SALT REACTOR CHEMISTRY

Fission product tellurium has been shown to be involved in the surface cracking of Hastelloy N that is exposed to the MSRE fuel salt.[1] In order to determine the role of tellurium in the corrosion of Hastelloy N, plans have been formulated for measuring the solubility of tellurium in MSBR fuel salt and for determining the effect of redox potential of the salt on the nature and concentration of tellurium species. Equipment has been built to expose metallurgical samples to tellurium vapor under various conditions. The first specimens will be exposed for 1000 hr under conditions such that the rate of tellurium deposition on the specimen is low. Exposed specimens will be given a preliminary inspection before detailed examinations and analyses are made by members of the Metals and Ceramics Division.

Equipment has been assembled for studying the exchange of deuterium and tritium with protonated species dissolved in the proposed coolant salt ($NaBF_4$), and for investigating the reactions related to potential corrosion by HF and BF_3 dissolved in molten $NaBF_4$. Various alternative coolant-salt mixtures such as BeF_2-NaF-LiF, ZrF_4-KF-NaF, and Li_2CO_3-Na_2CO_3-K_2CO_3 are being assessed and compared with respect to (1) compatibility with structural metals, (2) engineering performance (heat transfer, fluid flow, cost, etc.), (3) potential for tritium retention, and (4) compatibility with MSBR fuel salt and with steam. Laboratory space has been renovated and apparatus has been constructed for measurement of the solubility products of oxides of protactinium and other actinides in MSBR fuel salt.

3.2 MSBR FUEL PROCESSING

In order for the reactor to operate as a breeder, ^{233}Pa must be isolated from the region of high neutron flux during its decay to ^{233}U. Also, the rare-earth fission products must be removed on a 25- to 100-day cycle. Processes that use fluorination of the fuel salt and liquid-liquid extraction of the fluorinated salt with bismuth containing reductant appear to offer the best means toward this end;[2] consequently, we will resume studies designed to develop such an approach.

Work was resumed for study of the formation of frozen layers of salt for protecting continuous fluorinators from corrosion. The nonradioactive demonstration of continuous fluorination will require a heat source that is not subject to attack by gaseous fluorine within the molten salt in the fluorinator. It had been established earlier that autoresistance heating of the

1. H. E. McCoy, *MSR Program Semiannu. Progr. Rep. Aug. 31, 1972,* ORNL-4832, p. 63.

2. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973,* ORNL-4883, p. 14.

molten salt could be used for this purpose.[3] Six experiments previously carried out with $LiF\text{-}BeF_2$ (66-34 mole %) in a 48-in.-long, 6-in.-diam vertical test section yielded resistance values, heat generation rates, and general operating conditions that were in close agreement with predicted results.[4] A 6-in.-diam fluorinator simulation having a short (24-in.) test section had been constructed for verifying the final parameters for a frozen-wall fluorination experiment.[5] This experiment was resumed near the end of the current report period. Although completely successful operation with MSBR fuel carrier salt [$LiF\text{-}BeF_2\text{-}ThF_4$ (72-16-12 mole %)] has not yet been achieved, the results are encouraging, and it is believed that the system is operable.

Equipment was fabricated and installed for operating metal transfer experiment MTE-3B. In this experiment, we will use equipment very similar to that used for experiment MTE-3 and will determine the reason for low mass transfer rates seen in the latter experiment.[6] Salt and bismuth flow rates will be about 1% of the estimated flow rates required for removing rare earths from a 1000-MW(e) MSBR.

In the proposed flowsheet for processing MSBR fuel,[2] the fuel reconstitution method involves, first, reacting gaseous UF_6 and fluorine evolved in the fluorination step with UF_4 dissolved in salt and, then, reducing the resulting higher-valent uranium species to UF_4 with gaseous hydrogen. Experiments conducted with molten $LiF\text{-}BeF_2\text{-}ThF_4$ (72-16-12 mole %) at 600°C indicate that the stoichiometry of the reaction with UF_6 is[7]

$$UF_4(d) + UF_6(g) = 2UF_5(d) \qquad (1)$$

and that the reaction proceeds rapidly. It was also shown that gaseous hydrogen reacts with dissolved UF_5 as follows:

$$2UF_5(d) + H_2(g) = 2UF_4(d) + 2HF(g) \qquad (2)$$

This reaction proceeds more slowly than reaction (1). Gold was found to be sufficiently stable for use in studying reactions (1) and (2) but to be severely corroded when gaseous fluorine is introduced. We will continue these studies of the chemistry of fluorination and reconstitution. Laboratory facilities required for the safe handling of UF_6 and F_2 in fluorination and fuel reconstitution studies are being renovated. Apparatus for these studies has been designed, and fabrication has begun.

We have initiated a search for economical methods of providing gold equipment for carrying out engineering studies of the recombination of UF_6 and molten salt. Gold electroplating and cladding with thin gold foil were examined as methods for protecting nickel or stainless steel equipment from the corrosive effects of the intermediate compound UF_5.

Plans for providing chemical assistance to the Gas-System Technology Facility and the Coolant-Salt Technology Facility have been formulated. Laboratory facilities have been made available for conducting scouting tests to determine the compatibility of materials such as graphite and molybdenum with MSBR process fluids in support of the Processing Materials Program.

Conceptual designs are being drawn for a new engineering laboratory in which efforts to develop the fuel processing methods can be extended to larger scales. The process concepts have been established by laboratory experiments; reduction of these concepts to practice requires an extensive engineering development program since every aspect of the proposed process represents an extrapolation of only small-scale technology. The available work areas for chemical and engineering development of MSBR fuel reprocessing are small and widely separated. They are adequate only for laboratory work, small bench-scale engineering experiments, and tests of half-scale individual process equipment units. The proposed new laboratory will allow for the necessary engineering development of full-scale, integrated processing steps.

3.3 SALT PREPARATION FACILITY

The Molten-Salt Reactor Program is now being funded at a level that allows developmental work, using various compositions of molten salt, to proceed. The salt preparation facility will be reopened to satisfy this need.

The processing equipment located in Building 9201-3 was previously operated to blend and purify salt mixtures for use in a variety of programs as well as in much experimental and developmental work. The facility was shut down after the preparation of the salt charge for the Molten Salt Reactor Experiment. Because of the long downtime and the long prior service times of much of the equipment, we are renovating all units that will be used in the immediate future and reestablishing such documentation as is required.

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3. J. R. Hightower, Jr., *MSR Program Semiannu. Progr. Rep. Feb. 29, 1972,* ORNL-4782, p. 232.
4. J. R. Hightower, Jr., *MSR Program Semiannu. Progr. Rep. Aug. 31, 1972,* ORNL-4832, p. 180.
5. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973,* ORNL-4883, p. 29.
6. Ibid., p. 23.
7. M. R. Bennett and L. M. Ferris, *MSR Program Semiannu. Progr. Rep. Aug. 31, 1972,* ORNL-4832, p. 165.

4. Waste Management

4.1 GEOLOGIC DISPOSAL EVALUATION PROGRAM

The Chemical Technology Division's participation in radioactive waste disposal investigations has been redirected during the past year. The Radioactive Waste Repository Project has become the Geologic Disposal Evaluation Program, with a consequent change in emphasis from facility planning and design to broader-based studies of geologic disposal options. During the period of this report, more detailed investigations of the feasibility of the tentative site in southeast New Mexico have been undertaken along with an expanded scope which gives consideration to other salt deposits. In addition, a greatly expanded program covering borehole dissolutioning and advanced techniques for plugging abandoned wells has been initiated.

Geologic Investigations

Two exploratory boreholes are currently being drilled in southeast New Mexico. The hole that was being planned for last summer[1] was postponed until March 1974 as the result of an activation of interest in hydrocarbons in the vicinity of the study area. Specifically, a wildcat well (dry hole) was drilled 0.5 mile from the border of the tentative site. In order to increase the distance from this hole, the boundaries of the study area were moved approximately 2 miles. After the nine-month delay, a borehole (AEC No. 7) was initiated on March 19, 1974, at the northeast corner of the study area. The program for the hole included drilling to 1000 ft (the top of the salt formations), water testing in this hole, followed by casing of this portion of the hole, and coring from the salt top approximately 1000 ft to a total depth of approximately 4000 ft. The water tests conducted by the Hydrology Branch of the U.S. Geological Survey (USGS) indicated that there was very little water movement in the rocks overlying the salt at the location of the hole. The core recovery of the evaporite section was excellent, and preliminary analysis of the cores shows at least two very pure halite zones in the lower portion of the Salado formation. The second borehole, AEC No. 8, planned for the southwest corner of the site, will follow immediately after the completion of AEC No. 7; it will provide core from the land surface to approximately 2500 ft.

Other geologic investigations of the southeast New Mexico area during the year have concentrated on vulnerability of the salt formations to dissolutioning both from subsurface water movement and from downcutting surface streams. The results of the subsurface dissolutioning studies indicate that the most rapid lateral migration of the salt formation front is taking place in a west to east direction toward the site, but at a mean calculated rate of less than 2 miles in a million years. The accompanying vertical dissolutioning rate is estimated to be 80 ft in a million years. Considering these rates and the maximum estimates of surface erosion, the proposed disposal horizon at approximately 2000 ft appears to be safe for a period longer than 1,000,000 years.

In addition to the investigations of the southeast New Mexico site, consideration by the USGS was given to two other areas of bedded salt deposits in New Mexico, Clovis-Portales and Mescalero Plains. These areas were selected because the salt formations were present without the commonly associated hydrocarbon deposits. However, preliminary investigation of the salts indicated that they were not of sufficient thickness or purity to be considered.

The scope of the geologic investigations has been broadened for the coming year. It is anticipated that the program will be expanded to include assessment of salt domes (in the Gulf Coast region), salt anticlines (in the Paradox basin of southeast Utah and southwest Colorado), and other rock types, especially shales, granites, and limestones.

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973*, ORNL-4883, p. 33.

Borehole Dissolutioning and Plugging

The problem posed by abandoned boreholes penetrating through and beyond salt formations has been the subject of growing interest throughout this report period.

An extensive examination of existing plugging techniques and materials was conducted during the year, and this effort led to a sophisticated plugging demonstration of one of our exploratory holes in Kansas, AEC No. 1. The emplaced plug consisted of salt-saturated, sulfate-resistant Chem Comp cement opposite the salt formations, with short sections of epoxy positioned at the bottom and top of the salt to act as gaskets to absorb shock and maintain a seal in the critical salt section. To ensure maximum life of the plugging job, the steel casing in the upper 300 ft of the hole was removed by overcoring, and a neat Chem Comp cement was placed opposite the formations overlying the salt.

The future program in borehole dissolutioning and sealing includes investigations of new materials (e.g., rock melts, natural earthen materials, and pseudosalt plugs); explorations of actual cases of borehole dissolutioning in Kansas and theoretical studies to quantify the phenomenon; review of current practices in plugging; and investigation of techniques for emplacement and testing for durability of plugs.

Stored Energy

One of the questions that has been raised with respect to the suitability of salt for purposes of waste disposal is whether any stored energy which might be accumulated in the salt immediately surrounding a waste package due to gamma irradiation could be released in such a manner as to cause serious thermal excursions or other undesirable effects. Available information indicated that the amounts of stored energy and the conditions under which it could be released (annealed) were such that no safety hazards would be involved. To provide firmer and more detailed information, we conducted experiments in which samples of salt were irradiated under several different sets of exposure conditions of dose rate, dose, and temperature, and then analyzed for stored energy using a specially constructed calorimeter.[2] Postirradiation thermal annealing characteristics were investigated by exposing some of the irradiated samples at elevated temperatures prior to measuring the stored energy.

Our experimental results showed that energy storage in repository salt will depend on the temperature of the salt during irradiation as well as on the dose rate and the dose in the salt. Three different ranges of exposure temperatures with energy storage characteristics peculiar to the particular range were distinguished. Energy storage in the salt in the first range, which includes all temperatures above about 150°C, will be negligible. Some radiation energy can be stored in salt in the second range, which lies between about 120 and 150°C; extrapolations of our data indicate that the amount stored will reach saturation at 18 to 20 cal/g. Still larger amounts of radiation energy can be stored in the third temperature range, which is that below about 120°C; extrapolations of the few experimental data in this range indicate that the amount will reach saturation at about 60 cal/g. Semiempirical equations that correlate the experimental data for the respective temperature ranges and provide bases for extrapolations are as follows:

$$E = 17.8[1 - \exp(-9.3 \times 10^{-11} D)] - I^{-1}[2.06 \times 10^{26} \exp(-1.96 \times 10^{4}/T)] \times [1 - \exp(-9.3 \times 10^{-11} D)] ,$$

$$E = 17.8[1 - \exp(-9.3 \times 10^{-11} D)] ,$$

$$E = 60[1 - \exp(-8.5 \times 10^{-11} D)] ,$$

where E is the stored energy, cal/g; D is the radiation dose, rads; I is the dose rate, rads/hr; and T is the absolute temperature, °K.

In practice, the salt around each waste package in a repository will generally have a temperature greater than 150°C and, accordingly, will contain negligible amounts of stored energy. Some packages on the periphery of the repository will have salt temperatures less than those within the normal burial area due to their semi-isolation from thermal effects of other packages within the repository. However, the temperature of the salt around these peripheral packages will not be below 120°C in zones of significant dose.

If a package is effectively isolated from the thermal effects of other packages, the temperature of a fraction of the adjacent salt will be below 120°C for at least a portion of the period during which significant doses are accumulated. However, a preliminary analysis of the effects of a sudden release of 60 cal/g from isolated low-temperature packages indicates that no serious consequences would ensue. The salt would not melt during the release, and thermal and mechanical perturbations would be relatively small and brief.

2. G. H. Jenks and C. D. Bopp, *Storage and Release of Radiation Energy in Salt in Radioactive-Waste Repositories*, ORNL-TM-4449 (January 1974).

4.2 FRACTIONATION OF WASTES

A new program was originated this year to investigate the feasibility of fractionating high-level wastes generated by commercial nuclear fuel reprocessing plants into components that are more manageable in terms of long-term hazards and storage requirements. Specifically, the actinides and possibly some long-lived fission products are to be removed from high-level wastes to such a degree that the hazard of these wastes is substantially reduced at times of 1000 years or greater. During the current report period, the primary emphasis was centered on determining the degree of actinide removal necessary, the most promising process methods available, the primary unsolved separations problems, and the development program needed to accomplish these separations. Thus far, studies have been concerned with high-level waste from LWR fuel reprocessing; in the future, however, they will be expanded to include LMFBR and HTGR fuel reprocessing wastes. This program will provide part of the necessary technological basis for evaluation of waste management alternatives currently under study by the Atomic Energy Commission.

On the basis of the duration of the long-term hazard, there is potential merit in the use of separations processes that will greatly reduce the losses of fissile and fertile values to the high-level waste in conventional reprocessing of reactor fuels and, in addition, will separate the high-level waste into fission product and actinide fractions. Such separations could potentially alleviate the long-term storage of the remaining fission products since, following solidification and only 500 to 1000 years of storage, these materials would have a specific radiological toxicity comparable to deposits of naturally occurring minerals and ores. A storage period of 500 to 1000 years is a time span for which the effects of geologic, climatic, and other natural phenomena can reliably be extrapolated. On the other hand, the hazard index of untreated high-level wastes from conventional reprocessing remains as great as or greater than that of uranium minerals for more than 1,000,000 years. The actinides recovered from these wastes could be recycled to reactors for burnup to shorter-lived fission products or could be disposed of in a special manner that takes into consideration their relatively low heat generation rate but very long half-lives.

We have completed a preliminary determination of the actinide removals from spent reactor fuel required to reduce the hazard index[3] of waste at 1000 years to less than 5% of the hazard index of pitchblende ore and have made a partial evaluation of the feasibility of accomplishing this task. The feasibility study was directed primarily at high-level waste generated by the commercial reprocessing of LWR fuel. For pressurized-water reactors utilizing equilibrium plutonium recycle, the following removals are required from fuel irradiated to a burnup of 33,000 MWd/metric ton: 99.9% of the iodine, 99.9% of the uranium, 99.99% of the plutonium, 95% of the neptunium, and 99.9% of the americium and curium. Conceptual processes were developed from published data. Laboratory studies were utilized to determine applicability of processes where literature data are lacking. Results obtained from the study revealed a number of areas which will require considerable research and development in order to accomplish the necessary separations.

Calculations were made to determine the percentage removal of each actinide element (in different reactor fuels) that would be required to reduce the hazard index of the wastes to less than 5% of that of pitchblende after storage for about a thousand years (see Table 4.1). Further reduction of actinide content would not be warranted unless one also removed the very long-lived fission products: ^{99}Tc, ^{93}Zr, ^{135}Cs, and additional ^{129}I. Wastes from all of the fuel types require removal of uranium, plutonium, neptunium, americium, and curium; in addition, HTGR wastes require removal of thorium and protactinium. It was assumed in the calculations that all unrecovered actinides from the processing of 1 metric ton of LWR, LMFBR, and HTGR fuels were present in 2, 3, and 6 ft^3, respectively, of solidified high-level fission product

3. The hazard index of a mixture of radionuclides is defined as the quantity of water required to dilute a unit volume of the mixture to the ingestion Radiation Concentration Guides (RCG) given in the *Code of Federal Regulations,* Title 10, Part 20, Appendix B, Table II, for unrestricted use of water.

Table 4.1. Percentage removals required to reduce the hazard index of aged wastes to less than 5% of that of pitchblende[a,b]

Actinide	PWR-U[c]	PWR-Pu[c]	LMFBR[d]	HTGR[e]
Th				95.5
Pa				95.0
U	99.9	99.9	99.9	99.99
Np	95.0	95.0	70.0	95.0
Pu	99.95	99.99	99.99	99.9
Am and Cm	99.0	99.9	99.9	95.0

[a]Pitchblende is a mineral containing 60% uranium.
[b]Assumes 99.9% removal of fission product iodine.
[c]Burnup, 33,000 MWd/metric ton.
[d]Burnup, 41,200 MWd/metric ton.
[e]Burnup, 94,300 MWd/metric ton.

waste. It was also assumed that 100% of the tritium, krypton, and xenon, and 99.9% of the iodine, were removed during conventional reprocessing and did not report to the solidified waste.

In conventional, commercial reprocessing by solvent extraction, approximately 99.5% of both the fissile and the fertile values are recovered from solutions of either uranium-plutonium or uranium-thorium fuels. All other actinides are usually not recovered but are discharged to the high-level fission product waste along with the 0.5% of the unrecovered fissile and fertile values of the fuel. Minimum additional recovery factors of 5, 50, 20, 1000, and 1000 are needed for the uranium, plutonium, neptunium, americium, and curium, respectively, that are present in the high-level waste generated by the reprocessing of LWR fuels (33,000 MWd/ton, plutonium recycle). Separation processes presently in use give recoveries of 90 to 99% for neptunium, americium, and curium.

The current conceptual sequence for removing the actinides from LWR wastes initially involves recovery of about 95% of the neptunium along with the economic values of uranium and plutonium in a conventional plant using the Purex solvent extraction process (Fig. 4.1). Then, if technically feasible, essentially complete removal of the residual uranium, neptunium, and reactor-bred plutonium is accomplished using additional stages of Purex extraction. The actinides removed by this exhaustive extraction are recycled to the primary Purex plant. Next, the wastes are stored for a period of three to four years to reduce radiation damage to process reagents, solvents, or ion exchange resins in subsequent operations. During storage, plutonium grows back into the wastes by decay of curium and will

ORNL DWG 74-3054R

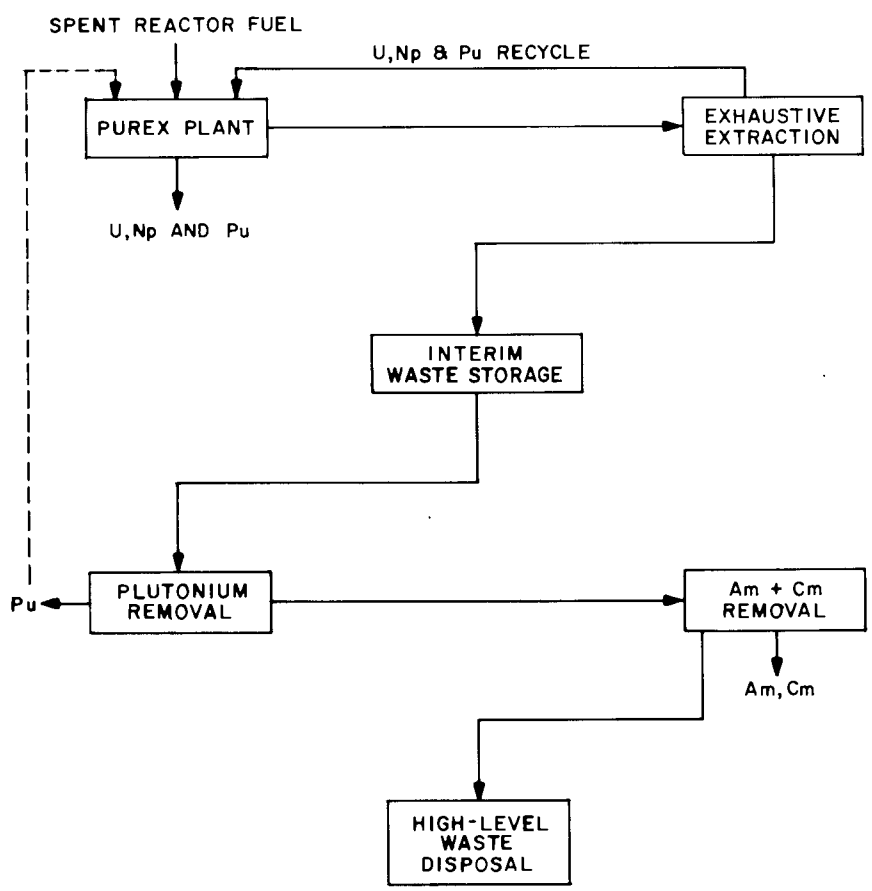

Fig. 4.1. Conceptual processing sequence for the removal of actinides from LWR reactor fuel.

again require removal. In the following step, yet undefined, it is visualized that the daughter plutonium and any plutonium remaining after the exhaustive extraction step would be removed. The plutonium recovered here, depending on its isotopic composition, may or may not be recycled to the primary Purex extraction. The americium and curium are removed following the final removal step for the plutonium, probably by solvent extraction or cation exchange chromatography (CEC). The candidate solvent extraction processes that are being considered involve extraction by tributyl phosphate (TBP) from feed solutions salted with aluminum nitrate and extraction by di(2-ethylhexyl)phosphoric acid from carboxylic acid solutions.

Studies of conceptual flowsheets for the removal of actinides by the proposed sequence have revealed a number of difficult problems that will have to be solved both in laboratory- and engineering-scale tests. These problems result from the actinide-bearing residues produced by incomplete dissolution of fuel and from the chemical changes that occur in solutions of actinides and fission products during processing and the recycle of process chemicals and solvents. More complete recovery of plutonium has been inhibited in conventional reprocessing by the presence of nonextractable forms which have not yet been identified but may consist of colloids, complex ions, precipitates, and sorbed species that are generated during the process steps. Certain fission products, such as zirconium, tin, and molybdenum, may be hydrolyzed and precipitated during the processing and must be satisfactorily dealt with (perhaps by prior removal) at process conditions of low acidity where actinides might be carried. Processes for recovering americium and curium require feed solutions of low acidity, and their losses to precipitates formed by phosphate ions from hydrolysis and degradation of TBP in the previous processing and by hydrolysis of fission products must be prevented. Methods are needed to provide improved valence control of neptunium for extraction. Alternatives for the ferrous sulfamate reductant that is presently employed for partitioning of uranium, plutonium, and neptunium will have to be developed since iron and sulfate interfere with recycle of low-level waste streams and with ultimate disposal. A consideration of paramount importance is the necessity for limiting the amounts and types of chemical reagents used and for recycling all of the low-level waste streams. This is an especially critical problem with available processes for americium and curium recovery.

Attainment of the required removal of plutonium and of americium and curium from the wastes will cause most of the difficulties in the processing. Problems caused by nonextractable forms of plutonium must be solved, and a satisfactory process for removing the americium and curium must be developed. Existing processes for removing americium and curium are deficient in one or more ways. Although several of the available processes have the potential for providing the final removal from the rare-earth fission products, methods for preparing satisfactory feed solutions to these processes will have to be developed. Conventional processes for separating americium and curium from fission products utilize high concentrations of metal salts or organic chemicals, and methods for eliminating these materials from the final fission product solid waste by appropriate recycle or combustion processes will have to be developed.

4.3 APPLICATION OF MASS TRANSPORT PHENOMENA TO THE LOSS OF RADIONUCLIDES FROM WASTE SOLIDS

We have derived several theoretical expressions, based on mass transport phenomena, that relate the radionuclides escaping from waste solids to diffusion, dissolution processes, surface conditions, and decay.[4] Representative available data for radioactive waste solids incorporated in cement, asphalt, ceramic, and glass media were analyzed using these theoretical expressions. The analyses show that an expression taking into account diffusion and concentration-dependent dissolution gives good agreement with the data for most of the products considered. In the main, these products can be categorized as waste solids of low solubility incorporated in inert matrices. The effective diffusivities obtained for the products analyzed are in the range of mid 10^{-17} to mid 10^{-12} cm^2/sec, the dissolution rate constants are in the range of high 10^{-9} to low 10^{-7} sec^{-1}, and the surface transfer constants are in the range of low 10^{-4} to low 10^{-3} sec^{-1}. Once determined, such parameters can be used to compare various waste products and to estimate releases from these products, in particular, long-term releases.

Solution of the mass transport equations for a semi-infinite medium for the model of diffusion with

4. H. W. Godbee and D. S. Joy, *Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment. Part I: Background and Theory,* ORNL-TM-4333 (February 1974).

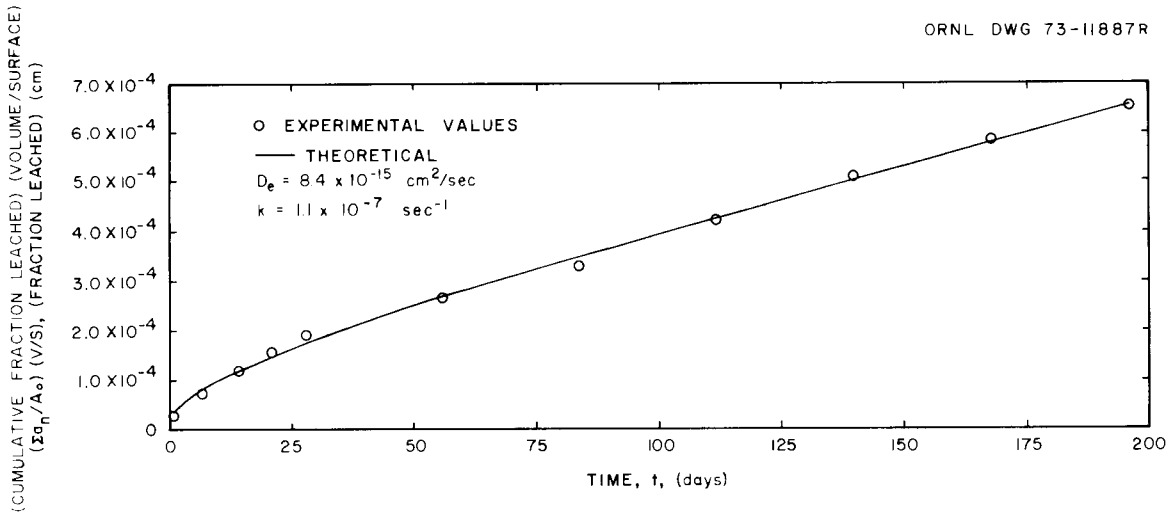

Fig. 4.2. Comparison of the amounts of ^{137}Cs leached from a borosilicate-glass product at 25°C with those predicted by an equation based on transport phenomena with a dissolution term. Experimental values were taken from ref. 5. Theoretical curve was calculated using Eq. (1) with $D_e = 8.4 \times 10^{-15}$ cm^2/sec and $k = 1.1 \times 10^{-7}$ sec^{-1}.

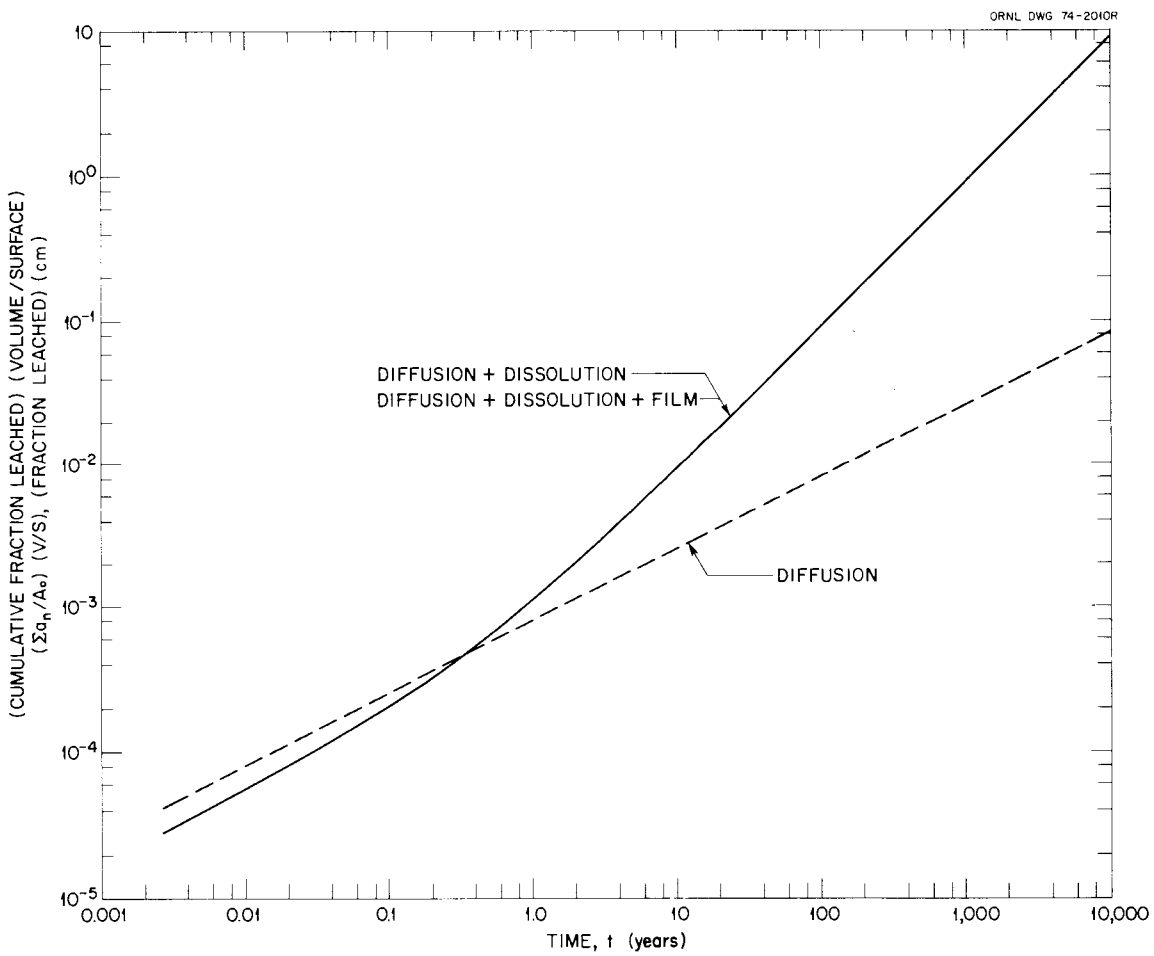

Fig. 4.3. Comparison of the long-term releases of ^{137}Cs (with radioactive decay neglected) from a borosilicate glass as predicted by models considering diffusion, diffusion plus dissolution, and diffusion plus dissolution plus a surface film. Equations and values of the parameters are given in ref. 4.

concentration-dependent dissolution gives

$$\frac{\Sigma a_n}{A_0}\frac{V}{S} = (D_e k)^{1/2}\left[\left(t+\frac{1}{2k}\right)\operatorname{erf}(kt)^{1/2} + \left(\frac{t}{\pi k}\right)^{1/2} e^{-kt}\right] \quad (1)$$

for the total amount leached. In this equation, $\Sigma a_n/A_0$ is the fraction leached, V/S is the specimen volume-to-surface ratio (cm), D_e is the effective diffusivity (cm^2/sec), k is a dissolution rate constant (sec^{-1}), t is time (sec), and erf is the error function. Data for the leaching of ^{137}Cs from a borosilicate glass[5] were fitted with Eq. (1) by a searching technique to give a D_e of 8.4×10^{-15} cm^2/sec and a k of 1.1×10^{-7} sec^{-1}. The amounts leached from the product, as given by the data and predicted by Eq. (1) with this D_e and k, are in good agreement (see Fig. 4.2). Predicted long-term releases from this product (neglecting radioactive decay of the ^{137}Cs) are presented in Fig. 4.3 for the models of diffusion, diffusion plus dissolution, and diffusion plus dissolution plus a surface film. The results show that the surface film has no significant effect on the amount leached. The difference in the amount leached as predicted by the model based on diffusion only and the amount leached according to the model based on diffusion plus concentration-dependent dissolution effectively illustrates that extrapolations concerning the leaching of sparingly soluble solids based on diffusion only should be viewed with reserve. The effect of radioactive decay on the amount of ^{137}Cs leached may be readily accounted for.[4]

4.4 PROJECTIONS OF RADIOACTIVE WASTES FROM THE NUCLEAR FUEL CYCLE

In light of the emphasis currently being placed on the development of nuclear energy resources, including the development and demonstration of the most practicable methods of managing the radioactive wastes that will arise from a diversified nuclear power economy, we have made a comprehensive set of projections of the radioactive wastes to be generated over the remainder of this century.[6] These new projections were based on a recent forecast of nuclear power growth in the United States[7] and on fuel mass-flow data developed for ^{235}U- and plutonium-enriched LWRs, an HTGR, and two reference LMFBR designs using the systems analysis computer code ORSAC.[8] Nuclear characteristics of the fuels and wastes were computed using ORIGEN.[9] The projected total installed nuclear electric capacity and the contribution of each of the three reactor types through the year 2000 are shown in Fig. 4.4.

To estimate the future magnitude of waste management operations, fuel cycle process flowsheets were constructed assuming present and near-future technology, and ten types of radioactive wastes were defined on the basis of their packaging, shipping, and probable disposal requirements. Finally, annual rates of generation, annual numbers of shipments, and accumulations of each type of waste through the end of the century were calculated. A summary of these projections for the year 2000 is presented in Table 4.2. The

5. J. E. Mendel and J. L. McElroy, *Waste Solidification Program, Vol. 10, Evaluation of Solidified Waste Products,* BNWL-1666 (July 1972).

6. J. O. Blomeke, C. W. Kee, and J. P. Nichols, *Projections of Radioactive Wastes to Be Generated by the U.S. Nuclear Power Industry,* ORNL-TM-3965 (February 1964).

7. *Nuclear Power 1973–2000,* WASH-1139(72) (Dec. 1, 1972).

8. F. G. Welfare et al., *The Oak Ridge Systems Analysis Code (ORSAC) Users' Manual,* ORNL-TM-3223 (June 1971).

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

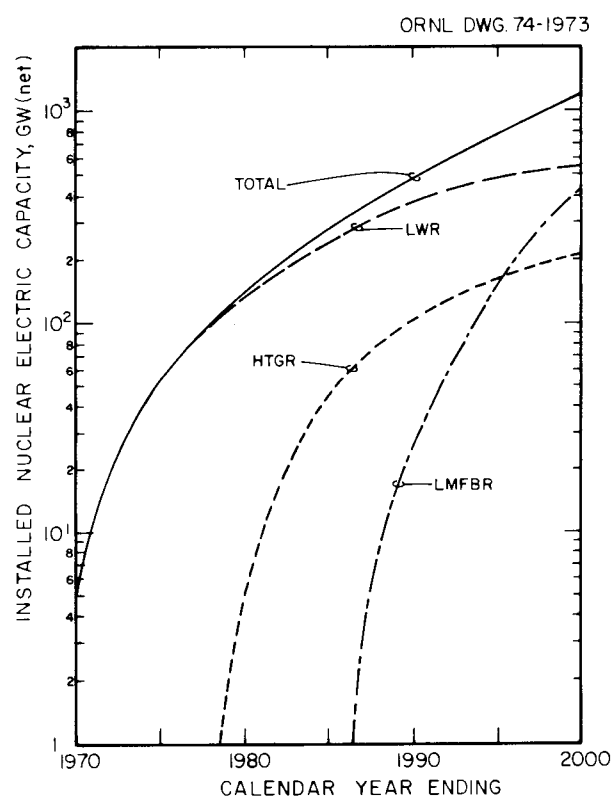

Fig. 4.4. Projected installed nuclear capacity in the United States.

Table 4.2. Fuel cycle wastes projected for the year 2000

Category of waste	Annual generation		Annual shipments	Total accumulated at repositories				
	Volume (thousands of cubic feet)	Activity (MCi)		Volume (thousands of cubic feet)	Activity (MCi)	Metric tons of actinides	Hazard (m^3 at RCG)[a]	
							Air	Water
High-level solidified	46	54,000	260[b,c]	140	16,000	410	2.8×10^{21}	1.1×10^{16}
Cladding hulls	60	320	540[c,d]	470	1,000	80	1.3×10^{19}	3.4×10^{13}
Noble gases	2.1[e]	220	200[c,d]	21[e]	1,500		5.0×10^{15}	
Iodine	0.07	0.0007	10[d,f]	0.71	0.007		3.6×10^{14}	1.2×10^{11}
Reactor tritium (water)	1,400	0.2	2,700[d,f]	19,000	1.7		8.4×10^{12}	5.6×10^{8}
FP tritium (solidified)	4.3	13	420[d,f]	41	87		4.3×10^{14}	2.9×10^{10}
Alpha solids	1,800	47	1,800[c,d]	12,000	220	26	1.7×10^{20}	2.7×10^{12}
Misc. α-β-γ solids	530	5.5	7,100[d,f]	4,000	24	0.9	3.8×10^{18}	9.7×10^{12}
Misc. β-γ solids	54,000	1.0	114,000[d,f]	330,000	4.1		2.4×10^{16}	2.0×10^{12}
Ore tailings	880,000	0.3		14,300,000	4.5	65,000	6.3×10^{18}	1.9×10^{13}

[a]These RCG (Radiation Concentration Guides) values correspond to Appendix B, Table II, of 10 CFR 20.
[b]Shipped 10 years after generation.
[c]Rail shipments are assumed.
[d]Shipped 1 year after generation.
[e]Pressurized at 2200 psi.
[f]Truck shipments are assumed.

hazards (inhalation and injection) as used here are defined in terms of the cubic meters of air or water that would be required to dilute all the radioactive constituents to the concentrations specified in the Radiation Concentration Guides[10] as being suitable for unrestricted use. Other definitions and principal assumptions used in this study are summarized below.

High-level wastes are composites of all the liquid waste streams arising from the reprocessing of spent fuels. These wastes contain most of the fission products, as well as significant amounts of the actinide isotopes, and are solidified into final volumes of 2, 3, and 6 ft^3 per ton of reprocessed LWR, LMFBR, and HTGR fuel respectively.

In addition to induced activity, the cladding hulls are assumed to contain 0.05% of the actinides and fission products present in the spent fuels. After compaction to 70% of their theoretical densities, the Zircaloy and stainless steel hulls occupy 2.1 ft^3 and 8.7 ft^3 per ton of LWR and LMFBR fuel respectively.

It is assumed that the mixed noble-gas fission products, krypton and xenon, are separated during reprocessing and packaged in standard 50-liter gas cylinders. Iodine is also separated during reprocessing, by virtue of its volatility, and then converted to KI for subsequent shipment and disposal.

Twenty thousand gallons of water per year, containing ^3H at a concentration of 5 μCi/ml, is assumed to be bled from the primary coolant circuit of each 1000-MW(e) LWR and shipped to disposal sites without additional treatment. Fission product tritium, separated by volatilization during reprocessing and recovered as tritiated water at a concentration of 200 Ci/liter, is subsequently fixed as $Ca(OH)_2$ before shipment and disposal.

Alpha solid wastes are defined as those solid materials that contain plutonium or other long-lived alpha emitters in concentrations greater than 10 μCi/kg and yet have sufficiently low external radiation levels after packaging that they can be handled directly. These wastes are generated in volumes of 10,000, 20,000, and 4000 ft^3 per ton of plutonium handled in fuel preparation, fabrication, and reprocessing, respectively. They contain an average of 0.25 g of plutonium or ^{233}U per cubic foot and are assumed to be reduced in volume for packaging and disposal by factors of 3 to 10.

Alpha-beta-gamma wastes are defined as those solid materials (other than high-level and cladding wastes) which contain long-lived alpha activities greater than 10 μCi/kg and have typical surface dose rates between 10 and 1000 millirems/hr after packaging. About 10,000 ft^3 of this type of waste, containing an average of 0.025 g of plutonium or ^{233}U per cubic foot, is generated at reprocessing plants per ton of plutonium or ^{233}U processed. It is compacted to the same degree as alpha waste.

Beta-gamma solid wastes are those diverse materials which are contaminated with low levels of beta- and gamma-emitting isotopes but contain less than 10 μCi of alpha activity per kilogram. These wastes, which are common to all nuclear facilities, generally contain from 0.001 to 1 Ci/ft^3; it is assumed that about 140,000 ft^3 will be generated per ton of plutonium or ^{233}U processed.

Projections of ore tailings are based on the assumption that 95% of the uranium and thorium is extracted from ores that assay 0.2% uranium or thorium. The unrecovered 5% and all radioactive daughters remain with the tailings, which average 0.16 yd^3 per ton of recovered U_3O_8 or ThO_2.

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10. *Code of Federal Regulations,* Title 10, Part 20, Appendix B, Table II.

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 their research work with these elements. TRU is the production, storage, and distribution center for the heavy-element research program in the United States. It functions integrally with the researchers and not merely as a supplier. Products are usually highly purified prior to shipment and are frequently provided in special chemical forms and/or in special devices as required by the experimenter. In addition to the normal production functions, various programs are pursued in cooperative ventures with other research laboratories to assist them in their work. Special isotopes are provided at their request, and hot-cell space 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 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 that are under the direction of the Chemical Technology Division, including the operation of TRU, isolation and purification of products, development of chemical processes, and some chemical studies of the actinide elements, are reported here. Target fabrication work, which is 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 that are being used in TRU. More detailed information is presented in a series of semiannual reports on production, status, and plans.[1,2]

Status and Progress

During the first four years that TRU was in operation, feed materials were primarily obtained from HFIR irradiations, 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 the Savannah River Plant (SRP) to recover californium for use in the Californium-I (Cf-I) program. This program is sponsored by the Production and Materials Management Division to evaluate the commercial market for ^{252}Cf. There were no further requests to process materials irradiated at SRP during the past year; hence operations at TRU were reduced accordingly. However, the amounts of transuranium elements produced in HFIR targets were maintained at a satisfactory level by irradiating isotopically heavier curium, most of which had been recovered from the Cf-I campaigns at TRU.

The primary role of TRU as supplier of research materials has continued; about 90 shipments were made this year to researchers throughout the country.

Production and Processing

During the current report period, two campaigns were carried out to process a total of 22 Cf-I curium-HFIR

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, 1973,* ORNL-4921 (March 1974).

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, 1973,* ORNL-4965 (in preparation).

targets. Key isotopes in the recovered materials are listed in Table 5.1. In addition, one campaign was made to purify 81 g of curium for the ORNL Isotopes Division, and another campaign was made specifically to recover transuranium elements from accumulated rework materials.

Product finishing operations normally 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 45 and 46, from previous campaigns, and from various rework materials. The amounts of materials undergoing product finishing operations included 17 g of ^{243}Am, 436 g of curium, 60 mg of ^{249}Bk, 470 mg of ^{252}Cf, 1650 μg of ^{253}Es (mixed isotopes), and about 1.5 pg of ^{257}Fm. High-purity daughter products that were recovered and purified included 36 mg of ^{248}Cm, 8 mg of ^{249}Cf, and 319 μg of ^{253}Es.

Processes and Equipment

Flowsheets used at TRU remained unchanged this year, and the status of the plant equipment remained good. We suspended chemical operations for a relatively short period of about three weeks to replace leaking and plugged lines. Also, the sampler equipment rack in cubicle 7 was replaced with a new rack containing vacuum tanks instead of pumps. Construction of several other replacement equipment racks was begun.

Table 5.1. Amounts of materials recovered in major campaigns in the Transuranium Processing Plant during the period April 1, 1973, through March 31, 1974

	Campaign 45	Campaign 46	Total
Completion date	10/73	3/74	
Material processed	10 Cf-I Cm-HFIR targets plus rework	12 Cf-I Cm-HFIR targets plus rework	
Amount recovered			
^{243}Am, g[a]	0.8	1.3	2.1
Total Cm, g[a]	81	83	164
^{244}Cm, g[a]	43	44	87
^{249}Bk, mg	21	17	38
^{252}Cf, mg	225	161	386
^{253}Es, mg	1.2	0.9	2.1
^{257}Fm, pg	1	0.5	1.5

[a]Americium and curium are not usually separated from each other.

Fabrication of Targets

Thirty-three targets were fabricated in order to recycle curium to the HFIR. Of these targets, 5 contained curium which had been recovered from research materials, 12 contained Cf-I curium, and 16 contained curium recovered from previous irradiation of Cf-I curium in the HFIR. Two special targets, containing various experimental pellets, were also fabricated.

5.2 SPECIAL PROJECTS

The facilities that are 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. Nine sources containing from 114 μg to 14 mg of ^{252}Cf were fabricated this year. Most of them were doubly encapsulated in type 304L stainless steel in a standard configuration.[3]

Two nonstandard sources were prepared. One of these, a small version of the special source prepared for the National Bureau of Standards (NBS),[4] was fabricated for Bettis Atomic Power Laboratory. While the external hardware was the same as that for the NBS source, the californium content was only 114 μg of ^{252}Cf and was confined to a very small volume; most was within a cylinder 1.3 mm in diameter by 3.8 mm tall.

The other special source was fabricated for Lawrence Livermore Laboratory (LLL). This source is actually a doubly encapsulated NSD-type source which was made a little shorter than usual and then fitted into an aluminum pneumatic rabbit housing supplied by LLL. At their request, we shipped the source to the NBS for

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.

a certified calibration. We were delighted to find that the NBS calibration was within 0.3% of our estimate.

Fabrication of Fission Chambers Containing ^{252}Cf

An activity new to TRU, the preparation of fission chambers loaded with ^{252}Cf, was undertaken during this report period. Although these chambers emit neutrons, as do all californium sources, the desired emanations are fission fragments. Accordingly, these new sources are designated FS- to distinguish them from our NS- series. For FS-1, the experimenter desired a nominal 30-ng source strength in a minimum cross-sectional area. Therefore, a very small aliquot (approximately 5 μl) containing the desired amount of ^{252}Cf was deposited in the center of the counter base and evaporated to dryness under a heat lamp. The stainless steel fission chamber was then assembled and welded in a glove box. The completed fission chamber was assayed by neutron counting to contain 31 ng of ^{252}Cf. The second fission source (FS-2) contained 15 μg of ^{252}Cf electroplated on a 1½-in.-diam platinum disk, which was then sealed into a doubly contained fission chamber. In addition, another fission source containing 1 to 2 μg of ^{252}Cf, which had been prepared earlier by the Isotopes Division, was recanned in the new type of outer container to match FS-2. All of these fission chambers were transferred to the Instrumentation and Controls Division, where they were filled with counter gas and the electronic characteristics were checked out.

Calibration of ^{252}Cf Sources

A new method for analyzing dead time was devised in which the counting data are fitted with a straight line, thereby making use of a large number of separate determinations. The dead time is then used to adjust the observed count rate to the absolute count rate with the following equation:

$$A = \frac{C}{1 - \tau C},$$

where A is the count rate that would be detected by a system with an infinitely fast response, C is the observed count rate, and τ is the effective dead time (i.e., the time required to process an incoming pulse and reset the system so that it is ready to receive another pulse). During the dead time, the counter is not "open for business." The details of the derivation may be found elsewhere.[5]

We applied this dead-time analysis to the neutron counters in the Target Decontamination Facility, where we calibrate our neutron sources and assay our californium shipping packages. When the pulse-shaping time was set to 2 μsec, as it has been most of the time since we started using these counters, the dead time was measured as 9.3 ± 0.3 μsec. However, when the pulse-shaping time was reduced to 1 μsec, the dead time was reduced by almost 50%. A shaping time of 1 μsec appears to be about the best compromise in our system between the need to maintain a low dead time at the count rates of interest and the need to provide noise-free amplification of the detector signal. We now routinely use the counters with a shaping time of 1 μsec, which results in a currently measured dead time of 5.42 ± 0.76 μsec. The correction for dead time in most cases is 1% or less.

Special Rabbit Irradiations

Two more HFIR hydraulic rabbits, each containing about 5 μg of ^{253}Es, were prepared as part of a continuing series for Argonne National Laboratory (ANL).

A new technique using magnesium diluent was developed to permit the fabrication of milligram quantities of ^{249}Bk into a HFIR hydraulic rabbit capsule for production of ^{250}Cf (details available in ref. 2).

A sample containing about 1.5 mg of ^{249}Bk was purified, and a HFIR hydraulic rabbit capsule was prepared, irradiated for 16 hr, and then processed – all within a five-day interval. 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.

The procedure went essentially as planned, and the resulting product was found to contain 237 μg of ^{250}Cf. The isotopic composition was:

Nuclide	Atom %
^{249}Cf	3.28
^{250}Cf	89.07
^{251}Cf	6.82
^{252}Cf	0.823
^{253}Cf	<0.002
^{254}Cf	<0.002

The ^{249}Bk residue from this irradiation, approximately 1 mg, was repurified and again fabricated into a

5. 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, 1973,* ORNL-4921 (March 1974), p. 18.

HFIR rabbit by the resin-loading technique. The product isolated from the second run contained 135 μg of ^{250}Cf and had essentially the same composition as the original ^{250}Cf product.

A special irradiation of 1.8 mg of ^{152}Sm was performed for A. M. Friedman of ANL. Although Dr. Friedman had requested a five-day irradiation, we scaled it back to 20 hr to produce an estimated 20 Ci of ^{153}Sm, based on cross sections from the General Electric "Chart of the Nuclides." The rabbit, upon discharge, was more radioactive than anticipated, and was thus allowed to cool an extra day before being shipped to ANL. Dr. Friedman estimates that he received about 150 Ci, which implies that the true activation cross section in the HFIR is an order of magnitude higher than the literature value.

Special HFIR Targets

A new experimental facility designed to hold one standard HFIR target (of the type used for transplutonium-element production) has been approved for use in the HFIR reflector. The purpose for locating the holder in one of the VXF holes of the beryllium reflector is to provide a flux significantly different from that in the target island. The contrast between the well-thermalized spectrum in the outer part of the reflector and the relatively hard spectrum in the target island will provide an opportunity to explore the relative importance of resonance and thermal absorptions in a number of key isotopes of the transplutonium production chain. The facility has been approved as suitable for the irradiation of a HFIR target, and subsequent approval of individual target assemblies can be made on the basis of adherence to the established criteria that pertain to HFIR target irradiations.

The initial experiment inserted into this VXF target holder was special target ST-8, which contained several samples and flux monitors. The samples and the purposes for which they were irradiated are as follows:

1. Two curium oxide pellets from pellet batch TRU-36, each containing 271 mg of curium. These pellets were used to study the production of ^{249}Bk and ^{250}Cf from ^{248}Cm.
2. Two old pellets, each containing approximately 1 μg of ^{252}Cf and several micrograms of ^{248}Cm. These pellets were used to study the production of ^{249}Bk from the ^{248}Cm, as well as the burnout of lighter californium isotopes. The same irradiation provided a check on the production of ^{253}Es.
3. Two special containers, each containing about 1 mg of ^{241}Am fixed on a bed of zeolite. These samples were used to test the Szilard-Chalmers type of enrichment of ^{242m}Am from the target isotope ^{241}Am.
4. Three similar containers with ^{141}Pr on zeolite. These samples were used to check the procedures for the above tests. The ^{141}Pr process has been found to perform satisfactorily in ORR irradiations. One of the capsules had a standard substrate; the other two contained different formulations for test purposes.
5. Three flux monitor assemblies containing 6-mg pieces of niobium wire and cobalt-aluminum alloy wire in small quartz ampuls.

The remaining space in the target was filled with dummy pellets and aluminum spacers.

The target was loaded into the reactor on July 22, 1973, and was irradiated for one cycle in position VXF-19. After discharge on August 15, 1973, it was returned to TRU for disassembly and analysis of the experiment.

Results show that while the thermal flux, as measured by the cobalt monitors, was roughly that anticipated, the burnup of the actinides suggested a much higher flux (about a factor of 2). Reconciliation of these data apparently involves the resonance spectrum. Probably the location of some fission sources (the curium pellets) in this part of the reflector increased the resonance flux appreciably above the calculated (unperturbed) value.

Production of Additional ^{253}Es

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 show that the best yield of ^{253}Es would be obtained from the portion of material near the midplane of a californium-loaded target which was subjected to two cycles of irradiation in the Control-Rod Access Plug Facility (in the beryllium reflector). Because this facility holds four targets, capability exists for the irradiation of a substantial amount of ^{252}Cf at one time, if it is assumed that we can fabricate pellets highly loaded with ^{252}Cf. To provide a check on the calculations, we have prepared a special target, ST-9 (T-29), which contains three ^{252}Cf pellets and three flux monitors located at various points along the rod. The average loading of ^{252}Cf in these pellets is about 2 μg. The target was completed without difficulty and was transferred to the HFIR for irradiation beginning with cycle 103. Preliminary results indicate close agreement with the calculations.

5.3 TRANSPLUTONIUM-ELEMENT RESEARCH

Systematic studies of actinide-element chemistry and comparative lanthanide chemistry are being carried out as additional quantities of the transplutonium isotopes become available. These investigations increase our basic understanding of the actinides and provide information applicable to systems where the actinides are encountered. This part of the USAEC Heavy Element Program includes work on the preparation of solid actinide compounds and the metals that are characterized by x-ray and electron diffraction, electron microscopy, thermogravimetry, differential thermal analysis, and gas chromatography. Several research efforts have also been carried out in collaboration with other ORNL divisions, other USAEC laboratories, and various scientific institutions in Europe.

Americium Metallides

Five americium metallides were prepared, and a paper summarizing the data on the compounds has been accepted for publication. The abstract follows:

"Americium Metallides: AmAs, AmSb, AmBi, Am_3Se_4, and $AmSe_2$," by J. W. Roddy, *J. Inorg. Nucl. Chem.*, in press. *Abstract:* The crystal structures of several americium metallides were determined using the long-lived americium-243 isotope. Three of the binary systems produced alloys near the equiatomic compositions AmAs, AmSb, and AmBi, which were found to have the NaCl-type structure. Two compounds were identified in the Am-Se system: (1) Am_3Se_4, which was found to have a bcc structure; and (2) $AmSe_2$ (less certain) with a tetragonal structure. The lattice parameters, calculated and observed d-spacings, and calculated and observed line intensities for these compounds are reported.

Preparation and Analysis of Actinide Metals by Electron Diffraction and X-Ray Analysis

Methods have been developed to prepare and analyze microgram or submicrogram amounts of actinide metals; the major interest is the transberkelium elements. In this work, numerous lanthanide and actinide metal deposits have been examined by electron diffraction and microscopy; also, some metal deposits have been collected on tungsten wires and quartz fibers and examined by x-ray diffraction.

Lanthanide metal deposits were initially studied as stand-ins for the actinide metals. Examination of these samples has shown the existence of a new crystalline form in addition to the structures that have been reported for the metal. Subsequently, efforts have been made to determine whether this crystalline material is a new metallic form, an impurity-stabilized phase, or a product other than metal. Additional experiments are planned.

The scarcity of ^{249}Cf and the einsteinium isotopes required that microtechniques be used for preparing the metallic state of these elements. However, the high volatility of californium and einsteinium metals at elevated temperatures and the high specific activity of the readily available einsteinium isotope (^{253}Es, $t_{1/2}$ = 20.6 days) create experimental difficulties in preparing and analyzing these metals. In the case of einsteinium metal, the high specific activity of einsteinium results in rapid degradation of the metal's crystallinity and in severe blackening of the film in the x-ray cameras. The use of electron diffraction for studying einsteinium metal deposits avoids or minimizes the above difficulties and appears to be the best approach for analyzing the einsteinium preparations.

Examination of californium and einsteinium metal deposits by electron diffraction has shown that the two metals are similar to each other. The melting points of californium and einsteinium metal were reported last year[6] to be 900 ± 30°C and 860 ± 30°C respectively. The electron diffraction data obtained for both materials indicated that they are divalent metals. From theoretical considerations, the metals were expected to be close to a transition point between their divalent and trivalent states; it may therefore be possible to obtain the metals in both states. A paper reporting the electron diffraction data obtained on californium metal has been accepted for publication in the *Journal of Inorganic and Nuclear Chemistry.*[7]

Actinide Oxysulfates and Oxysulfides

X-ray diffraction and thermogravimetry studies have been carried out on the sulfates, oxysulfates, and oxysulfides of the transplutonium elements. The oxysulfate and oxysulfide can be prepared by thermal decomposition of the sulfate salt, or the products can be encountered during calcination of Dowex 50 resin loaded with the actinide metal ion. The particular product obtained is dependent on the temperature and atmosphere employed during calcination.

A paper summarizing the data collected on the californium oxysulfate-oxysulfide system has been accepted for publication in the *Journal of Inorganic and Nuclear Chemistry.*[8] The oxysulfate was found to be

6. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973,* ORNL-4883, p. 43.

7. R. G. Haire and R. D. Baybarz, "Crystal Structure and Melting Point of Californium Metal," *J. Inorg. Nucl. Chem.* (in press).

8. R. D. Baybarz, J. A. Fahey, and R. G. Haire, "The Preparation, Crystal Structures, and Some Properties of Californium Oxysulfate and Oxysulfide," *J. Inorg. Nucl. Chem.* (in press).

stable in air up to 860°C; at higher temperatures, it decomposes to the sesquioxide, the reaction being dependent on both the time and temperature of the heating. The oxysulfide was obtained by heating either the loaded Dowex 50 resin beads or the hydrous sulfate salt in atmospheres containing hydrogen or in vacuum at 800°C. Lattice parameters were determined for each compound. For the orthorhombic oxysulfate, the parameters are a_0 = 4.187 ± 0.002 Å, b_0 = 4.072 ± 0.002 Å, and c_0 = 13.009 ± 0.006 Å. The cell dimensions for the trigonal oxysulfate are a_0 = 3.844 ± 0.002 Å and c_0 = 6.656 ± 0.004 Å.

The oxysulfates and oxysulfides of the other transplutonium elements up to californium have also been prepared, and these compounds, together with the californium products, have been found to form series comparable to those known for the corresponding lanthanide compounds.

The Dihydride and Mononitride of Californium

The dihydride (CfH_{2+x}) and mononitride (CfN) of californium have been prepared from californium metal, and the compounds have been analyzed by x-ray diffraction. Since only microgram amounts of the products were available, identification of the products was made solely on the basis of the x-ray diffraction results and the reaction conditions. The lattice parameters of these compounds are in accord with those reported for the other transplutonium dihydrides and mononitrides. The lattice parameters obtained for the fcc structures were as follows: (1) a_0 = 5.232 ± 0.005 Å for CfH_{2+x}, and (2) a_0 = 4.984 ± 0.002 Å for the CfN product. Additional preparations are needed to confirm these values.

Studies of the Actinide Hydroxides

Electron microscopy, electron diffraction, and x-ray analysis studies on the actinide hydroxides have been continued on a limited basis. The initial work on these materials centered on the preparation and determination of the crystal structure and morphology of the actinide hydroxides and a comparison of their chemistry with the comparable lanthanide compounds. More recent efforts have been aimed at examining the self-irradiation damage in the hydroxide microcrystals.

Studies have shown that with ^{244}Cm, the average lifetime of the curium trihydroxide crystals was less than one day; however, with ^{241}Am, many of the americium hydroxide crystals were still crystalline after three months. With ^{249}Bk, the life of the berkelium trihydroxide crystals was found to be similar to that of the ^{244}Cm product – that is, much shorter than anticipated since berkelium decays by beta emission. The initial work on ^{147}Pm trihydroxide crystals was reported last year.[6] Periodic examinations of promethium crystals during 20 months of aging (^{147}Pm, $t_{1/2}$ = 2.6 years, beta decay) have shown evidence of only moderate crystal damage, confirming that self-irradiation by beta particles was less damaging to the crystals than observed for corresponding compounds containing alpha emitters. The shorter life of the berkelium hydroxide crystals has been attributed to air oxidation of the berkelium compound. Several of the different hydroxide crystals will be observed for additional aging periods.

Collaborative Research with the Transuranium Research Laboratory

Several programs of mutual interest were carried out jointly with members of the Chemistry Division. One of these efforts, which was done in collaboration with J. R. Peterson, consultant from the University of Tennessee, and J. Fuger, University of Liege (Belgium), involved the preparation of several single 0.5-mg pieces of berkelium metal which were used for measuring the heat of solution of the metal in hydrochloric acid. Another project was concerned with electron spectroscopic measurements on berkelium, californium, and einsteinium compounds that yielded several electron binding energies for the core and valence electrons for each element. This work was done in collaboration with M. Krause (Chemistry Division), and additional experiments with these elements in different chemical states are planned.

Collaborative Research with Los Alamos Scientific Laboratory

Several collaborative research projects have been carried out with personnel at the Los Alamos Scientific Laboratory. One area of mutual interest involves preparation and investigation of the fluoride compounds of the tetravalent actinides. Some of the results obtained in these investigations have been published under two subject headings: californium tetrafluoride[9] and revised lattice parameters for the actinide tetrafluorides.[10] Additional experimental work on the

9. R. G. Haire and L. B. Asprey, "The Preparation and Lattice Parameters of Californium Tetrafluoride," *Inorg. Nucl. Chem. Lett.* 9, 869 (1973).

10. L. B. Asprey and R. G. Haire, "On the Actinide Tetrafluoride Lattice Constants," *Inorg. Nucl. Chem. Lett.* 9, 1121 (1973).

actinide fluoride system has been completed, but the data have not been fully analyzed. The latter efforts are concerned with the absorption spectra of californium tetrafluoride and the lattice parameters of complex fluoride salts of tetravalent berkelium and californium, that is, $Na_7M_6F_{31}$, $LiMF_5$, etc. (M = actinide). The preparation and study of the californium metal system constituted another area of joint research.[11] This study has resulted in the identification of two double-hexagonal close-packed (dhcp) structures for californium metal; one structure has been assigned to the divalent form and the other to a trivalent form of the metal. The latter structure has lattice parameters slightly smaller than those reported for the dhcp form of berkelium metal.

Collaborative Research with Europäisches Institut für Transurane (Euratom, Karlsruhe, Germany)

Several research projects were initiated with the Transuranium Institute at Karlsruhe, Germany, while one member of the Division was at the Institute on a one-year Alexander von Humboldt Fellowship. One area of investigation concerned the determination of the vapor pressures of americium, curium, and californium metal. In addition, studies were made on the high- and low-temperature phases of high-purity americium and curium metal. Also, several intermetallic actinide compounds were prepared with platinum and beryllium, and their crystal structures were examined by x-ray analysis. Results of these studies will be published in the near future.

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11. R. G. Haire and L. B. Asprey, "Studies on the Californium Metal System," submitted for publication in *Inorganic and Nuclear Chemistry Letters.*

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, as well as in the *Gas-Cooled Reactor Programs Annual Progress Report for the Period Ending December 31, 1973* (ORNL-4975).

7. Preparation of $^{233}UO_2$

ORNL's contract with Bettis Atomic Power Laboratory (BAPL) to prepare $^{233}UO_2$ involves (1) purifying several hundred kilograms of ^{233}U (presently 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 $^{233}UO_2$ scrap generated at ORNL and the $^{233}UO_2$-ThO_2 scrap generated at BAPL. The routine production of UO_2 powder at a plant capacity of 50% was begun in June 1973. The program is expected to continue until June 1975.

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 31.6 kg of ^{233}U from recycle UO_2 and ammonium diuranate in 13 dissolutions. This recycle material was generated as a result of overheating in the microwave oven (ammonium diuranate) and incomplete reduction in the calcining furnace (UO_2); recycle UO_2 was also accumulated from cleanup of the glove boxes after each week's operation. In addition, some UO_2 was returned by BAPL for recovery.

All 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 to the ion exchange system for purification. The product from the dissolution of ammonium diuranate was further purified in the solvent extraction system before being returned to storage. Two of the dissolutions were "cleanout" dissolvings to account for all uranium charged previously.

Thirty dissolutions were made in the scrap dissolver to recover 36.6 kg of ^{233}U and 1039 kg of thorium from UO_2-ThO_2 scrap generated at BAPL. The amount of scrap charged to the dissolver in each case varied from 50 to 100 kg of mixed oxide, and the dissolvent consisted of 12 M HNO_3–0.04 M F^-–0.1 M $Al(NO_3)_3$. The dissolvent was held at 105°C until the thorium concentration reached 1.0 to 1.2 M. These solutions were accumulated for use as feed to the solvent extraction system.

7.2 ^{233}U PURIFICATION SYSTEMS

Six runs were conducted in the solvent extraction purification system to purify 117 kg of uranium. These runs were made as necessary to recover and purify uranium from the dissolution of scrap, recycle material from the ion exchange system, and recycle material from previous solvent extraction runs.

Uranium losses to the raffinate were high (0.3%) during initial operations, apparently because of insufficient pulsing in the column. In an effort to ameliorate this situation, we have installed a larger pulser; with this new equipment, future losses are expected to be less than 0.2% of the feed. The separation factor of the thorium from uranium was approximately 10^4.

Approximately 602 kg of uranium was purified in 25 runs made in the ion exchange equipment. It was necessary to process eight batches of material through two cycles of ion exchange in order to sufficiently remove the thorium and ^{224}Ra. Near the end of the report period, we replaced the dual-column system with a single column containing 1.8 times the volume of resin used previously. Operation of the single-column system has resulted in excellent decontamination from thorium and radioactive daughters from ^{232}U decay.

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

A total of 189.5 kg of UO_2 was prepared and transferred to BAPL in 12 shipments during the year. One batch (20.4 kg) failed to meet the radiation

specification; however, this specification was waived by BAPL. The material is processed through the conversion system in 1.0-kg (uranium) batches. Of the 190 batches processed, we rejected 4 due to a loss of hydrogen to the furnace caused by a restriction in the hydrogen supply line and 2 due to ignition in the microwave oven. The latter was attributed to incomplete removal of ammonia following the precipitation step.

8. Separations Chemistry Research and Development

New separations methods are being developed, principally for uses in radiochemical processing but also for other purposes extending from extractive metallurgy to biochemistry. The program divides into three parallel, interdependent, and frequently overlapping activities: (1) descriptive chemical studies (Sects. 8.1, 8.5–8.7) of the reactions of substances to be separated and of separations agents, of the controlling variables in particular separations, and of potential new reagents and methods; (2) development (Sects. 8.2–8.6) of selected methods into specific complete processes, both where no process exists and where existing processes can be improved, carried when warranted to the point that large-scale performance can be predicted; and (3) fundamental chemical studies (Sect. 8.7) of the species, equilibria, and mechanisms involved in separations systems, both to increase knowledge and to help define potential applications.

8.1 NEW SEPARATIONS AGENTS

Octylphenyl phosphoric acid (OPPA) is a commercially available[1] mixture of mono- and diester acids and neutral impurities. It is the extractant of choice in a process for recovering uranium from phosphoric acid (cf. Sect. 8.2) and has shown potential for other applications. Solubility loss measurements showed that the monoester diacid is selectively lost to phosphoric acid solutions. Since uranium extraction from phosphoric acid is more efficient with the mixture than with either component alone, a source of separated mono-OPPA will be needed for makeup. We have prepared essentially pure (>99%) mono-OPPA by two methods, one based on ethylene glycol extraction and crystallization, the other on removal of the impurity by precipitation. The former also yielded pure (>98%) di-OPPA.

Commercial di(2-ethylhexyl) phosphoric acid (HDEHP) typically contains impurities that interfere with inter- and intragroup separations of trivalent lanthanides and actinides.[2] All published methods for its complete purification are too cumbersome and expensive for large-scale process use. We have devised a system of scrubbing commercial HDEHP that can remove even the more persistent contaminants in four or five stages.

We have obtained samples of two new types of organophosphorus polymers and have established liaison with the specialty manufacturer[3] for obtaining further types. The samples now being tested are both insoluble solids, a polyphosphonium salt and a polyphosphine oxide. Analogous structures in liquid reagents are expected to be available.

We are examining several unusual means of implementing separations reactions for use in the "single atom" chemistry of accelerator-produced heavy elements (cf. Sect. 8.7). One of these is the adaptation of liquid-liquid extraction to distribution between the surfaces of two slightly wetted films. Tests to date have been with an aqueous hydrochloric acid solution on the face of a hydrophilic plastic film[4] vs an organic quaternary ammonium salt solution on the face of a hydrophobic plastic film[4] or a collodion film containing the quaternary ammonium salt. The films were contacted briefly, on the order of 5 sec. While poor reproducibility and physical performance (transfer of reagent) have been observed thus far, the distributions found for ^{59}Fe, ^{109}Cd, ^{64}Cu, and ^{133}Ba have been consistent with their behavior in conventional solvent extraction.[5]

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1. Mobil Chemical Co., P.O. Box 26683, Richmond, Va. 23261.
2. Boyd Weaver and Richard Shoun, "Heavy Actinide Element Partitioning by Extraction with Monoacidic Phosphorus Esters – HEPEX," *Ind. Eng. Chem., Process Design Develop.* **10**, 582 (1971).
3. Weston Chemical, Borg-Warner Corp., Montvale, N.J.
4. Research Laboratories, Eastman Kodak Co., Rochester, N.Y.
5. F. G. Seeley and D. J. Crouse, "Extraction of Metals from Chloride Solutions with Amines," *J. Chem. Eng. Data* **11**, 424 (1966).

8.2 RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID

Information from phosphate producers indicates that a large tonnage of low-grade phosphate rock exists in which the concentration of iron is too high (~2% Fe_2O_3) for economic conversion to fertilizer via the wet-process acid route. However, if one-half to two-thirds of the iron could be removed from acid produced from this rock, the acid could be processed economically. This would expand the potential reserves of fertilizers, which are in short supply, and also increase the recoverable supply of uranium.

The octylphenyl phosphoric acid (OPPA) extractant, used in the first cycle of our alternative extraction process for recovering uranium from wet-process phosphoric acid,[6-8] extracts ferric iron very strongly and may be useful for not only recovering uranium but also upgrading the acid by removal of iron.

A McCabe-Thiele analysis of the extraction of iron from a commercial wet-process acid liquor containing 9 g of Fe(III) per liter, with 0.4 *M* OPPA in Amsco 450 (0.15 *M* monoester, 0.25 *M* diester form), indicates that 98% of the iron could be removed in three ideal extraction stages when operating with an aqueous/organic feed ratio of 1/3. Under these conditions the uranium would be completely extracted, provided at least 0.5 to 1 g of Fe(II) per liter is present to ensure that the uranium is in the extractable tetravalent state. Preliminary tests indicate that the iron can be effectively stripped from the solvent into an acidic solution that contains a reductant to reduce the Fe(III) to Fe(II). It is envisioned that the iron could be continuously removed from the stripping circuit as a solid, while the stripping solution acid is recycled. The uranium would then be stripped from the solvent by oxidizing it to the less extractable hexavalent state with sodium chlorate in 10 *M* H_3PO_4, as in the original OPPA process.[6]

8.3 SEPARATION OF RADIUM FROM URANIUM ORE TAILINGS

The purpose of this project is to investigate the leaching characteristics of radium from uranium ores and sulfate-leached ore tailings for two alternative objectives: (1) to find a means of removing the radium (and other radionuclides) in an economically practicable manner or (2) to find a means for significantly reducing the leachability of the radium. Previously reported tests,[9,10] 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 required the use of fairly concentrated HNO_3 or HCl solutions (3 *M*) or large volumes of selected salt solutions. Three samples of actual plant tailings slurries have now been wet-classified and sampled for radium concentration vs particle size, confirming an earlier observation that 80 to 90% of the radium is present in the −325 mesh (<44-μ) fraction, that is, the "slimes."

In an attempt to further elucidate the dissolution mechanism, leaching tests were made on sea sand that had been ground to −325 mesh, washed successively with 0.1 *M* HCl solution and H_2O to prevent adsorption of radium on the freshly exposed surfaces, and then coated with either $RaSO_4$ alone or $RaSO_4$ in combination with $CaSO_4$ and/or $BaSO_4$. At a leaching solution to solids ratio of 30:1, the dissolution of $RaSO_4$ (alone) increased from 11% to 98% over the HCl concentration range 0.0001 to 1.0 *M*. The presence of $CaSO_4$ increased the solubility of $RaSO_4$, while the presence of $BaSO_4$ decreased its solubility. The presence of excess sulfate (Na_2SO_4) depressed the solubility of $RaSO_4$, as expected, when both $CaSO_4$ and $BaSO_4$ were absent; however, very little change was noted in the solubility of $RaSO_4$ (>90%) over the sulfate concentration range 0.01 to 1.0 *M* when $CaSO_4$ was present.

Leaching of four coated-sand samples with 1 *M* NaCl–0.1 *M* HCl solutions at widely varying solution/solid ratios (Fig. 8.1) indicated a much lower $RaSO_4$ solubility than expected (~3×10^{-10} g/ml). Not only is the $RaSO_4$ associated with $BaSO_4$, and thus dependent upon the solubility of the latter, as reported by Lind,[11] but it appears that there is some association with the $CaSO_4$, even in the presence of $BaSO_4$, which *increases* the effective solubility of the $RaSO_4$.

When samples of actual "slimes solids," the −150 mesh fraction of the sulfate-leached ore tailings, were

6. F. J. Hurst and D. J. Crouse, "Recovery of Uranium from Wet-Process Phosphoric Acid by Extraction with Octylphenylphosphoric Acid," *Ind. Eng. Chem., Process Design Develop.*, in press.

7. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973*, ORNL-4883, pp. 56–57.

8. *Chem. Develop. Sect. B Semiannu. Progr. Rep. Mar. 1, 1973 to Aug. 31, 1973, Part I*, ORNL-TM-4370, pp. 368–78.

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

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

11. S. C. Lind, J. E. Underwood, and C. F. Whittemore, "The Solubility of Pure Radium Sulfate," *J. Amer. Chem. Soc.* **40**(3) (March 1918).

leached with 1 *M* NaCl–0.1 *M* HCl solutions in the same manner as the coated-sand samples, the $RaSO_4$ appeared to be less dependent on the $BaSO_4$. When 90% of the radium had been leached out, only about 10% of the barium but 100% of the calcium had been dissolved (Fig. 8.2).

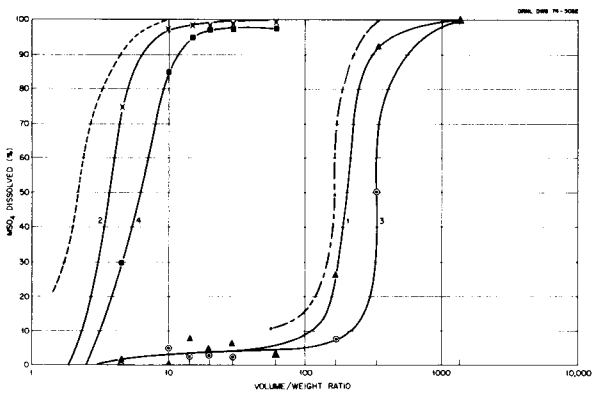

Fig. 8.1. Effect of volume/weight ratio on the leaching of Ra, Ca, and Ba sulfates from coated sand with 1 *M* NaCl–0.1 *M* HCl solution. Sand samples: –325 mesh sea sand coated with (1) 0.055 g of $CaSO_4$, 0.0011 g of $BaSO_4$, and 3000 pCi of $^{226}RaSO_4$ per gram (Δ); (2) 0.055 g of $CaSO_4$ and 3000 pCi of $^{226}RaSO_4$ per gram (×); (3) 0.0011 g of $BaSO_4$ and 3000 pCi of $^{226}RaSO_4$ per gram (○); (4) 3000 pCi of $^{226}RaSO_4$ per gram (□). Contact: solids and leachant mixed for 20 hr at room temperature on Burrell shaker. -----, Ca analysis; –·–·–, Ba analysis.

8.4 SEPARATION OF ALPHA EMITTERS FROM FUEL REPROCESSING WASTES

In support of the Waste Fractionation Program (Sect. 4.2), we have devised a tentative flowsheet for segregation of at least 99.9% of the americium and curium in a 2 *N* HNO_3 waste solution. The process includes the following principal steps:

1. Evaporation of the waste solution to adjust the HNO_3 concentration to 6–8 *N* and to reduce the volume.
2. Removal of zirconium and molybdenum by extraction with di(2-ethylhexyl) phosphoric acid (HDEHP) in an aromatic hydrocarbon diluent.
3. Complete destruction of the HNO_3 with excess formic acid.
4. Coextraction of the actinides and fission product rare earths with a solvent of the same composition as used in step 2. Extraction from the weakly acidic HCOOH solution is much more efficient than from the lowest HNO_3 concentration attainable.
5. Separation of the actinides from the rare earths by a countercurrent partitioning system in which the HDEHP extract is the feed and the aqueous phase is a dilute solution of glycolic (hydroxyacetic) acid and sodium diethylenetriaminepentaacetate

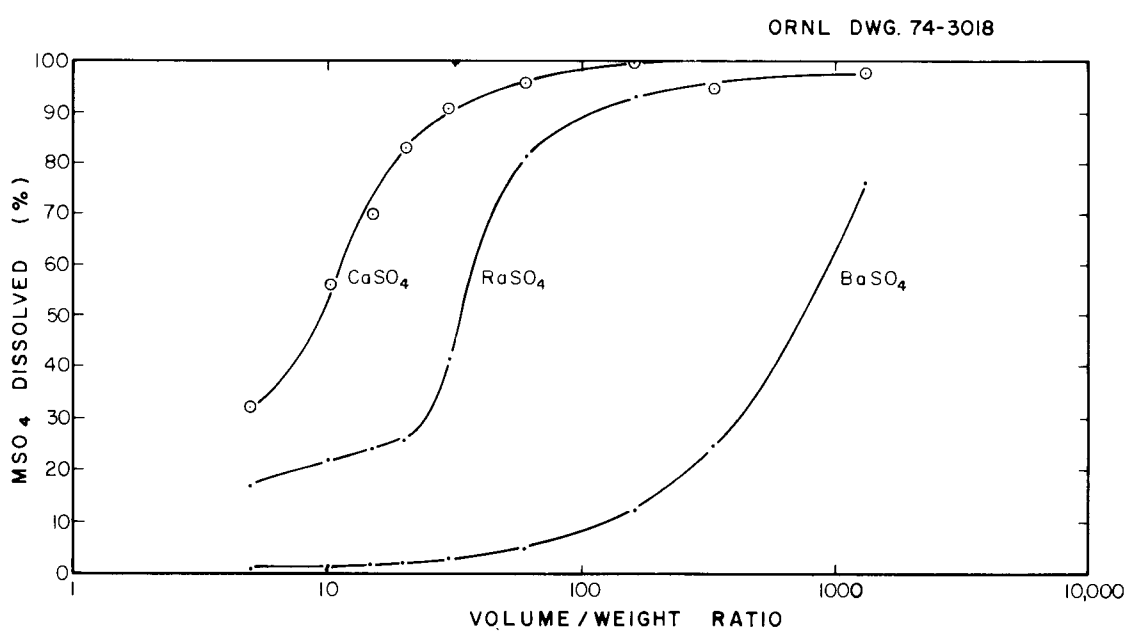

Fig. 8.2. Effect of volume/weight ratio on the leaching of Ra, Ca, and Ba sulfates from slimes solids tailings with 1 *M* NaCl–0.1 *M* HCl solution. Slimes solids: $CaSO_4$, 0.184 g/g; $BaSO_4$, 0.0018 g/g; $^{226}RaSO_4$, 3333 pCi/g. Contact: solid and leachant mixed for 20 hr at room temperature on Burrell shaker.

(Na_5DTPA). The rare earths remain in the solvent. This is a version of the Talspeak process.[12] Substitution of glycolic acid for lactic acid greatly shortens the time required for stagewise equilibrium. Operation at 50°C instead of 25°C further improves the extraction kinetics and accelerates phase separation. The resultant lower distribution coefficients decrease the required aqueous flow by a factor of about 2.

6. Recovery of the americium from the aqueous effluent by any of several methods to be evaluated in future work.

8.5 HIGH-RESOLUTION SEPARATIONS

The use of ion exchange resins of very small particle size and high column pressures ("pressurized ion exchange") has been shown to have a number of important advantages over conventional ion exchange in some applications. It has been applied successfully in analyzing body fluids,[13] separating actinides,[14] and purifying ^{233}U.[15] We are examining some hydrometallurgical separations known to be difficult in order to determine whether the unique advantages of pressurized ion exchange might greatly broaden the acceptance of ion exchange in such applications. Experimental work has been started on separating nickel from cobalt, using 15- to 25-μ Dowex 50W-X8 resin at 200 to 400 psig.

In the industrial Caron process,[16] the nickel-cobalt oxide ore is subjected to a reductive roast to convert the nickel and cobalt to the metallic state. The calcine is leached under oxidizing conditions with an ammonium hydroxide–ammonium carbonate solution to dissolve the metals as their ammine complexes. The nickel and cobalt are recovered from solution and separated from each other by precipitation techniques. Several cation exchange resins were tested previously by the Bureau of Mines[17] for separation and recovery of nickel and cobalt from ammoniacal liquors. It was found that the resins had a moderately good loading capacity for nickel and cobalt, provided the ammonia and carbonate concentrations were not high. Also, the resins sorbed nickel more strongly than cobalt, but the selectivity was not adequate to allow a clean-cut separation.

The liquor being used as feed material for our tests was obtained from a user of the commercial process. The nickel is present as the blue divalent hexammine complex $[Ni(NH_3)_6]^{2+}$, whereas the cobalt appears to be present in three forms: the yellow trivalent hexammine complex $[Co(NH_3)_6]^{3+}$ (Co-3), the red trivalent aquopentammine complex $[Co(NH_3)_5(H_2O)]^{3+}$ (Co-2), and an unidentified red trivalent complex, possibly $[Co(NH_3)_4(H_2O)_2]^{3+}$ (Co-1). The former two cobalt complexes are present in about equal amounts (40%); the latter accounts for the remaining 20%. With ammonium carbonate solutions, the complexes are eluted in the order: Co-1 > Co-2 > Co-3. Conversely, with ammonium bicarbonate solutions the nickel is eluted before the cobalt species, which is the preferred order of elution for separation of the minor (cobalt) component. In this case the Ni/Co-2 separation factor is about 2.5, adequate to permit efficient separation of the metal ions. Unfortunately, however, the separation factor between the nickel and the minor red cobalt complex (Co-1) is only about 1.3, so that complete separation between nickel and cobalt would be difficult. Although an effort to achieve the nickel-cobalt separation by converting all of the cobalt to the yellow hexammine form was not successful, it was possible to convert all of the cobalt to a single, unidentified red complex by reducing the Co(III) ammine to Co(II) with a small amount of nickel metal, permitting a Ni/Co separation factor of about 3. Elution of a sample of reduced liquor with bicarbonate solution resulted in the same elution order as that obtained with the ammonium carbonate solutions.

When the yellow cobalt complex was removed by passing the feed liquor through a bed of Dowex 50 resin, it did not re-form within the time required for systematic investigations of the behavior of the other species. Results of the investigations showed significant effects from carbonate or bicarbonate concentration,

12. B. Weaver and F. A. Kappelmann, *Talspeak: A New Method of Separating Americium and Curium from the Lanthanides by Extraction from an Aqueous Solution of an Aminopolyacetic Acid Complex with a Monoacidic Organophosphate or Phosphonate,* ORNL-3559 (August 1964); *J. Inorg. Nucl. Chem.* **30**, 263 (1968).

13. C. D. Scott, "Automated High Resolution Analysis for the Clinical Laboratory by Liquid Column Chromatography," *Advan. Clin. Chem.* **15**, 1 (1972).

14. D. O. Campbell, "Chromatographic Separation of Transplutonium Elements Using High Pressure Ion Exchange," *Ind. Eng. Chem., Process Design Develop.* **8**, 95 (1970).

15. R. H. Rainey, *Laboratory Development of a Pressurized Cation Exchange Process for Removing the Daughters of ^{232}U from ^{233}U,* ORNL-4731 (December 1972).

16. J. R. Boldt, Jr., *The Winning of Nickel,* p. 425, Van Nostrand, Princeton, N.J., 1967.

17. I. W. Nicholson, P. T. Brooks, and J. B. Clemmer, "Innovations in Processing Nickel-Cobalt Ores," presented at the Rocky Mountain Minerals Conference, sponsored by the A.I.M.E., Salt Lake City, Utah, Sept. 17–19, 1958.

temperature, and loading, and also cross effects from differing combinations of these variables.

Complexation with EDTA prevented sorption of nickel from ammonium carbonate solution by Dowex 50W-X8 resin, while the sorption of cobalt (all three complex species present) was unaffected, even when most of the free ammonia and carbon dioxide was removed from the solution by boiling. In order to completely mask the nickel and prevent its sorption, it was necessary to add at least one mole of EDTA per mole of nickel. Seventy percent of this EDTA was recovered from the cobalt-free eluent by acidification after boiling to remove residual ammonia and carbon dioxide. Both the rate and completeness of precipitation and recovery of the relatively expensive EDTA must be increased before this flowsheet can become economically feasible.

8.6 BIOCHEMICAL SEPARATIONS

Exploratory work to improve and provide for scaleup of a process to isolate "colony stimulating factor" (CSF) from human urine[18,19] was continued throughout part of this report period. CSF is a humoral regulator, as yet unidentified, that stimulates the development of stem cells into immature forms of white blood cells; hence it is of high potential importance to biology and medicine.

Use of the improved dialysis procedure reported last year,[18] programmed gradient elution chromatography on diethylaminoethyl cellulose, and simple sorption-desorption on calcium phosphate gel eliminated 99.9% of the contaminating proteins and 90% of the initial volume. The absolute amount of assayable CSF increased threefold, presumably because of elimination of an inhibitor. Thus the measurable specific activity of the CSF was increased by a factor of 3000 through application of these three steps.

8.7 DISTRIBUTION EQUILIBRIA, KINETICS, AND MECHANISMS

"Single-Atom" Chemistry

The versatile techniques of liquid-liquid extraction, extraction chromatography, and ion resin chromatography are being adapted to study the chemistry of cyclotron-produced transfermium elements. Most of the work to date has been concerned with nobelium, and a paper has been submitted for publication in the *Journal of Inorganic and Nuclear Chemistry*. The abstract follows:

"Comparative Solution Chemistry, Ionic Radius, and Single Ion Hydration Energy of Nobelium," by R. J. Silva, W. J. McDowell, O. L. Keller, Jr., and J. R. Tarrant. *Abstract:* The chemistry of nobelium has been examined by comparing its behavior with other elements in solvent extraction and ion exchange systems, by confirming that its normal valence is +2 by acid dependence of its solvent extraction behavior, by derivation of its ionic radius using both experimental and theoretical methods and by calculation of the single ion heat of hydration. In the experimental work about 500 to 1000 atoms per experiment of cyclotron produced ^{255}No ($T_{1/2}$ = 223 sec) were used. Its extraction behavior in a tri-*n*-octylamine-HCl system was compared with that of divalent mercury, cadmium, copper, cobalt and barium and it was found to be most similar to the relatively non-complexing alkaline earths. Comparison to the alkaline earths in a cation exchange resin-HCl system indicated it to be most like Ca^{2+} and comparison with these elements in a di(2-ethylhexyl) phosphoric acid (HDEHP) liquid-liquid extraction system showed nobelium to have an extraction behavior between that of Ca^{2+} and Sr^{2+}. The extraction of nobelium into HDEHP as a function of pH allowed a direct determination of the valence as +2 in confirmation of previous indications. The ionic radius of No^{2+} was estimated from a linear correlation of ionic radius with distribution coefficient for several divalent ions. A value of 1.0 Å was obtained from ion exchange data and 1.1 Å from liquid-liquid extraction data, with theoretical calculations giving a value of 1.1 Å. The single ion heat of hydration, obtained from a Born type calculation, was −355 Kcal/(g·atom).

Methods are being developed for studying the citrate, oxalate, and acetate complexes of nobelium for determining the reduction potential of No^{2+} and for automating and shortening the chemical procedures to make them applicable to nuclides of still shorter half-lives.

Liquid Scintillation Alpha Spectrometry

Continued use of, and outside interest in, liquid scintillation alpha spectrometry has led to a continued effort to improve this method of alpha counting. The most recent improvement has resulted from the application of pulse-shape discrimination to the liquid scintillation method. It is possible electronically to differentiate between the liquid scintillation pulses produced by beta or gamma radiation and those produced by alpha radiation. Up to 99% of the beta or gamma pulses can be rejected (or counted separately). This results in a marked improvement in the ease with which alpha spectra can be quantitatively resolved, since with liquid scintillation spectra the beta-gamma background is often superimposed on the alpha spectrum. Further, in low-count-rate samples such as those

18. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973*, ORNL-4883, p. 68.

19. E. R. Stanley and D. Metcalf, *Aust. J. Exp. Biol. Med. Sci.* **47**, 453 (1969).

from health physics and environmental monitoring, pulse-shape discrimination results in a dramatic reduction of background to values as low as 0.01 count/min under an alpha peak. This reduces the lower detection limit for alpha counts to approximately the same value. A paper describing the pulse-shape discrimination is in press.[20]

Our present principal emphasis is on developing application of liquid scintillation alpha spectrometry to the "single-atom" transfermium chemistry. Meanwhile, cooperation continues with the Environmental Sciences and Health Physics Divisions, and a detailed paper on the analysis of environmental and physiological samples has been accepted for publication. The abstract follows:

"Plutonium and Uranium Analysis in Environmental Samples: A Combined Solvent Extraction–Liquid Scintillation Method," by W. J. McDowell, D. T. Farrar, and M. R. Billings, *Talanta,* in press. *Abstract*: A method for the analytical determination of uranium and/or plutonium by a combined high-resolution liquid scintillation–solvent extraction method is presented. Assuming a sample count equal to background count to be the detection limit, the lower detection limit for these and other alpha-emitting nuclides is 1.0 dpm with a Pyrex sample tube, 0.3 dpm with a quartz sample tube using present detector shielding or 0.02 dpm with pulse-shape discrimination. Alpha counting efficiency is 100%. With the counting data presented as an alpha energy spectrum, an energy resolution of 0.2 to 0.3 MeV FWHM and an energy identification to ± 0.1 MeV are possible. Thus, within these limits, identification and quantitative determination of a specific alpha emitter independent of chemical separation are possible. The separation procedure allows greater than 98% recovery of uranium and/or plutonium from solution samples containing large amounts of iron and other interfering substances. In most cases uranium, even when present in 10^8-fold mole excess, may be quantitatively separated from plutonium without loss of the plutonium. Potential applications of this general analytical concept to other alpha counting problems are noted. Special problems associated with the analysis of plutonium in soil and water samples are discussed. Results of tests to determine the pulse-height and energy resolution characteristics of several scintillators are presented. Construction of the high-resolution liquid scintillation detector is described.

Iodine Chemistry

The Iodox process utilizes the strong oxidizing power of concentrated nitric acid to convert elemental iodine and volatile organic iodides to the nonvolatile iodic acid (HIO_3 or HI_3O_8). The effect of nitrite (or nitrogen oxides) on this reaction was examined by means of equilibrium measurements at nitric acid concentrations of 14, 16, and 18 *M*. A small amount of nitrite held the iodine as I_2 at 14 *M* HNO_3, but not at 18 *M*.

The solutions were prepared by adding known quantities of KI or HIO_3 and HNO_2 to the nitric acid. For the nominal reaction,

$$I_2 + 5HNO_3 + H_2O \rightleftharpoons 2HIO_3 + 5HNO_2 ,$$

$$Q' = \frac{[HIO_3]^2 [HNO_2]^5}{[I_2]} , \qquad (1)$$

$$\frac{[I_2]}{[HIO_3]^2} \propto [HNO_2]^5 .$$

$[I_2]$ was determined spectrophotometrically (with nitrite interference balanced out in the reference cell), $[HIO_3]$ by difference from the total iodine, and the stoichiometric nitrite $[HNO_2]_{st}$ (i.e., all reduced nitrogen calculated as equivalent nitrite) by balance from the nitrite added and the measured extent of reaction. While the actual reduced nitrogen product must depend on the nitric acid concentration in accordance with the equilibria among HNO_3, NO_2, NO, and/or N_2O, the concentration of the reduced nitrogen in a given solution will be directly proportional to $[HNO_2]_{st}$. Thus, if the product were NO_2 only,

$$I_2 + 10HNO_3 \rightleftharpoons 2HIO_3 + 10NO_2 + 4H_2O ,$$

$$\frac{[I_2]}{[HIO_3]^2} \propto [NO_2]^{10} \approx \{2[HNO_2]_{st}\}^{10} ; \qquad (2)$$

if NO only,

$$3I_2 + 10HNO_3 \rightleftharpoons 6HIO_3 + 10NO + 2H_2O ,$$

$$\frac{[I_2]}{[HIO_3]^2} \propto [NO]^{10/3} \approx \{{}^2/_3[HNO_2]_{st}\}^{3.33} ; \qquad (3)$$

and if N_2O only,

$$4I_2 + 10HNO_3 \rightleftharpoons 8HIO_3 + 5N_2O + H_2O ,$$

$$\frac{[I_2]}{[HIO_3]^2} \propto [N_2O]^{5/4} \approx \{{}^1/_4[HNO_2]_{st}\}^{1.25} . \qquad (4)$$

Logarithmic plots of $[I_2]/[HIO_3]^2$ vs $[HNO_2]_{st}$ (Fig. 8.3) show slopes of 5 at 14 *M* HNO_3, 2.7 at 16 *M*, and 2.5 at 18 *M*, suggesting increasing significance of N_2O and accounting at least qualitatively for the decreased effectiveness of the added nitrite in preserving the I_2 at the higher nitric acid concentration.

20. J. H. Thorngate, W. J. McDowell, and D. J. Christian, "An Application of Pulse Shape Discrimination to Liquid Scintillation Alpha Spectrometry," *Health Phys.*, in press.

These equilibrium values also correlate well with the potentials of nitric-nitrous acid mixtures. Figure 8.4 (solid lines) shows plots of added (stoichiometric) nitrite concentration vs the resulting potential (bright platinum vs saturated calomel electrode). Nernstian behavior was followed with slope in accordance with the expected two-electron change:

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \rightleftharpoons 2NO_2^- + 2H^+ . \quad (5)$$

The equilibrium values of $[NO_2^-]_{st}$ interpolated on the 14, 16, and 18 *M* HNO_3 lines of Fig. 8.3 at 25, 50, 80, and 90% iodine conversion are plotted on the corresponding HNO_3 lines of Fig. 8.4. Here they map into a consistent family of straight lines, giving a simple direct relation of percent conversion to nitric acid concentration and potential.

The solubility of HI_3O_8 was determined in nitric acid solutions pertinent to the Iodox process, and a paper summarizing the results has been accepted for publication. The abstract follows:

"The Solubility of HI_3O_8 in Concentrated Nitric Acid," by R. H. Rainey and J. C. Mailen, *J. Chem. Eng. Data,* in press. *Abstract:* The solubility of HI_3O_8 was determined in 12 to 20 *M* nitric acid over the temperature range of 25 to 100°C. The results can be expressed by the least-squares equation: $\ln S\ (g\ HI_3O_8/\ell) = 13.276 - 0.4515\, C_{HNO_3}(M) - 1170.35/T(°K)$. The solid phase was identified as HI_3O_8 by X-ray diffraction.

In the Iodox process, concentrated (hyperazeotropic) nitric acid is used to absorb iodine from a gas stream. The acid is then reconcentrated, cooled, filtered to remove part of the iodine, and recycled. The solid phase was identified as HI_3O_8 over the entire acid range tested, so that the solubility of HI_3O_8 will determine the amount of iodine recycled with the process acid. There was no indication of perturbation at the azeotrope, and traces of molecular I_2 were detected at 100°C only.

The hyperazeotropic nitric acid is to be prepared by distillation in the presence of magnesium nitrate to break the azeotrope, and densities of the molten

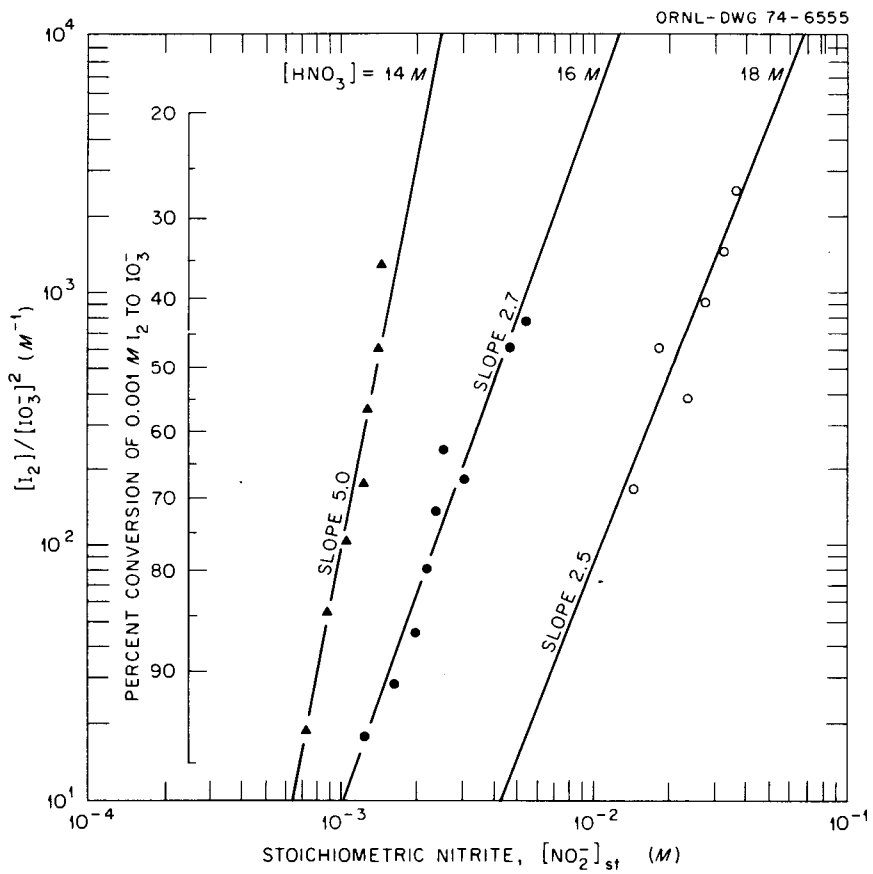

Fig. 8.3. Inhibiting effect of nitrite on the conversion of iodine to iodic acid in concentrated nitric acid. Slope gives exponent *n* in the relation $\log [I_2]/[IO_3^-]^2 = \log [NO_2^-]_{st}^{\,n} + \text{const}$.

magnesium nitrate are needed for process control. The density of magnesium nitrate containing water at approximately 3 to 6 moles of H_2O per mole of Mg was determined from the melting point to about 240°C. The results are given by the following equations,

$$d(3H_2O) = 1.8284 - 0.000705t\ (^\circ C)\ ,$$

$$d(6H_2O) = 1.6556 - 0.000818t\ (^\circ C)\ ,$$

with correlation coefficients of 0.9935 and 0.9929 respectively.

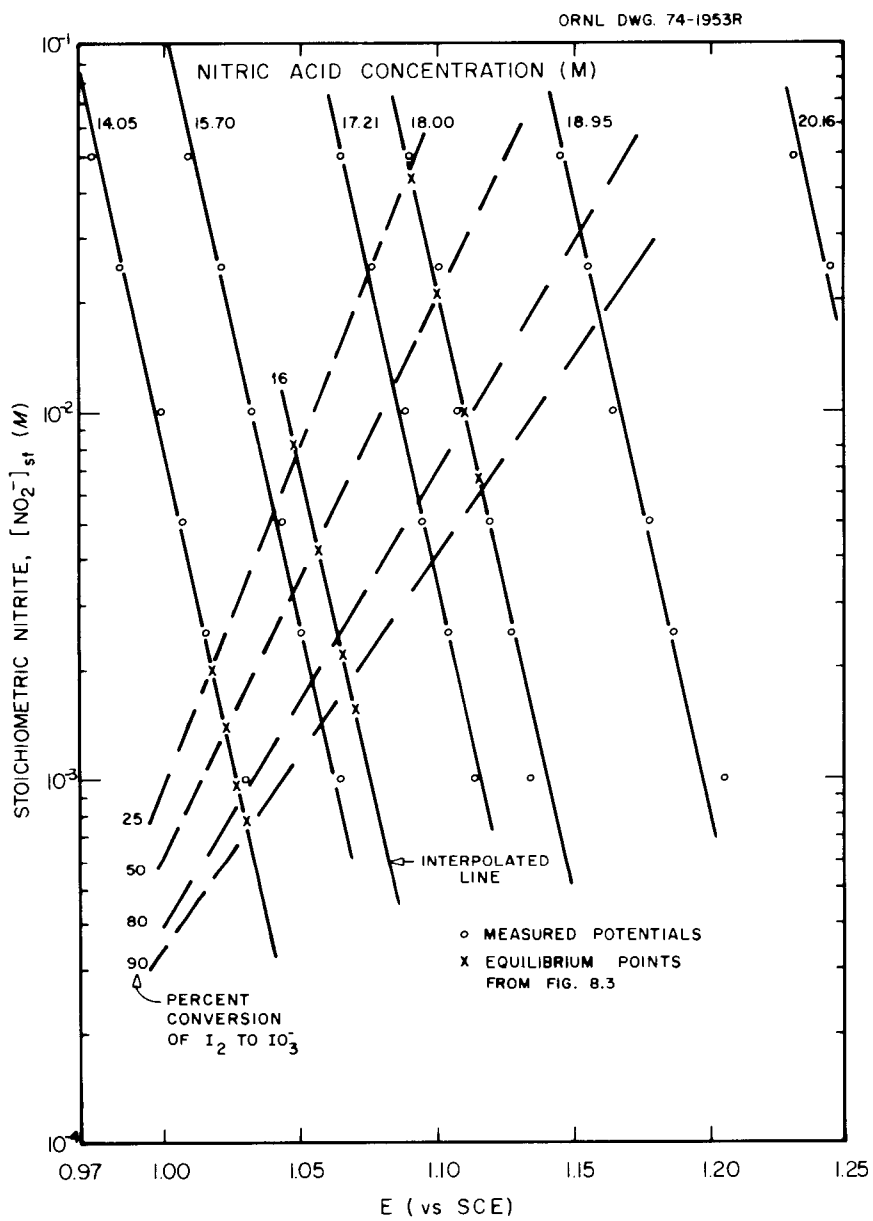

Fig. 8.4. Correlation of iodine–iodic acid conversion with potential of nitric acid–nitrous acid mixtures. Potential was measured in the absence of iodine.

9. Biochemical Technology

MACROMOLECULAR SEPARATIONS

9.1 PURIFICATION OF ERYTHROPOIETIN

The long-range goal of this program is to develop a feasible chemical flowsheet for preparing milligram quantities of erythropoietin (Epo) for use in clinical testing for the relief of anemia. Epo is the hormone that is a primary regulator of erythropoiesis. During this report period, we have prepared and supplied partially purified samples of Epo to Dr. E. Goldwasser, Argonne Cancer Research Hospital, for evaluation.

The current flowsheet consists of the following steps: (1) treatment of sheep with phenylhydrazine to induce anemia and a high concentration of Epo in their blood, (2) DEAE-cellulose chromatography of the desalted sheep plasma to produce "step 1 Epo," (3) carboxymethylcellulose chromatography to produce "step 2 Epo," and (4) ethanol–lithium chloride fractional precipitation to obtain "step 3 Epo."

Phenylhydrazine has been administered to a total of 187 sheep over a 24-month period. The procedure for inducing anemia, particularly the use of a scaled dose on day 5 to titrate the sheep to a hematocrit of 12 ± 3%, has worked quite satisfactorily. Only 19 (or 11%) of the animals expired prior to the recovery of blood. The average hematocrit of the remaining 168 sheep was 11.8% on day 8. These sheep have yielded a total of 499 liters of plasma, or an average of 3 liters per animal.

The Epo content of the pooled plasma after dialysis or dilution averaged 2.9 ± 2.0 units/ml (average plus or minus standard deviation). The results from batch to batch varied widely, from 0.4 to 9.4 units/ml, with a standard deviation of 48%. The 499 liters of plasma yielded a total of 1,486,600 units of Epo. The 168 sheep weighed a total of 8497 kg; thus, 175 units of Epo was obtained per kilogram of sheep.

The recovery of "step 1 Epo" after DEAE-cellulose chromatography was 55%, or 824,000 units of Epo with a purification factor of 30 to 40. This low recovery was largely due to loss from sheep plasma to the desalted DEAE feed. Therefore, new methods of desalting have been investigated.

The carboxymethylcellulose recovery of "step 2 Epo" was 73%, with a product purification factor of 3.8; this product contained a total of 323,000 units of Epo at a concentration of 7.7 units/A_{280}.

Poor results were obtained with the subtractive antibody procedure. No useful separation was achieved because the sheep Epo–rabbit antibody titer was very dilute.

The assays for Epo concentration were carried out in vivo by the exhypoxic polycythemic mouse procedure; our results are reported in terms of units calibrated against Epo standards (international units) obtained from WHO.

9.2 SEQUENCE STUDIES ON PHENYLALANINE tRNA FROM CALF LIVER

Most tRNA primary base sequence studies have been concerned with tRNAs derived from bacterial sources. Only recently have these studies been extended to mammalian systems. The mammalian tRNAs are generally more complex in that they contain larger families of isoacceptors, making the purification of a specific tRNA more difficult; these tRNAs also contain more modified bases.

By combining various chromatographic techniques, including BD-cellulose, reversed-phase, and Sephadex A-50 chromatography, we have separated and purified milligram quantities of several tRNAs from calf liver.[1] We have prepared sufficient quantities of $tRNA^{Ser}$ and $tRNA^{Phe}$ to begin investigating the primary base sequence of these tRNAs. Extensive rechromatography on reversed-phase (RPC-5) columns indicated that the $tRNA^{Ser}$ contained two isoacceptors which would be extremely difficult to separate, while the $tRNA^{Phe}$ preparation appeared more homogeneous. Therefore, the $tRNA^{Phe}$ product was chosen for sequence studies.

1. R. L. Pearson, C. W. Hancher, J. F. Weiss, D. W. Holladay, and A. D. Kelmers, *Biochim. Biophys. Acta* **294**, 236 (1973).

The total base composition was obtained by nucleoside analysis,[2] and oligonucleotides from a pancreatic ribonuclease digest were separated by reversed-phase chromatography.[3] Preliminary results were obtained on the base composition of the oligonucleotides, and some of the oligonucleotides were further digested with ribonuclease T_1 to aid in structure assignment.

Base Composition of Calf Liver $tRNA^{Phe}$

Approximately 12 A_{260} units of calf liver $tRNA^{Phe}$ was digested to the nucleoside level with snake venom phosphodiesterase and bacterial alkaline phosphatase. The resulting digest was separated into its constituent nucleosides by chromatography on an Aminex A-6 column.[2] The results are summarized in Table 9.1. The values shown are the averages for two analyses. In addition to the nucleosides listed, at least two unidentified peaks were obtained. Dihydrouridine was not determined.

The values, in nanomoles per milliliter, were calculated from the peak areas, and these values were normalized by assuming that 31.7 nanomoles/ml for uridine represents 9.0 uridine residues per tRNA molecule. This allows comparison of the results with the structure of rabbit liver $tRNA^{Phe}$ determined by Keith et al.[4]

The major base composition of calf liver $tRNA^{Phe}$ was found to be very similar to that of rabbit liver $tRNA^{Phe}$.

Pancreatic Ribonuclease Digestion of $tRNA^{Phe}$

Approximately 60 A_{260} units of calf liver $tRNA^{Phe}$ in 1.0 ml of 0.05 *M* Tris-HCl, pH 7.3, was digested with 50 μl (5.0 mg/ml) of pancreatic ribonuclease for 4 hr at 38°C. The digest was chromatographed in two separate runs on an RPC-5 column to separate the oligonucleotides.[3]

A typical chromatogram is shown in Fig. 9.1. The eluate fractions were pooled and neutralized, and the eluent was removed by lyophilization. The base composition of each peak fraction was then determined after digestion with snake venom phosphodiesterase and bacterial alkaline phosphatase to nucleosides, as described above. In addition, aliquots of several of the peak fractions were further digested with ribonuclease T_1; these digests were chromatographed on an RPC-5 column, and the base composition of the resulting products was determined.

Results of these analyses are incomplete. However, preliminary data[5] offer supporting evidence for the similarity in structure of $tRNA^{Phe}$ from calf liver and rabbit liver.

2. R. P. Singhal and W. E. Cohn, *Biochim. Biophys. Acta* **262**, 565 (1972).
3. B. Z. Egan, *Biochim. Biophys. Acta* **299**, 245 (1973).
4. G. Keith, F. Picaud, J. Weissenbach, J. P. Ebel, G. Petrissant, and G. Dirheimer, *FEBS Lett.* **31**, 345 (1973).
5. *Chemical Develop. Sect. B Semiannu. Progr. Rep. Mar. 1, 1973, to Aug. 31, 1973, Part I*, ORNL-TM-4370, pp. 270–80.

Table 9.1. Base composition of calf liver $tRNA^{Phe}$ and comparison with that of rabbit liver $tRNA^{Phe}$

Constituent nucleoside	Calf liver $tRNA^{Phe}$		Rabbit liver $tRNA^{Phe}$ (residues/molecule)[b]
	Nanomoles/ml	Residues/molecule[a]	
Uridine	31.7	9.0	9
Pseudouridine	13.4	3.8	4
Ribothymidine	2.31	0.7	1
Guanosine	71.9	20.4	19
Cytidine	63.4	18.0	17
Adenosine	55.6	15.8	16

[a]Calculated assuming that the uridine residues are identical (9.0 per molecule) for calf liver and rabbit liver $tRNA^{Phe}$.

[b]Based on a structure reported by G. Keith, F. Picaud, J. Weissenbach, J. P. Ebel, G. Petrissant, and G. Dirheimer, *FEBS Lett.* **31**, 345 (1973).

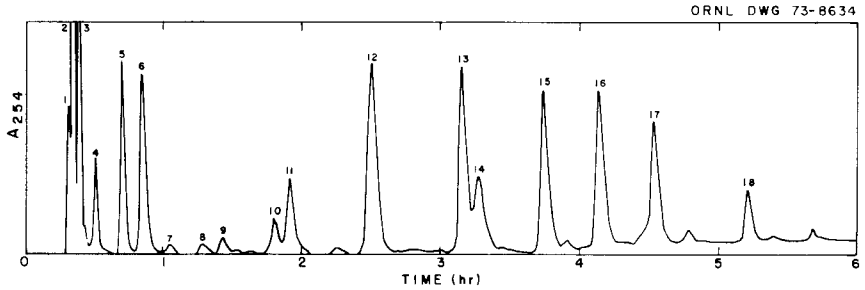

Fig. 9.1. Reversed-phase chromatogram of a pancreatic ribonuclease digest of calf liver tRNA^{Phe}. Column, 0.63 cm in diameter by 97 cm long, RPC-5; eluent, 500 ml of 0.40 to 2.5 *M* ammonium acetate–acetic acid gradient, pH 4.4; temperature, 37°C; flow rate, 1.15 ml/min.

HIGH-RESOLUTION ANALYTICAL SYSTEMS

It is apparent that developments in medical science are slowly moving toward an understanding of some diseases on the molecular level. The effort to achieve a more complete understanding of detailed human biochemistry is being aided by the development of new analytical methods and instruments applicable to studies of complex human physiologic fluids. To take advantage of such developments in the clinical laboratory, it will be necessary to have automated, high-resolution analytical systems to determine many molecular constituents in a single sample. These systems will include a means for separating the complex mixtures into their individual molecular constituents and monitoring devices for quantitating the separated molecular compounds.

A number of high-resolution analytical systems utilizing liquid chromatography (LC) as a means of separation are being developed.[6–13] Several analyzers have advanced through the prototype phase and are being evaluated at other laboratories. Automated data processing systems designed for monitoring liquid chromatographic systems have been fabricated, and computer programs to make full use of these systems have been developed.[14–16] The complete systems are undergoing evaluation in "working" clinical laboratories.

Applications of the LC systems to the analysis of physiologic samples from clinically normal subjects and those having a variety of pathologic conditions have yielded many interesting results.[17–20] Data obtained from these and other high-resolution analytical systems should ultimately broaden our understanding of human

6. S. Katz, S. R. Dinsmore, and W. W. Pitt, Jr., "A Small, Automated High-Resolution Analyzer for Determination of Carbohydrates in Body Fluids," *Clin. Chem.* 17, 701 (1971).

7. W. W. Pitt, Jr., C. D. Scott, and G. Jones, "Simultaneous Multicolumn Operation of the UV-Analyzer for Body Fluids," *Clin. Chem.* **18**, 767 (1972).

8. 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).

9. C. D. Scott, D. D. Chilcote, and N. E. Lee, "Coupled Anion Exchange and Cation Exchange Chromatography of Complex Biochemical Mixtures," *Anal. Chem.* **44**, 84 (1972).

10. C. D. Scott and W. Wilson Pitt, Jr., "Differential Chromatography Using Dual, Coupled Parallel Columns," *J. Chromatogr. Sci.* **10**, 740 (1972).

11. D. D. Chilcote and J. E. Mrochek, "Chromatographic Analysis of Naturally Fluorescing Compounds: I. Rapid Analysis of Nanogram Amounts of Indoles in Physiologic Fluids," *Clin. Chem.* **18**, 778 (1972).

12. D. D. Chilcote, "Column-Chromatographic Analysis of Naturally Fluorescing Compounds: II. Rapid Analysis of Indoleacetic Acid and 5-Hydroxyindoleacetic Acid in Biological Samples," *Clin. Chem.* **18**, 1376 (1972).

13. D. D. Chilcote and J. E. Mrochek, "Rapid Chromatographic Analysis of Nucleosides and N-Bases in Physiologic Fluids," *Anal. Lett.* **6**, 531 (1973).

14. D. D. Chilcote and Charles D. Scott, "Use of a Small Dedicated Computer with a High-Resolution Liquid Chromatograph," *Chem. Instrum.* **3**, 113 (1971).

15. D. D. Chilcote and J. E. Mrochek, "Use of Automatic Digital Data Acquisition and On-Line Computer Analysis in High-Resolution Liquid Chromatography," *Clin. Chem.* **17**, 751 (1971).

16. D. D. Chilcote, "Computer Technique for Identification of Chromatographic Peaks," *Clin. Chem.* **19**, 826 (1973).

17. J. E. Mrochek and W. T. Rainey, Jr., "Identification and Biochemical Significance of Substituted Furans in Human Urine," *Clin. Chem.* **18**, 821 (1972).

18. J. E. Mrochek, S. R. Dinsmore, and D. W. Ohrt, "Monitoring Phenylalanine-Tyrosine Metabolism by High-Resolution Liquid Chromatography," *Clin. Chem.* **19**, 927 (1973).

19. T. P. Waalkes, S. R. Dinsmore, and J. E. Mrochek, "Urinary Excretion by Cancer Patients of the Nucleosides, N^2,N^2-Dimethylguanosine, 1-Methylinosine, and Pseudouridine," *J. Nat. Cancer Inst.* **51**, 271 (1973).

20. J. E. Mrochek and W. T. Rainey, Jr., "Gas Chromatography and Mass Spectrometry of Some Trimethylsilyl Derivatives of Urinary Glucuronides," *Anal. Biochem.* **57**, 173 (1974).

biochemistry and the changes to be expected from certain diseases.

9.3 ENGINEERING DEVELOPMENT

Twenty prototype systems of the UV- and carbohydrate analyzers[6,21] are now in use. Although the engineering development was hampered during this report period because of reduced funding, some efforts were continued to adapt previously developed systems and detectors to new biochemical analyses.

Nucleoside Analyzer

A modified, two-column UV-Analyzer designed for nucleoside separation and analysis was constructed during the year. The "nucleoside analyzer" was designed to analyze the early part (the first 5 hr) of a urine chromatogram using only dilute (0.015 *M*) buffer eluent. A short (25-cm) column was coupled through a timer-actuated valve to a longer (100-cm) column; both columns contained anion exchange resin (Aminex A-27). The analytical procedure involves loading the sample on the short column, eluting through both columns with dilute buffer for 5 hr, followed by an automated uncoupling of the two columns. Concentrated (6 *M*) buffer is pumped through the short column to strip it, while elution of the longer column is continued with dilute buffer. After the short column has been stripped for 2 hr, the two columns are automatically recoupled, and dilute buffer is passed through them for 2 hr to regenerate the system for the next sample. All operations are timer-actuated, and the system is completely automated. Excellent resolution for the front end of the urine chromatogram has been demonstrated, and the system has proved to be reliable in day-to-day operation.

Application of Cerate Oxidimetry to Carbohydrate Detection

Existing color-development detection methods[6,22,23] for carbohydrates limit the utility of the separation system because of peak broadening and lack of sensitivity. Peak broadening is generally caused by mixing problems arising from the addition of multiple reagent streams of differing viscosities to the column effluent. However, the color-development detection systems do have the advantage of specificity for carbohydrates.

A recently developed system,[9,24] which relies on the production of fluorescent cerium(III) by oxidation of products in chromatographic column eluents with cerium(IV), appeared to have promise as a detection device for carbohydrates. Although this system is relatively nondiscriminatory, its sensitivity and resolution capability (single reagent stream of similar viscosity mixed with the column effluent) appear to more than overcome this lack of specificity. Results of tests indicate that the sensitivity is improved by at least one order of magnitude over that obtained with the phenol–sulfuric acid detector,[9] with a concomitant gain in resolution for a series of 16 carbohydrate standards. The detector, coupled with the usual borate buffer elution of an anion exchange column,[9] is being tested for its utility in the analysis of protein-bound carbohydrates in human serum. We are currently investigating changes in column geometry and gradient, with the ultimate goal being the development of a carbohydrate system capable of a complete analysis in 6 to 8 hr.

9.4 APPLICATIONS AND EXPERIMENTAL RESULTS

The development of the automated liquid chromatographic analyzer (UV-Analyzer) has been essentially completed with the fabrication of a computer-based data acquisition and analysis system capable of collecting and analyzing six channels of information from two UV-Analyzers. Software development for the computer system has progressed sufficiently that it can be utilized to identify some chromatographic peaks and print out their concentrations and names.

Work related to the isolation and identification of new molecular constituents in physiologic body fluids is continuing. Current emphasis is on the identification and comparative monitoring of acetaminophen metabolites in serum and urine. This work illustrates the capability of liquid chromatographic systems for separating and simultaneously monitoring a large number of

21. Charles D. Scott, Robert L. Jolley, and Wayne F. Johnson, "Prototype Systems for the Automated, High-Resolution Analysis of UV-Absorbing Constituents and Carbohydrates in Body Fluids," *Amer. J. Clin. Pathol.* **53**, 701 (1970).

22. L. H. Koehler, "Differentiation of Carbohydrates by Anthrone Reaction Rate and Color Intensity," *Anal. Chem.* **24**, 1576 (1952).

23. O. Samuelson, in *Ion Exchange*, ed. by J. A. Marinsky, Marcel Dekker, New York, 1969.

24. S. Katz, W. W. Pitt, Jr., and G. Jones, Jr., "Sensitive Fluorescence Monitoring of Aromatic Acids after Anion-Exchange Chromatography of Body Fluids," *Clin. Chem.* **19**, 817 (1973).

nonvolatile constituents, both conjugated and unconjugated, in a single physiologic sample.

Description of the Automated Data Acquisition System

The computer system is equipped with 12K words of fast memory, a dual cassette tape transport, a real-time clock, an automatic program loader, a digital input/output interface, and an analog input subsystem (ADC). These interfaces enable the computer to simultaneously collect data from two chromatographs while analyzing stored data from one chromatographic analysis.

Computer programming for the system is facilitated by the high-level language FOCAL. This language has been expanded to include commands to specify data acquisition rate, initiate or terminate data collection from either analyzer, access data recorded for either analyzer, write or read processed results onto or from cassette tape, and access the real-time clock for program sequencing and timing. Data from the liquid chromatographic columns are obtained by an automated foreground subprogram which is scheduled to operate periodically by the real-time clock. Double buffering of the input data (two analog signals from photometers and associated digital control inputs) into a block of the memory for each active analyzer is performed by the foreground subprograms at the specified data rate. As the input data blocks are filled, they are written into a ring buffer on the data storage cassette for processing by a FOCAL language program[25] which was modified to operate the new system.

Computer Software

FOCAL language programs for the analysis of chromatographic data and deconvolution of overlapping peaks are described in refs. 14–16 and 26. Modifications to these programs have improved their automated capabilities and added certain specific options which are selected by the operator. A new FOCAL program has been written to enable the computer to identify certain chromatographic peaks, based on elution position, by using reference compounds which are normally present in urinary samples and to print out concentrations of reference and identified compounds using library data from standards.[16]

25. C. D. Scott and S. Katz, *Body Fluids Analysis Program Progress Report for the Period September 1, 1968, to February 28, 1969*, ORNL-TM-2551 (1969).

26. N. G. Anderson, *The Molecular Anatomy Program First Semiannual Progress Report March 1, 1972–August 31, 1972*, ORNL-4815 (1972).

Identification of Urinary Constituents

Thirteen new uv-absorbing compounds isolated from urine samples have been identified during the past year, increasing the total number of identified constituents to 132. (The total is 144 when identified carbohydrates are included.) A list of the new compounds and the origins of the samples in which they were found are given in Table 9.2.

Applications

Studies involving the application of high-resolution liquid chromatography to the investigation of complex physiologic fluids are continuing. One of the more interesting aspects of these studies involved an investigation of the metabolism of a commonly used analgesic, acetaminophen (Tylenol^{R}), in clinically normal subjects. In this study, seven metabolites of the drug were identified in urine samples, and their concentrations were monitored as a function of time after 1950 mg of the drug had been ingested by two clinically normal adult males. In addition, we obtained serum samples which enabled a comparison of concentrations of the free drug and some of its metabolites in both urine and serum (see Fig. 9.2).

A new metabolite of acetaminophen was isolated and identified. The excretion of this metabolite, S-(5-acetamido-2-glucuronosidophenyl)cysteine (CAAPGL), amounted to 5% of the ingested dose (1950 mg) for the 41-year-old subject and 1.6% for the 58-year-old subject. This conjugate and the unconjugated compound S-(5-acetamido-2-hydroxyphenyl)cysteine (CAAP) may have important roles as detoxified products of a presumed toxic metabolite of acetaminophen.[27–29] Other urinary metabolites that were identified and monitored include 2-methoxy-4-glucuronosidoacetanilide, 4-glucuronosidoacetanilide, 2-methoxy-4-hydroxyacetanilide sulfate, 4-hydroxyacetanilide sulfate, and 2,4-dihydroxyacetanilide sulfate.

Results of the study showed that after 2 hr the concentration of 4-glucuronosidoacetanilide in the se-

27. J. R. Mitchell, D. J. Jollow, W. Z. Potter, D. C. Davis, J. R. Gillette, and B. B. Brodie, "Acetaminophen-Induced Hepatic Necrosis. I. Role of Drug Metabolism," *J. Pharm. Exp. Ther.* **187**, 185 (1973).

28. J. R. Mitchell, D. J. Jollow, W. Z. Potter, J. R. Gillette, and B. B. Brodie, "Acetaminophen-Induced Hepatic Necrosis. IV. Protective Role of Glutathione," *J. Pharm. Exp. Ther.* **187**, 211 (1973).

29. J. E. Mrochek, S. Katz, W. H. Christie, and S. R. Dinsmore, "The Metabolism of Acetaminophen in Man as Determined by High-Resolution Liquid Chromatography," *Clin. Chem.* (in press).

Table 9.2. Urinary compounds identified during the period April 1, 1973–March 31, 1974

Compound	Origin of sample
β-(3-Methoxy-4-hydroxyphenyl)hydracrylic acid	Normal and pathologic urines
α-Methoxy-α-(3-methoxy-4-hydroxyphenyl)acetic acid	Lesch-Nyhan syndrome and adult leukemia
4-Hydroxyacetanilide (sulfate conjugate)	Metabolite of acetaminophen
2-Methoxy-4-hydroxyacetanilide (sulfate conjugate)	Metabolite of acetaminophen
S-(5-Acetamido-2-hydroxyphenyl)cysteine	Metabolite of acetaminophen
S-(5-Acetamido-2-glucuronosidophenyl)cysteine	Metabolite of acetaminophen
2,4-Dihydroxyacetanilide (sulfate conjugate)	Metabolite of acetaminophen
1,3-Dimethyluric acid	Normal and pathologic urines – dietary
1,7-Dimethyluric acid	Normal and pathologic urines – dietary
3-Methyluric acid	Normal and pathologic urines – dietary
6-Methylthioguanosine	Metabolite of 6-thioguanine in cancer patients
3-Methoxy-4-hydroxycinnamic acid (glycine conjugate)	Pathologic samples
1-β-D-Arabinofuranosyluracil	Metabolite of cytosine arabinoside in cancer patients
4-Aminoimidazole-5-carboxamide	Cancer patient

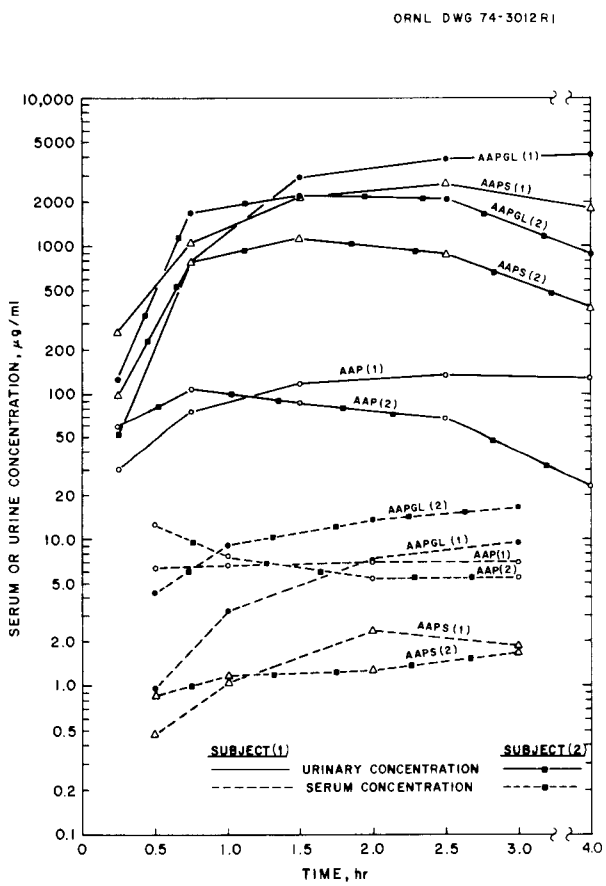

Fig. 9.2. Comparisons of urinary and serum concentrations of acetaminophen (AAP) and its glucuronide (AAPGL) and sulfate (AAPS) conjugates.

rum exceeded that in the free drug (see Table 9.3). This suggests that analytical procedures utilizing extraction coupled with gas chromatographic analysis would not accurately measure the total amount of acetaminophen in the blood since the hydrophilic glucuronide would not be extracted.

Research such as this illustrates the value of liquid chromatography in drug investigations. A large spectrum of compounds can be monitored, enabling not only a study of individual metabolites but also an investigation of drug-induced effects on endogenous compounds. The data obtained will aid in interpretations for mechanisms of drug action and enable formulation of new and possibly more effective drug structures.

LC Monitoring of tRNA Degradation Products

The identification of two additional products of tRNA degradation, 1-methylguanosine (m^1G) and 7-methylguanine (7-MeG), in urine samples from clinically normal subjects prompted a reexamination of the LC-determined excretion data[19] for pseudouridine (ψ), 1-methylinosine (m^1I), and N^2,N^2-dimethylguanosine (m^2_2G). These data were placed on a more comparable basis by converting them to excretion rates per unit of body weight per 24 hr. Analysis of the data revealed that children (aged 4 to 13) excreted these degradation products of the tRNA macromolecule at a level about 60% higher than the adults (see Table 9.4).

Analytical results obtained for the urinary excretion of ψ, m^1I, and m_2^2G by adult cancer patients were generally elevated as compared with their normal adult counterparts, as shown in Fig. 9.3. Whether or not the elevated urine levels for these compounds are derived from tumor cell tRNA or are a secondary effect of the tumor on the host is not known. The possibility that the increased levels of these compounds in urine may be useful in following and assessing the clinical course of cancer patients was not determined by these initial measurements. In a recent report on Hodgkin's disease, the increased urinary excretion of ψ correlated with poor prognostic implications for the patient.[30] Previous studies with chronic lymphatic leukemia indicated a correlation between urinary excretion changes for ψ and response to treatment.[31]

30. K. J. Pinkard, I. A. Cooper, R. Motteram, et al., "Purine and Pyrimidine Excretion in Hodgkin's Disease," *J. Nat. Cancer Inst.* **49**, 27 (1972).

31. A. Hogan, A. Creuss-Callaghan, and J. J. Fennelly, "Studies of Pseudouridine Changes in Chronic Lymphatic Leukemia during Therapy," *Ir. J. Med. Sci.* **3**, 505 (1970).

Table 9.3. Comparisons of serum concentrations of acetaminophen and its metabolites in two clinically normal male adults

Time after drug ingestion[a] (hr)	Subject[b]	Serum concentration (μg/ml)			
		AAP[c]	AAPGL[c]	AAPS[c]	MAAPS[c]
0.5	1	6.2	1.0	0.5	N.D.[d]
	2	12.4	4.3	0.9	0.2
1.0	1	6.6	3.2	1.0	0.1
	2	8.6	9.1	1.2	0.04
2.0	1	7.0	7.2	2.4	2.1
	2	5.4	13.4	1.2	N.D.[d]
3.0	1	7.0	9.4	1.9	0.2
	2	5.5	16.6	1.6	N.D.[d]

[a]Each subject ingested 1950 mg of acetaminophen, equivalent to 23 mg per kilogram of body weight.

[b]Subject 1 was 41 years old; subject 2 was 58 years old.

[c]AAP = acetaminophen; AAPGL = 4-glucuronosidoacetanilide; AAPS = 4-hydroxyacetanilide sulfate; MAAPS = 2-methoxy-4-hydroxyacetanilide sulfate.

[d]N.D. = not detectable.

Table 9.4. Urinary excretion of pseudouridine, N^2,N^2-dimethylguanosine, 1-methylinosine, 1-methylguanine, and 7-methylguanine by normal control subjects

Subjects	Average excretion rate [mg kg^{-1} $(24\ hr)^{-1}$]				
	ψ	m_2^2G	m^1I	m^1G	7-MeG
Adults[a]	0.94 (0.16)[b]	0.06 (0.014)	0.06 (0.009)	0.07 (0.018)	0.10 (0.023)
Children[a]	1.53 (0.38)	0.10 (0.022)	0.10 (0.031)	0.11 (0.032)	0.16 (0.048)

[a]Values given for ψ, m_2^2G, and m^1I represent a total of 17 adults (ages, 15–33) and 9 children (ages, 4–13); values given for m^1G and 7-MeG represent 5 adults and 7 children.

[b]Parentheses enclose the standard deviations.

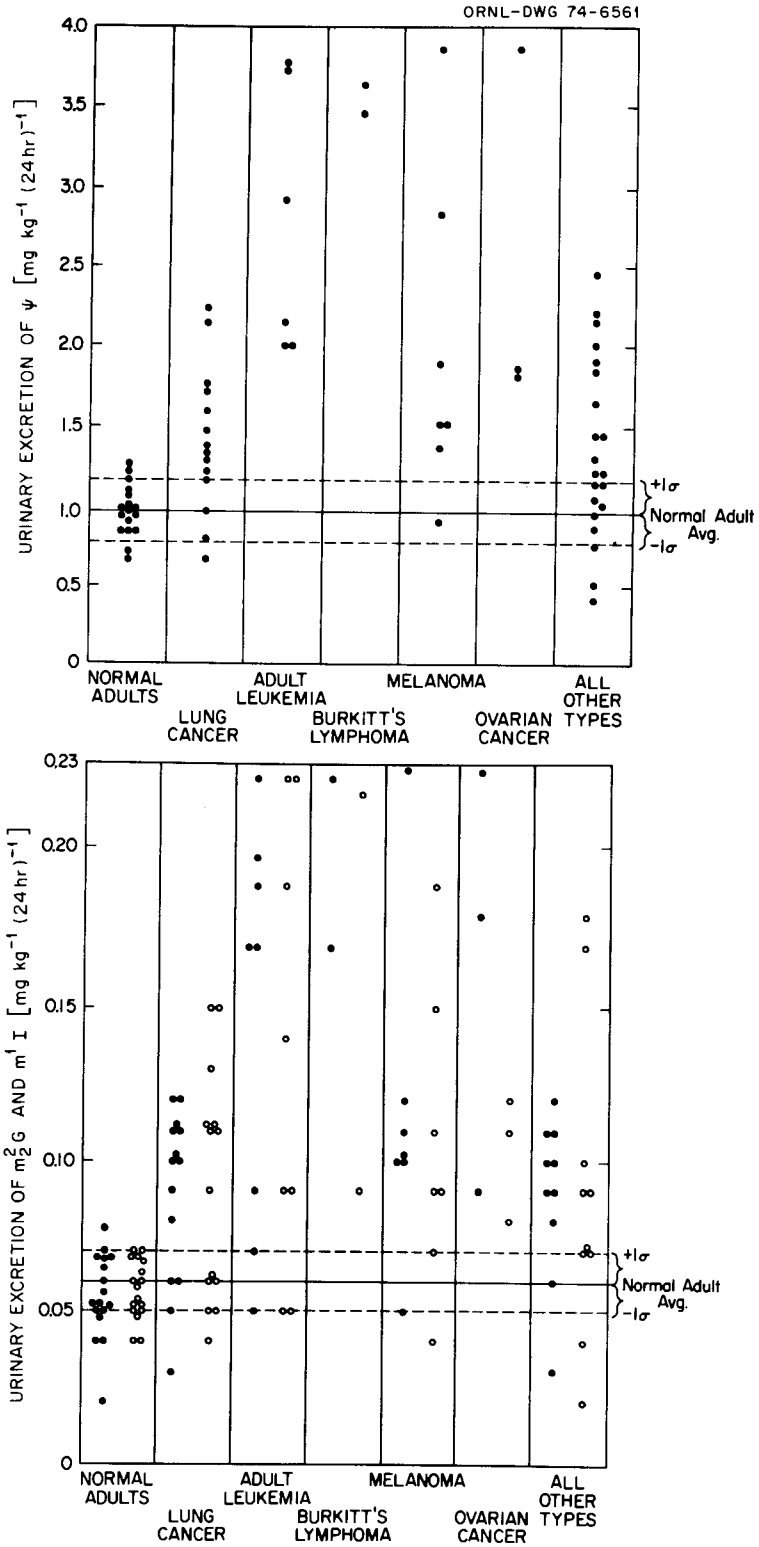

Fig. 9.3. Urinary excretion of pseudouridine (ψ), N^2,N^2-dimethylguanosine (m^2_2G), and 1-methylinosine (m^1I) by clinically normal adults and cancer patients.

WATER POLLUTION STUDIES

The continually expanding population and industrialization of the United States have greatly increased the need for multiple reuse of surface waters with their concomitant concentrations of trace organic compounds. The organic compounds found in the aquatic environment have numerous diverse sources; while many of these are the result of man's activities, some are attributable to natural processes. Regardless of the source, whether domestic, industrial, or agricultural wastes, atmospheric washout, runoff, or by-products of natural biota, it is imperative that identities, quantities, and toxicologic effects of the individual contaminants be established. The impact of these contaminants on the water ecosystems and, indeed, mankind, cannot be accurately assessed without quantitative information concerning the specific compounds and the effects of various treatment processes such as chlorination. No adequate systems for removal or recovery of the organic content can be designed without that prior knowledge.

Although little is known about the significance, from the standpoint of the health of the general population, of the very low concentrations (micrograms per liter) of stable organic and organochlorine compounds found in public water supplies, experimental evidence indicates that some of them may be carcinogenic, mutagenic, or teratogenic. Organic contamination in waters has generally been determined in terms of gross organic content, with relatively limited attempts being made to identify the individual molecular species. Because of its sensitivity and capability for analyzing for many low-molecular-weight, refractory organics in aqueous samples, high-resolution anion exchange chromatography was a natural choice for adaptation to the problem of analyzing for trace organics found in polluted waters. The high-resolution analytical systems previously developed for the analysis of the molecular constituents of physiologic fluids have been successfully applied to the analysis of various polluted waters.

9.5 EFFLUENTS FROM SEWAGE TREATMENT PLANTS

The separation and identification of soluble organic pollutants in the effluents of sewage treatment plants have been continued. Thirty-nine stable organic compounds from four samples of effluent from the primary stage of domestic sanitary sewage treatment plants were isolated and identified. These compounds, their concentrations, and the analytical procedures used for their identification are given in Table 9.5. Ten stable organic compounds from two samples of effluent from the secondary stage of domestic sanitary sewage treatment plants have been isolated and identified (see Table 9.6). In addition to the identified compounds, more than 75 compounds have been characterized with respect to some or all of the following: molecular weight, gas and liquid chromatographic retention times, uv spectra, and mass spectra.

A significant effort has been made toward determining the effects of chlorinating sewage effluents. As a part of this study, six samples of effluents from a domestic sewage treatment plant were chlorinated with ^{36}Cl-tagged chlorination agents to 1 to 2 ppm chlorine residual. After chlorination, the samples were concentrated and chromatographed on an anion exchange column. Analysis of the resulting chromatograms (by means of ultraviolet absorbance and radioactivity measurements) showed the separation of at least 62 chlorine-containing constituents, some of which were probably stable chloro-organic compounds. The concentrations of these constituents ranged from 0.02 to 14 μg of chlorine per liter of original effluent.

Seventeen chloro-organic compounds, tentatively identified by cochromatography of standards, are listed in Table 9.7. The biotoxicities of two of these compounds, 5-chlorouracil and 4-chlororesorcinol, are being investigated in a cooperative effort with the Environmental Sciences Division. Acute toxicity as well as chronic effects (e.g., survivorship and fecundity) are being determined for the zooplankton *Daphnia magna* and carp eggs.[32]

9.6 NATURAL WATERS

The identification and quantification of trace organic compounds present in various natural waters are being studied using high-resolution anion exchange chromatography. The sites chosen for obtaining natural waters for the study, and the bases of selection, are listed in Table 9.8. During this report period the technique for concentrating the water samples prior to analysis was further evaluated; samples were taken at least once from each of the six selected sites; the samples were concentrated and run on the analytical system; known samples of humic acid were obtained and analyzed as reference material on the same system; and development of a group of suitable internal standard compounds was begun.

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32. C. W. Gehrs, L. D. Eyman, R. L. Jolley, and J. E. Thompson, "Effects of Stable Chlorine-Containing Organics on Aquatic Biota," *Nature* (in press).

Table 9.5. Molecular constituents identified in the effluent of the primary stage of a domestic sewage plant

Compound	Identification method[a]	Concentration (μg/liter)
Ethylene glycol	AC, GC, MS	
Maltose	AC, GC	
Galactose	AC, GC	
Glucose	AC, GC	
Glycerine	AC, GC, MS	
Urea	AC, GC, MS	
N^1-Methyl-4-pyridone-3-carboxamide	AC, UV, GC	10
Phenylalanine	AC, GC, MS	90
Uracil	AC, CC, UV, GC, MS	40
5-Acetylamino-6-amino-3-methyluracil	AC, CC, UV, GC	140
N^1-Methyl-2-pyridone-5-carboxamide	AC, CC, UV, GC	20
Thymine	AC, CC, GC, MS	~7
Theobromine	AC, CC	
7-Methylxanthine	AC, CC	~90
Inosine	AC, CC, UV, GC, MS	50
Hypoxanthine	AC, GC, MS	25
Xanthine	AC, CC, UV, GC, MS	70
Copper(II) acetate (binuclear)	MS	
Adenosine	AC, CC, UV, GC, MS	
1,7-Dimethylxanthine	AC, CC	
3-Methylxanthine	AC, CC	
Caffeine	AC, CC, UV, MS	~10
Guanosine	AC, CC, UV, GC, MS	50
1-Methylxanthine	AC, CC, UV	70
Uric acid	AC, GC, MS	20
Orotic acid	AC, UV, GC, MS	5
Succinic acid	AC, GC, MS	
Phenol	AC, GC, MS	6
3-Hydroxyphenylhydracrylic acid	AC, UV, GC, MS	10
Phenylacetic acid	AC, GC	~10
4-Hydroxyphenylacetic acid	AC, UV, GC, MS	190
Benzoic acid	AC, GC, MS	
2-Hydroxybenzoic acid	AC, GC, MS	7
4-Hydroxybenzoic acid	AC, GC, MS	
3-Hydroxybenzoic acid	AC, GC, MS	~40
3-Hydroxyphenylpropionic acid	AC, GC, MS	~20
Indican	AC, GC, F	~2
o-Phthalic acid	AC, UV, MS	200
p-Cresol	AC, GC, MS	20

[a]AC, anion exchange chromatography· CC, cation exchange chromatography; UV, ultraviolet spectrum; GC, gas chromatography on two columns; MS, mass spectroscopy; F, fluorescent spectrum.

Table 9.6. Identification of molecular constituents in the effluent of the secondary stage of a domestic sewage plant

Compound	Identification method[a]	Concentration (μg/liter)
Glycerine	AC, GC, MS	
Uracil	AC, CC, UV	30
5-Acetylamino-6-amino-3-methyluracil	AC, CC, UV	30
1-Methylinosine	AC, CC, UV	80
Inosine	AC, CC, UV	20
7-Methylxanthine	AC, CC, UV	5
1-Methylxanthine	AC, GC	6
1,7-Dimethylxanthine	AC, CC, UV	~6
Succinic acid	AC, GC, MS	
p-Cresol	AC, GC, MS	90

[a]AC, anion exchange chromatography; GC, gas chromatography on two columns; CC, cation exchange chromatography; UV, ultraviolet spectrum; MS, mass spectroscopy.

Table 9.7. Tentative identifications and concentrations of chlorine-containing constituents in chlorinated sewage plant effluents

Peak elution volume (ml)	Tentative identification	Reference standard elution volume (ml)	Concentration of organic compound (μg/liter)
72.4 ± 2.7	5-Chlorouracil	72[a]	4.3
80.2 ± 4.0	5-Chlorouridine	81	1.7
86.2 ± 4.2	8-Chlorocaffeine	86	1.7
102 ± 3.3	6-Chloroguanine	109	0.9
218	8-Chloroxanthine	218	1.5
302 ± 5.9	2-Chlorobenzoic acid	307 ± 9[b]	0.26
312 ± 5.9	5-Chlorosalicylic acid	310	0.24
334 ± 6.4	4-Chloromandelic acid	338	1.1
403 ± 1.7	2-Chlorophenol	400	1.7
415 ± 3.8	4-Chlorophenylacetic acid	411	0.38
436 ± 5.4	4-Chlorobenzoic acid	434 ± 11[c]	1.1
444 ± 4.4	4-Chlorophenol	446	0.69
464 ± 8.7	3-Chlorobenzoic acid	455 ± 10[c]	0.62[d]
	and/or		
	3-Chlorophenol	456	0.51[d]
496 ± 8.7	4-Chlororesorcinol	495	1.2
527 ± 15.6	3-Chloro-4-hydroxybenzoic acid	540	1.3
547 ± 20.2	4-Chloro-3-methylphenol	550	1.5

[a]Average of two determinations.
[b]Average of seven determinations plus or minus standard deviation.
[c]Average of four determinations plus or minus standard deviation.
[d]Value based on the assumption that the chlorine is present as the pure compound of one and not as a mixture of both.

Table 9.8. Initial sampling sites for the measurement of the molecular organic contaminants in polluted water

Geographic location	Physical location	Reasons for selection
Oak Ridge, Tennessee	Walker Springs Watershed	Well characterized ecologically and relatively undisturbed
Watts Bar Reservoir, Kingston, Tennessee	Cooling water inlet[a] to TVA steam plant	Reasonably unpolluted water routinely chlorinated for anti-fouling purposes
Fort Loudoun Lake, Knoxville, Tennessee	U.S. Navy and Marine Corps Reserve Training Center	Downstream from major city sewage treatment plant
Lake Marion, South Carolina	Santee Dam	Example of waters with high natural organic content
Mississippi River, Memphis, Tennessee	Cooling water intake[a] of Allen Steam Plant	Nation's major watershed and site of samples taken for other studies
South Fork of Holston River, Kingsport, Tennessee	Just above junction with North Fork	Downstream from large industrial organic chemical plant

[a]Inlet chosen to provide base line for later studies of effects of chlorination.

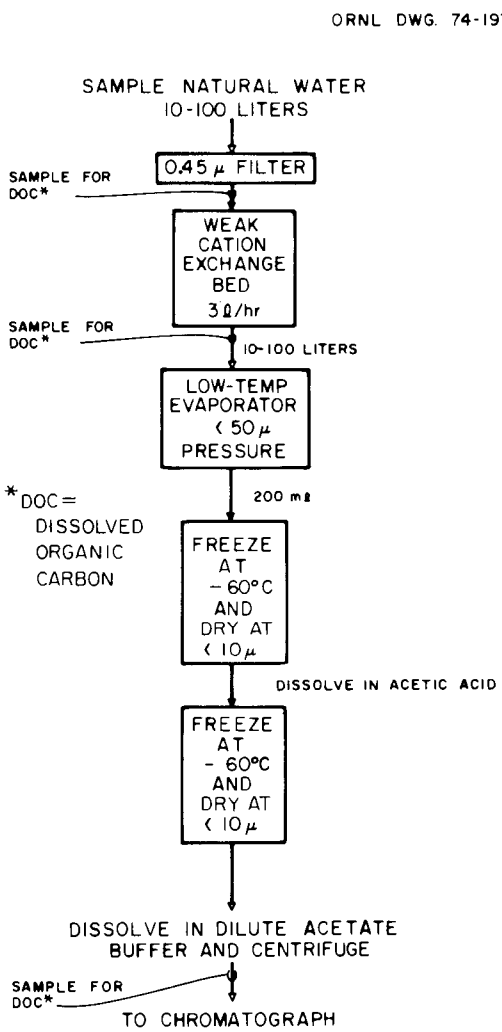

Fig. 9.4. Procedure for concentration of polluted water prior to high-resolution liquid chromatography.

Table 9.9. Identification of molecular constituents in natural waters

Sample site	Compound	Identification method[a]
Fort Loudoun Lake	Glycerine	AC, GC, MS
	Urea	AC, GC, MS
Lake Marion	Glycerine	AC, GC, MS
	Glycine	AC, GC, MS
	Urea	AC, GC, MS
Watts Bar Lake	Glycerine	AC, GC, MS
	Diethylene glycol	AC, GC, MS
	Xylitol	AC, GC, MS
	Mannitol	

[a]AC, anion exchange chromatography; GC, gas chromatography; MS, mass spectrometry.

The concentration technique that had been adequate for sewage plant effluents was found to be unsatisfactory for natural waters because of the greater concentration factor needed and the consequent larger quantity of insoluble salts that were produced. It was found that the concentration technique, in addition to the filtration, vacuum distillation, and freeze-drying steps, required filtration of the natural water through an ion exchange column to remove those cations which form the bulk of the inorganic insoluble compounds. The concentration technique adopted is shown in Fig. 9.4.

Concentrated samples from the six sites (Table 9.8) have been analyzed on an anion exchange chromatograph having a cerate oxidative detector in series with an ultraviolet photometer. In addition, concentrates from three sites have been chromatographed on a

preparative scale, and the column eluate fraction has been subjected to a multianalytical technique[33] in an effort to identify individual contaminants. Identifications made to date are shown in Table 9.9.

CENTRIFUGAL FAST ANALYZER DEVELOPMENT

The basic objective of this effort is the development of fast analytical systems for clinical and related uses. The first system developed under the auspices of this program was the GeMSAEC Fast Analyzer, which uses a centrifugal field to transfer small aliquots of samples and reagents into their respective rotating cuvets, where they are mixed and then are rapidly and sequentially monitored by a stationary photometer or fluorometer. Most of the routine operating functions of the analyzer, including automated sample and reagent loading and on-line data acquisition, storage, and computation, have been developed to the extent that the analytical system is useful for the rapid routine analysis of very small serum samples using both end-point and kinetic techniques. To demonstrate that such a system is practical and reliable, a 15-cuvet Centrifugal Fast Analyzer has been routinely operated for the past three years in the ORNL Clinical Laboratory. In addition, approximately 200 commercial systems have been placed in various clinical laboratories around the world.

9.7 ENGINEERING DEVELOPMENT

During this report period, our efforts in this area were primarily focused on the continued development of a miniature analytical system that is based around a miniature Centrifugal Fast Analyzer. The components of this system include an analyzer, several rotors, a rotor cleaning station, an automated sample-reagent loader, and an on-line data system. The system was evaluated by comparing its performance directly with that of the 15-cuvet GeMSAEC Centrifugal Fast Analyzer. The results of this evaluation were so successful that the miniature system has replaced the older analyzer and is now being used routinely in the clinical laboratory in the ORNL Health Division (Fig. 9.5). To obtain an additional independent evaluation, a duplicate system is being fabricated and will be installed and evaluated in the clinical laboratory of the National Institutes of Health, Bethesda, Maryland.

Both surface and right-angle fluorescence monitors are being developed in an effort to broaden the application of the miniature analyzer; the right-angle monitors can also be used for nephelometric measure-

33. J. E. Mrochek, W. C. Butts, W. T. Rainey, and C. A. Burtis, "The Separation and Identification of Urinary Constituents Using Multiple-Analytical Techniques," *Clin. Chem.* **17**, 72 (1971).

Fig. 9.5. A miniature Centrifugal Fast Analyzer system in routine operation in the clinical laboratory of the ORNL Health Division. Also included in this system, but not shown, are an automated sample-reagent loader and a rotor cleaning station.

Fig. 9.6. A portable analytical system consisting of a portable Centrifugal Fast Analyzer and data system.

ments. Methods of loading liquids into the rotors continue to be of interest; consequently, the technique of dynamic introduction of liquids has been extensively studied, its important parameters have been identified and optimized, and various analytical applications have been investigated. A rotor that is capable of accepting and automatically processing a whole-blood sample is being developed, and a prototype is currently being evaluated.

A portable Centrifugal Fast Analyzer is also under development, and a second prototype is currently being evaluated. This prototype, which is contained in and on a 4-in.^{3} cabinet, is battery operated and capable of either photometric or fluorometric measurement. A portable data system is being developed to complement the portable analyzer, and the combination (Fig. 9.6) should result in a system that is capable of operation in almost any field situation.

9.8 ANALYTICAL APPLICATIONS

A simple and rapid procedure for determining blood groups has been developed for use with the miniature and portable Centrifugal Fast Analyzers. In this procedure, aliquots of red blood cells and antisera are transferred, mixed, and incubated within their respective cuvets in the rotor of the analyzer. They are next centrifuged at 4000 rpm for 30 to 45 sec in order to pack the cells; this is followed by an abrupt braking. Nonagglutinated cells (negative reaction) are resuspended by this dynamic braking step, whereas most agglutinated cells (positive reaction) remain packed at

the edge of the rotor. The absorbance of each cuvet is measured after braking. Those cuvets with high absorbances (1.3 absorbance units to infinite absorbance) are considered to represent a negative reaction; those cuvets with low absorbances (0 to 0.5 absorbance unit) are considered to represent a positive reaction.

Direct ABO and Rh blood grouping has been investigated by comparison with manual slide blood grouping as performed by the ORNL Health Division. Also, reverse ABO and Rh blood grouping has been performed on serum. Additional applications of the system include cross matching and the direct and indirect Coombs tests.

A blood-cell washing rotor has been developed to facilitate the cross matching and the direct and indirect antiglobulin (Coombs) tests. This rotor was evaluated by coating Rh_0-positive red blood cells (Rh_0^+ RBC) with anti-Rh_0 under conditions not conducive to agglutination of the cells. After several cell washing operations, these labeled cells were found to be very sensitive to antihuman immunoglobulin, whereas nonlabeled cells (Rh_0^+ RBC) were not.

An additional effort involves the use of a Centrifugal Fast Analyzer to automate various immunological assays. For example, the miniature analyzer with the right-angle optical monitor has been used in the development of a 3-min kinetic IgG assay. Other assays under consideration include those for IgA, IgM, C′3 complement component, and α_1-antitrypsin, as well as many others for which specific antibodies are available.

GENETIC MONITORING

Mutations in man may be caused by environmental conditions such as ionizing radiation, chemical pollutants, etc., as well as by natural causes. Therefore, it is desirable to monitor the mutation rate so that dangerous increases can be detected. One technique used for monitoring involves the high-resolution gel electrophoresis of the enzymes present in red blood cells (RBC). However, a rapid means of separating stabilized blood into plasma, washed cells, and cell lysate is needed if RBC are to be analyzed in a genetic screening program. Previously, this operation required a tedious

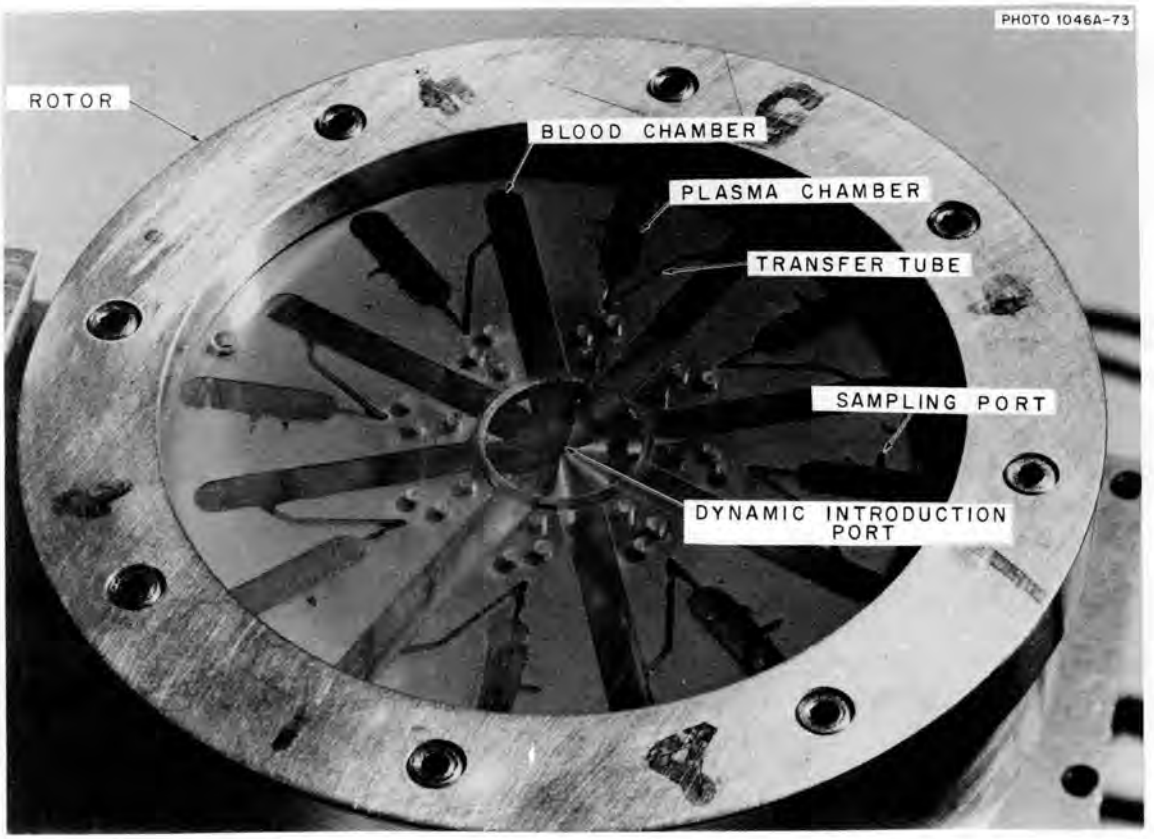

Fig. 9.7. Top view of first prototype of the blood separation rotor.

ORNL DWG 73-6913R

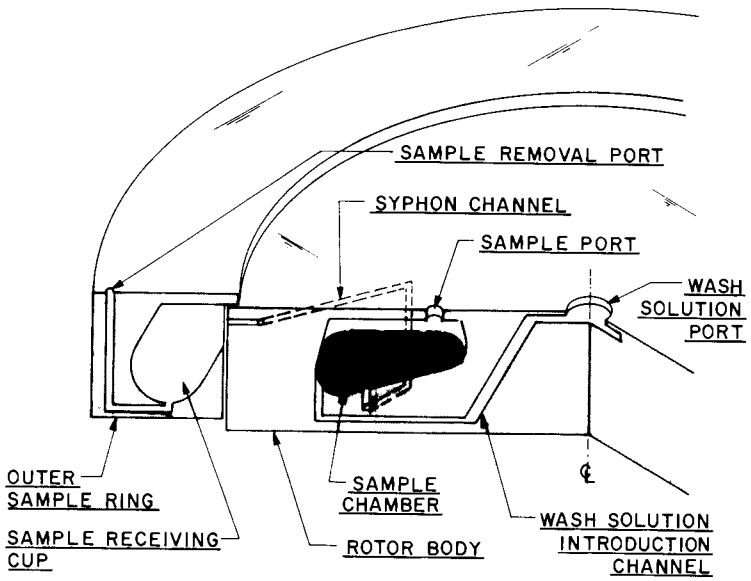

Fig. 9.8. Design of advanced rotor and sample ring for whole-blood processing.

series of manual operations including centrifugations, mixings, and pipettings. To simplify and automate this operation, a blood processing system consisting of a process centrifuge with an appropriately designed rotor is being developed.

The first prototype rotor (Fig. 9.7) separated stabilized blood into plasma and cell fractions, washed the cell fractions, lysed the blood cells, and allowed sampling of both the plasma and the lysed cells. After this unit had been evaluated, a second rotor which incorporated additional automated features was designed (Fig. 9.8) and fabricated. As with the earlier version, the new system has provisions for blood separation, washing of RBC, and lysing; however, it differs in that it utilizes removable outer chambers for collecting samples of plasma, RBC, and lysate in three successive operations.

The important feature of the new system is that collected plasma, RBC, and lysate can be sampled either at the end of the process or while other separation processes are in progress. Thus, sampling in this system does not limit further separation and preparation steps as it did in the initial design. The system is now undergoing evaluation by Dr. Jim Neel and his group at the University of Michigan, Ann Arbor.

BIOLOGICAL PRODUCTION OF FUEL GASES

Increasing interest in a "hydrogen economy" based on hydrogen as a medium of energy transport has increased efforts to develop alternatives to the present hydrogen production methods. It is well known[34] that certain bacteria in the proper environment will produce hydrogen. The hydrogen-producing process has been demonstrated in aqueous solutions of cellular extracts containing ferredoxin and hydrogenase, using sodium dithionite as the reducing agent.[35–41] Hydrogen was formed as the reduction product from the water, and $Na_2S_2O_4$ was presumably oxidized to a higher oxide, as yet unidentified. It has been reported[42] that such higher oxides can be reduced to dithionite by thermal decomposition. Thus, a cyclic process can be considered such that

$$Na_2S_2O_4 + H_2O \xrightarrow[\text{hydrogenase}]{\text{ferredoxin}} H_2\uparrow + Na_2S_2O_x \ ,$$

34. W. D. McElroy and B. Glass, eds., *A Symposium on Inorganic Nitrogen Metabolism,* Johns Hopkins Press, Baltimore, 1956.
35. H. C. Peck, Jr., and H. Gest, *J. Bacteriol.* **71**, 70 (1956).
36. H. C. Peck, Jr., and H. Gest, *J. Bacteriol.* **73**, 569 (1957).
37. J. E. Carnahan and J. E. Castle, *J. Bacteriol.* **75**, 121 (1958).
38. J. E. Carnahan, L. E. Mortenson, H. F. Mower, and J. E. Castle, *Biochim. Biophys. Acta* **44**, 520 (1960).
39. L. E. Mortenson, R. C. Valentine, and J. E. Carnahan, *Biochem. Biophys. Res. Commun.* **7**, 448 (1962).
40. R. C. Valentine, L. E. Mortenson, and J. E. Carnahan, *J. Biol. Chem.* **238**, 1141 (1963).
41. E. Knight, Jr., and R. W. F. Hardy, *J. Biol. Chem.* **241**, 2752 (1966).
42. M. Boros and B. Lorant, *Seifen-Oele-Fette-Wachse* **89**, 531 (1963).

$$Na_2S_2O_x \xrightarrow{630-710^\circ C} O_2\uparrow + Na_2S_2O_4 ,$$

resulting in the net production of hydrogen (and oxygen) from water.

We have investigated the stability of the dithionite and enzymes, the reaction kinetics and efficiency of the enzymatic reduction step, and the chemistry associated with the thermal decomposition and chemical reduction of sodium hyposulfite and sodium dithionate.[43]

Procedures

Several grams of *Clostridium pasteurianum* bacteria were grown, and crude extracts of the necessary enzymes were prepared by lyophilization, grinding, and extraction of the cells. Enzymatic activity was retained for several weeks when the preparations were stored frozen (−20°C) under argon or in a vacuum.

Since both the dithionite and the enzymes, particularly hydrogenase, are sensitive to oxygen, most experimental operations and preparations were carried out in a glove box or in closed vessels under argon. Solutions were buffered with potassium phosphate. Hydrogen was measured with a gas chromatograph.

Kinetics

Rates of hydrogen production were obtained as a function of temperature, enzyme concentration, solution pH, and substrate concentration. In general, the hydrogen production rate decreased with time during a run; therefore, the rate obtained refers to the initial rate.

No attempt was made to quantitatively measure the amount of ferredoxin and hydrogenase in the cell extracts. Enzyme concentration was measured in terms of the volume of cell extract. On this basis, an approximately first-order relationship between hydrogen production rate and enzyme concentration was obtained.

The observed effect of pH on the rate of hydrogen production is actually the sum of several effects. The pH affects both the stability of the enzyme and the decomposition of sodium dithionite. Under the conditions considered, the optimum pH for the maximum hydrogen production rate appeared to be about 6.8.

The effect of temperature on the hydrogen production rate of the catalyzed reaction may be influenced by the thermal inactivation of the enzymes. No decrease in the initial hydrogen production rate was observed in the temperature range 35 to 50°C, indicating that initial inactivation of the enzymes was not significant. In this temperature range the initial hydrogen production rate followed the Arrhenius relationship; a plot of the logarithm of the hydrogen production rate vs $1/T$ gave a straight line. An apparent activation energy of 14 kcal per gram-mole of hydrogen was calculated.

The rate of hydrogen production was measured at different dithionite concentrations in the range 0.5 to 230 g/liter. At pH 6.6 and 35°C, and at constant enzyme concentration, the maximum rate of hydrogen production was observed at approximately 3 g of $Na_2S_2O_4$ per liter. Higher concentrations of dithionite appeared to inhibit the reaction.

Regeneration of Dithionite

Recycling the oxidized substrate to recover the dithionite would make the enzymatic method for producing hydrogen much more attractive. The oxidation products of the dithionite reaction have not yet been identified. However, possible products were postulated to be $Na_2S_2O_5$, $Na_2S_2O_6$, and/or $Na_2S_2O_7$. There are conflicting reports in the literature as to the products and the mechanism of the thermal decomposition of these compounds.[42,44]

We have studied the thermal decomposition of $Na_2S_2O_5$ by differential thermal analysis and thermogravimetric analysis in vacuum and in oxygen, argon, and hydrogen. The gases produced were analyzed by mass spectrometry. In each case, SO_2 was produced at temperatures below 250°C. A sample of $Na_2S_2O_6$ also produced SO_2 when heated in a vacuum. These results indicate that thermal decomposition of the higher oxides is not a feasible method for recovering the dithionite.

We also investigated the chemical reduction of $Na_2S_2O_5$ and $Na_2S_2O_6$ with zinc. While dithionite can be produced in this way, temperatures of 1350 to 1500°C would be required to recover the zinc.

Several alternative reducing agents are being evaluated as a replacement for $Na_2S_2O_4$ as substrate for the hydrogen-producing reaction.

43. C. D. Scott et al., *Experimental Engineering Semiannu. Progr. Rep. Sept. 1, 1973 to Feb. 28, 1974,* ORNL-TM-4602 (in preparation).

44. L. Erdey, J. Simon, S. Gal, and G. Liptay, *Talanta* 13, 67 (1966).

10. Spectrophotometric Studies of Solutions with Radioactive Materials

10.1 SPECTRAL STUDIES OF THE ACTINIDES

The results of investigations on the photochemical reduction of UO_2^{2+} and on the dioxouranium(V) intermediate species have been reported in two papers accepted for publication in the *Journal of Inorganic and Nuclear Chemistry*. The abstracts of the papers follow:

"Photoreduction of the Uranyl Ion with Laser Light and Ethanol. I. Quantum Yields and Medium Effects," by J. T. Bell and S. R. Buxton. *Abstract:* The photoreduction of the uranyl ion in sulfuric acid with laser light and ethanol is discussed. Quantum yields of ~0.6 and 0.5 were measured for the production of U(IV) with an argon ion laser and with a neon laser, respectively. The effects of ethanol and sulfuric acid concentrations to increase the quantum yields are discussed.

"Spectrophotometric Studies of Dioxouranium(V) in Aqueous Media. I. The Perchlorate Medium," by J. T. Bell, H. A. Friedman, and M. R. Billings. *Abstract:* The spectrum of UO_2^+ in aqueous perchlorate medium is described as two absorption bands at 9400 and 7380 A, with higher energy absorption beginning at ~6500 A and increasing at shorter wavelengths to at least 5000 A. Thermodynamic values of k, ΔF°, ΔH°, and ΔS° for the disproportionation of UO_2^+ were determined to be 7×10^4, −6.6 kcal, −18.6 kcal, and −40 e.u., respectively. The value of S° for UO_2^+ was determined to be −11 e.u.

A third paper is in review before being submitted to the *Journal of Inorganic and Nuclear Chemistry*. An abstract follows:

"Photoreduction of the Uranyl Ion with Laser Light and Ethanol. II. The Effects of Temperature and Uranyl Concentration on the Uranyl-Ethanol Reaction," by J. T. Bell and S. R. Buxton. *Abstract:* The effects of temperature and UO_2^{2+} concentration on the quantum yield for the photochemical reduction of UO_2^{2+} to U^{4+} with laser light and ethanol are presented. As the temperature was increased, the quantum yield decreased through a minimum for the lower UO_2^{2+} concentrations (<0.1 *M*) but steadily increased for the higher UO_2^{2+} concentrations (>0.5 *M*). The quantum yield at each temperature in the range 25 to 87°C was strongly dependent on UO_2^{2+} concentrations less than 0.2 *M*, and almost independent of UO_2^{2+} concentrations greater than 0.3 *M*. The essential considerations of the UO_2^{2+}-ethanol dark reaction and of various effects on the UO_2^{2+} absorbance at the specific argon laser wavelengths are also discussed. The UO_2^{2+}-ethanol reaction will occur in the dark, especially at the higher temperatures, and the activation energy for the reaction was determined to be 10.2 kcal. The equilibrium quotient at 25°C for the UO_2^{2+}-ethanol dark reaction was determined to be about 10^{-7}. The effects of temperature and of UO_2^{2+} concentration on the UO_2^{2+} absorbance at the laser wavelengths are not equal to the same effects on the absorption at the peak wavelengths. The photochemical reduction of the U(V) intermediate is suggested to play a primary role in the mechanism of the photochemical reduction of UO_2^{2+} to U^{4+}.

Investigations of the photochemistry of aqueous plutonium species resulted in the discovery of three photochemical plutonium reactions. Plutonium(VI), as PuO_2^{2+}, is reduced with ethanol and light to PuO_2^+; Pu^{4+} is reduced by ethanol and light to Pu^{3+}; and Pu^{4+} is oxidized by heat, and perhaps light, and nitrate to PuO_2^{2+}. The reactions are not detectable with 4765-Å laser light but are easily observed with light from a mercury arc source. Quantum yields for the reactions are estimated to be less than 0.1.

The quantum yield for the photochemical reduction of PuO_2^{2+} to Pu^{4+} in a perchlorate medium with ethanol and filtered ultraviolet light was determined to be 0.01. The filtered light was calibrated with a solution of UO_2SO_4 in 3 *M* H_2SO_4 and 1.1 *M* ethanol which would absorb all of the filtered ultraviolet light imposed on the sample. Then, the same sample cell was filled with a perchloric acid solution that contained PuO_2^{2+} ions and had an ethanol concentration of 1.1 *M*. This solution would also absorb all of the light in contact with the sample. The amounts of photoreduced Pu^{4+} and U^{4+} were then compared, and the quantum yield for the plutonium reaction was calculated assuming a value of 0.6 for the quantum yield for uranyl photoreduction.

10.2 SPECTROPHOTOMETRIC STUDIES OF I_2 AND H_2O IN CONDENSED GASES

Preliminary studies of the chemistry of HTGR fission products in liquid and gaseous CO_2 have shown that I_2

is not very stable in CO_2, that H_2O is associated with CO_2, and that H_2O further decreases the stability of I_2 in the three-component system.

The H_2O-CO_2 binary system was studied to establish techniques for analyzing water in the three-component system. However, early results indicated molecular association of H_2O and CO_2, and a more rigorous investigation was initiated because of the possible entrapment of T_2O in the KALC process.[1] The concentration of water in liquid or gaseous CO_2 can be observed by the intensity of the 1.88-μ absorption band, which is characteristic of the H-O-H structure. The molar absorptivity of this band for H_2O in liquid CO_2 was determined to be 4.0 for the 5 to 25°C range by differential techniques, and by combining the literature data for the solubility of H_2O in CO_2 with our observed absorbance data. The vapor-phase association of H_2O with CO_2 was studied by observing the 1.88-μ band for the vapor phase over liquid H_2O at CO_2 pressures of 400 to 900 psi. The amount of H_2O vapor over pure H_2O at these temperatures cannot be detected by these techniques, but the amount of H_2O in the vapor increased with the CO_2 pressure. The data have been interpreted by assuming that the following equilibrium is established in the vapor phase:

$$nCO_2 + H_2O \overset{K_n}{\rightleftharpoons} (CO_2)_nH_2O\,. \qquad (1)$$

The concentration of H_2O in the vapor phase was assumed to be constant, and the absorbance at 1.88 μ was assumed to represent the $(CO_2)_nH_2O$ species only, because H_2O could not be detected without the CO_2 overpressure. If these assumptions are valid, a logarithmic plot of product concentration vs CO_2 concentration should be linear with a slope of n and an intercept of ln K'_n, where K'_n is the product of the concentration quotient, K_n, and the H_2O concentration. The logarithmic plots at 15, 25, and 40°C are shown in Fig. 10.1. This analysis indicates that there is molecular association of H_2O with CO_2 and that the association does not disrupt the H-O-H structure of the water. Furthermore, the CO_2/H_2O mole ratio in the vapor-phase association product is indicated to be 1 or 2, depending on the temperature and the CO_2 pressure.

The visible absorption spectrum of I_2 in liquid CO_2 was observed to be similar to the spectrum of I_2 in CCl_4 and n-hexane; that is, CO_2 appeared to be a nonpolar solvent for I_2. The I_2 band was at 5141 Å in liquid CO_2, a shift of approximately +20 Å as compared with that in CCl_4. The intensity of the I_2 band decreased with time, indicating that the I_2 was reacting, and the addition of water to the CO_2 increased the rate of I_2 reaction, as shown in the last column in Table 10.1. The concentration of H_2O in liquid CO_2 was monitored by the 1.88-μ band with a molar absorptivity of 4.0; this H_2O band also decreased in the three-component system, indicating that the H_2O was reacting with the I_2.

Table 10.1. The rate[a] of decreasing iodine concentration in liquid CO_2 at various iodine and water concentrations

10^4 × iodine concentration (moles/liter)	10^4 × water concentration (moles/liter)	10^3 × negative slope of plot of apparent molar absorptivity vs time
2.624	15.9	3.82[b]
		1.48
3.978	19.3	4.44[b]
		2.23
1.974	22.1	5.00[b]
		2.36
2.707	31.4	5.38
4.486	43.1	5.89
6.603	44.9	7.86
4.544	74.8	21.4
5.301	78.1	16.5
29.61		12.3

[a]The rate is expressed as the slope of the plot of the apparent molar absorptivity vs time (in hours).

[b]When two values are given, there were two straight-line segments intersecting at about 11 hr.

1. M. E. Whatley, *Calculations on the Performance of the KALC Process*, ORNL-4859 (May 1973).

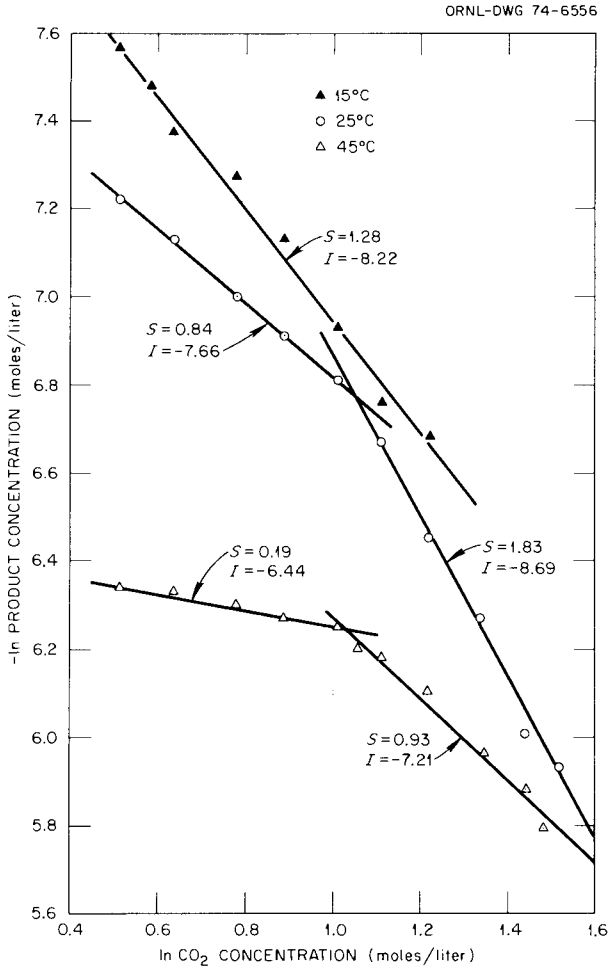

Fig. 10.1. Logarithmic plots of the concentrations of CO_2 and of the CO_2-H_2O association product for the vapor-phase reaction of CO_2 and H_2O at 15, 25, and 45°C.

11. Actinide Oxides and Carbides

11.1 COLLOIDAL SYSTEMS

The theoretical model described last year[1] was successfully applied to the cases of colloidal particles of different sizes and with large surface potentials. A paper has been submitted to the *Journal of Colloid and Interface Science.* The abstract follows:

"Variational Method for the Double Layer Potential. I. Description of the Method," by I. L. Thomas. *Abstract:* A variational method is developed which gives the solution to the Poisson-Boltzmann equation for the double layer in terms of analytical functions. This method will give solutions for two unlike interacting particles for small or large potentials. The potential of two interacting like particles is calculated and compared with the result of Verwey and Overbeek.

The investigation of the oxidation of urania sols was completed, and a paper has been prepared for submission to the *Journal of Colloid and Interface Science.* The abstract follows:

"Oxidation Effects on the Electrokinetic Behavior of Urania Sols," by J. P. McBride, L. E. Morse, J. F. Talley, and C. F. Coleman. *Abstract:* Tests by ultracentrifugation and moving boundary electrophoresis of the effects of partial oxidation on urania sols showed that the resulting U(VI) (at least up to 25% oxidation) neither diffuses throughout the UO_2 crystallites nor forms a surface layer, but dissolves in the intermicellar solution. The changes in ionic strength, due mainly to the changing U(VI) concentration, were calculated and found to correlate well with the zeta potentials determined from the electrophoretic mobilities. Comparisons with a theoretical model of colloid particle interaction showed that the range of zeta potentials is consistent with the observed effects on viscosity and stability of the sols.

11.2 CARBIDE HYDROLYSIS

As a prelude to the study of the hydrolysis of uranium monocarbide, the general literature of the hydrolysis of both actinide and lanthanide carbides was reviewed and reported.[2] On reaction with water, all of these carbides yield a variety of hydrocarbons, hydrogen, and hydrous oxides. Uranium monocarbide reacts with pure water and most acid and alkaline solutions to produce primarily methane, hydrogen, and hydrated UO_2. Superficially, this would indicate a simple method for processing uranium monocarbide fuel. However, it has been reported that UC fuel irradiated to a burnup of 0.6 at. % or more does not react with water;[3] and while it can be dissolved in rather concentrated nitric acid solutions, subsequent processing is complicated by the formation of soluble organic compounds (e.g., oxalic and mellitic acids). In dilute nitric acid (0.001 to 0.5 *M*) even the unirradiated UC is unreactive.[4]

The present research was started to establish the reason for the passive behavior of UC, and electrochemical methods appeared to offer an attractive method. For these studies, irregularly shaped pieces of UC were mounted in epoxy resin, and electrical connection was made through the back side of the resin. The front was metallographically polished under kerosene and rinsed in acetone. The pieces were then stored in a vacuum desiccator until used. All experiments were conducted at 20°C.

The open-circuit potentials of UC in water, 0.05 *M* H_2SO_4, 0.1 *M* HCl, and 0.1 *M* HNO_3 were measured as a function of time. In the experiments with the first three media, initial potentials were within 0.1 V of the saturated calomel electrode (S.C.E.) and no visible reaction was noted. Over a period of 2 to 8 hr, the potentials gradually decreased to −0.5 to −0.7 V vs S.C.E., and reaction (gas evolution) was obvious. On the other hand, no reaction of UC with 0.1 *M* HNO_3 was noted during the first 18 hr; shortly afterward, however, the potential dropped below −0.5 V vs S.C.E. and gas evolution began. No reaction was observed in 1.0 *M* HNO_3 throughout the two-day test. In all cases,

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973,* ORNL-4883, p. 88.

2. J. C. Griess, *The Hydrolysis of Lanthanide and Actinide Carbides – A Survey of Recent Literature,* ORNL-TM-4480 (February 1974).

3. M. J. Bradley et al., *Inorg. Chem.* **3,** 454 (1964).

4. L. M. Ferris and M. J. Bradley, *J. Amer. Chem. Soc.* **87,** 1710–14 (1965).

reaction began at the interface between the UC and the epoxy resin, where a crevice probably existed.

Anodic polarization curves obtained potentiostatically in 0.05 *M* H_2SO_4 showed an active dissolution region (−0.7 to −0.5 V vs S.C.E.), followed first by a region of apparent passivity (~−0.4 to −0.1 V vs S.C.E.) and then by a transpassive region, that is, a potential region where uranium dissolved in its highest valency. This behavior is the same as that noted with some metals and alloys. Materials showing this type of behavior are usually susceptible to crevice attack. In a restricted crevice the solution composition, and potential with respect to the solid, is not the same as that of the bulk solution. Thus the potential of the carbide in the crevice may be in the active region, although its potential elsewhere may be in the passive region.

The polarization data generally indicate that UC would undergo only very slight reaction with aqueous solutions if the potential between the solution and the UC could be kept in the range of −0.4 to −0.1 V vs S.C.E. Payer[5] has suggested that irradiation in a neutron flux produces passivity of UC by virtue of the noble metals (Ru, Pd, Rh) formed in fission. Electrochemically the noble metals have low cathodic overvoltages, and this fact facilitates the polarization of UC into the passive region. Although the results obtained in this investigation indicate that such a mechanism is possible, our results do not prove it. If such a mechanism is the cause of passivity, the dissolution of passive UC could probably be accomplished by cathodic polarization into the active region or by anodic polarization into the transpassive region. In the latter case, however, the products would probably include soluble organic materials, as was noted in nitric acid dissolution.

In support of the noble-metal hypothesis of passivity, we showed that polycrystalline UC exposed in water containing either 60 ppm of platinum as H_2PtCl_6 or 30 ppm of ruthenium as $RuCl_3$ remained passive for many days, whereas in pure water, reaction began within a few hours. In the former cases, some of the metal deposited on the UC. However, we subsequently observed that in water at room temperature the addition of either H_2SO_4 or HCl at 0.001 to 0.5 *M* or K_2SO_4 or KCl at 0.1 *M* also inhibited reaction. Thus, at this time, we are not certain whether it was the effect of the salt or the noble metal in the salt that produced the passivity. A definitive answer could presumably be obtained by alloying low levels of ruthenium, palladium, or rhodium with UC and observing reactivity of the UC in aqueous solutions, but this study was interrupted before such an experiment could be conducted.

5. J. Payer, Ph.D. dissertation, Ohio State University, Columbus, 1971.

12. Chemical Engineering Research

12.1 HYDRODYNAMICS OF PACKED LIQUID-LIQUID EXTRACTION CONTACTORS

Past studies of countercurrent flow in packed columns have been concerned, for the most part, with systems using organic solvents and aqueous solutions since these types of fluids have been used in most solvent extraction applications. Our more recent measurements[1,2] have provided information on variations in physical properties for systems of high density difference, as well as data for high-density halocarbons (CCl_4 and CH_2Br_2). These new results have made it possible to develop a general correlation covering a wide range of physical properties. Such a correlation is needed as solvent extraction applications incorporating a wide range of conditions become increasingly important. The column packing in this study was restricted to Raschig rings. Although considerable data are available for other packing materials, especially Berl saddles, there is not sufficient information on any other single packing to permit an analysis and correlation of the magnitude presented here.

Examination of both the literature and new ORNL results indicated that flooding data can be approximated reasonably well as a straight line when the square root of the superficial flow rate of one phase is plotted vs the square root of the flow rate of the other phase. This behavior has also been reflected in several previous correlations, and the new correlation was developed on this basis. The flooding points from each data set were fitted to a straight line with the form

$$V_{c,f}^{1/2} + k_1 V_{d,f}^{1/2} = k_2 \ , \qquad (1)$$

where

$V_{c,f}$ = superficial continuous-phase velocity at flooding,

$V_{d,f}$ = superficial dispersed-phase velocity at flooding,

k_1, k_2 = constants.

The resulting parameters, k_1 and k_2, for each set of data were evaluated by a least-squares regression, and these parameters were assumed to be power functions of the fluid and packing properties. In this evaluation we used only those data sets in which the uncertainties in k_1 or k_2 did not exceed 30% of their most probable value. The resulting flooding correlation was:

$$V_{c,f}^{1/2} + (0.844\ \Delta\rho^{0.145} \times d_p^{0.298}\mu_c^{-0.084}\epsilon^{-0.078})V_{d,f}^{1/2} = 23.8\ \Delta\rho^{0.269} d_p^{0.494}\mu_c^{-0.084}\epsilon^{0.5} \ , \qquad (2)$$

where

$\Delta\rho$ = difference in densities of the two phases,

d_p = packing diameter,

μ_c = viscosity of continuous phase,

ϵ = void fraction of packing.

This equation, which is based on more extensive data and a wider range of physical properties than any previous correlation, should be more reliable in predicting flooding rates for new systems where no data exist. Its advantages will be most evident for systems with high density differences; however, since it is not a dimensionless correlation, care must be taken to choose correct units.

Comparison of the new correlation with previous correlations. Table 12.1 compares the fit of the new correlation to selected data with that of some of the previous correlations. The fractional error, e_f, in each correlation has been evaluated for each intercept as

1. L. E. McNeese, *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 9,* ORNL-TM-3259 (December 1972), p. 216.

2. L. T. Jester et al., *Flooding Characteristics of a Packed Column with Countercurrent Liquid-Liquid Flow with High Density Difference,* ORNL-MIT-162 (Dec. 19, 1972).

Table 12.1. Fractional error of the proposed flooding rate correlation and previous correlations

Investigator	Data at low V_d	Data at low V_c
Watson and McNeese (this study)	0.276	0.209
Breckenfeld and Wilke[a]	0.825	0.829
Crawford and Wilke[b]	0.903	0.904
Dell and Pratt[c]	0.324	0.628

[a]R. R. Breckenfeld and C. R. Wilke, *Chem. Eng. Progr.* **46**, 187 (1950).

[b]J. W. Crawford and C. R. Wilke, *Chem. Eng. Progr.* **47**, 423 (1951).

[c]F. R. Dell and H. R. C. Pratt, *Trans. Inst. Chem. Eng. (London)* **29**, 89 (1951).

follows:

$$e_f = \frac{V_{\text{calc}}^{1/2} - V_{\text{meas}}^{1/2}}{V_{\text{meas}}^{1/2}} .$$

The overall fractional error, f, for each correlation listed in Table 12.1 is defined as

$$f = \frac{\Sigma e_f^2}{n-1} , \tag{3}$$

where n = number of data points. The fractional error is written in a form that resembles a standard deviation.

The new correlation, Eq. (2), is in good agreement with both low- and high-density-difference data and is more accurate than any of the other three correlations listed in Table 12.1 for both high- and low-density data. The fractional error is approximately 0.2. The fractional error for the most accurate of the previous correlations, that of Dell and Pratt, is approximately 0.3 at low values of V_d and becomes greater at high V_d values. Both of the other correlations tested were considerably less accurate, with fractional errors ranging from approximately 0.88 to 0.90.

Summary. We have proposed and tested a new correlation which predicts flooding rates for Raschig-ring-packed columns with significantly greater accuracy than previous correlations over a wide range of fluid properties. The earlier correlations had been developed from data obtained from systems using low values for density difference and covering a narrow range of values. Although the new correlation was developed solely from data for Raschig rings, it can also be used to extrapolate measurements made with other packing materials (e.g., Berl saddles). The dependence of flooding rates on parameters such as density difference, viscosity, packing (nominal) diameter, etc., should be similar for many other packing materials.

12.2 PERFORMANCE OF OPEN BUBBLE COLUMNS[3]

Measurements of gas holdup and axial dispersion in open bubble columns having diameters of 1, 1.5, 2, 3, and 6 in. have been made[4] over a wide range of operating conditions and liquid properties. During this report period, these data along with a large collection of the best data in the literature have been reduced to generalized correlations based on dimensionless groups.

It has been observed that the hydrodynamic performance of open bubble columns is characterized by two flow regimes with an intermediate transition region. At low superficial gas velocities, the gas rises in the form of discrete single bubbles. This flow regime is called the "bubbly regime." At very high superficial gas velocities, the gas surges through the column in large cylindrical slugs occupying nearly the entire cross section of the column. This flow regime is called the "slugging regime." In the intermediate transition region, discrete bubbles coalesce as they rise through the column to form slugs near the top. We have found that it is useful to distinguish between the two regimes of flow in correlating hydrodynamic results.

In the bubbly flow regime the axial dispersion coefficient has been correlated using dimensionless groups as follows:

$$N_{\text{Pe}} = 11.12 N_{\text{Re}}^{0.82} N_{\text{Ar}}^{0.45} , \tag{4}$$

where

N_{Pe} = Peclet number = DU/E,

N_{Re} = Reynolds number = DU/ν,

N_{Ar} = Archimedes number = $D^3 g/\nu^2$,

D = column diameter,

U = superficial gas velocity,

E = axial dispersion coefficient,

ν = liquid kinematic viscosity,

g = acceleration of gravity.

3. Part of this work was done by J. W. Tester, Director of the MIT School of Chemical Engineering Practice.

4. L. E. McNeese, *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 9*, ORNL-TM-3259 (December 1972), pp. 52–148.

In the slugging regime the axial dispersion coefficient has been correlated using dimensionless groups as follows:

$$N_{Pe} = 0.387 N_{Re}^{0.25} N_{Su}^{-0.13} , \quad (5)$$

where

N_{Su} = Suratman number = $D\rho\sigma/\mu^2$,

ρ = liquid density,

σ = interfacial tension,

μ = liquid viscosity.

The transition between bubbly flow and slugging flow may be reliably predicted from the intersection of Eqs. (4) and (5). The observed Peclet number tends to follow the lower (greater axial mixing) value of the Peclet number across the transition.

Using this method for predicting the transition in flow regime, it has been possible to correlate data for gas phase holdup in each regime as follows:

in the bubbly regime,

$$\theta = 0.322 \left(\frac{\rho U^4}{g\sigma}\right)^{0.219} ; \quad (6)$$

in the slugging regime,

$$\theta = 0.848 \left(\frac{U^2}{gD}\right)^{0.362} ; \quad (7)$$

where θ = gas holdup fraction.

The correlations for axial mixing and gas holdup comprise a thorough description of the hydrodynamic performance of open bubble columns. During this report period, a study of the mass transfer performance of open bubble columns has been initiated using equipment that had been used previously for the hydrodynamic studies. The liquid-film-controlled absorption of CO_2 into water was chosen as the system for initial study; the results obtained thus far are limited to data for the 1.5-in.-diam column. Details of the experimental procedure and data analysis have been reported elsewhere.[5-7]

Carbon dioxide in an inert diluent gas (argon or air) was metered through a single ¼-in. orifice in the bottom of the column and contacted with distilled water, which was introduced at the top of the column. The height of the liquid in the column was adjusted by varying the elevation of an overflow on the liquid exit line. Water samples were taken from the bottom of the column as well as from points along the length of the column and were titrated for CO_2 concentration.

The effects of axial mixing on mass transfer performance were isolated by using values of the axial dispersion coefficient from the correlations given above and the solutions to the dispersion equation given by Miyauchi and Vermeulen.[8] Column end effects (resulting largely from enhanced mass transfer at the inlets) were isolated by plotting the number of transfer units observed (corrected for axial dispersion) vs column height. In general, this gave a linear relationship which could be extrapolated to zero column height to obtain the number of transfer units resulting from end effects.

Values of the mass transfer coefficient, $K_L a$, after corrections for axial dispersion and end effects, are presented in Fig. 12.1 as a function of superficial gas velocity. The effect of superficial liquid velocity was found to be small; hence the results obtained with various liquid flow rates are presented in Fig. 12.1. It was convenient to operate the column with approxi-

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

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

7. D. J. Conklin et al., *Axial Mixing in Open Bubble Columns, Part V: Mass Transfer Effects,* ORNL-MIT-174 (1973).

8. T. Miyauchi and T. Vermeulen, *Longitudinal Dispersion in Solvent Extraction Columns: Mathematical Theory,* UCRL-3911 (1957).

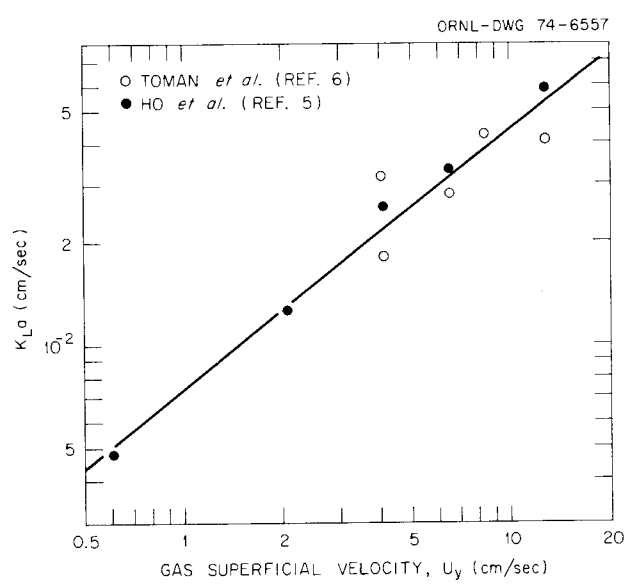

Fig. 12.1. Mass transfer coefficients in a 1.5-in.-diam column.

mately the same extraction factor for each run. Therefore an appropriate extraction factor, which permitted accurate evaluations of mass transfer coefficients (with the existing uncertainties in the CO_2 analyses), was chosen.

Concentration profiles obtained from liquid samples along the length of the column have been compared with predictions from the Miyauchi-Vermeulen dispersion equations. There was reasonably good agreement between predictions and observations, validating our use of the dispersion model. Moreover, it was clear that the assumption of complete mixing in the liquid phase (which has always been made in previous studies of mass transfer performance in open bubble columns) is not tenable. That the data do not support a plug-flow model of the liquid phase was evident from the concentration discontinuity at the liquid inlet. The presence of an end effect at the gas inlet was shown by the deviation from the Miyauchi-Vermeulen model at the bottom of the column. Finally, the mass transfer coefficients derived from the observed concentration profiles are in good agreement with those obtained from the overall column performance and corrected for dispersion and end effects. This agreement between the two independent experimental and analytical methods demonstrates the validity of our approach.

Studies to be carried out in the immediate future will involve various larger diameter columns. Subsequent studies will consider gas-film-controlled systems (NH_3-H_2O) and variations in liquid properties (viscosity, etc.).

12.3 MECHANICALLY AGITATED LIQUID-LIQUID CONTACTORS

A critical operation in the proposed MSBR reprocessing plant is the extraction of rare earths from the fluoride fuel carrier salt to an intermediate bismuth stream. One method for performing this extraction involves the use of a stirred-interface contactor in which bismuth and fluoride salt phases are not dispersed but are agitated in order to facilitate the mass transfer of rare earths across the salt-bismuth interface.

Previous reports[9-11] have shown that a water-mercury contactor using the reaction

$$Pb^{2+}[H_2O] + Zn[Hg] \rightarrow Pb[Hg] + Zn^{2+}[H_2O]$$

is suitable for studying mass transfer rates in systems characterized by two phases with high density differences. These studies have indicated that, although results generally follow the predictions of the Lewis correlation, significant deviations do exist. Therefore, it was considered necessary to study geometric variations and mass transfer rates in rectangular cells similar to those proposed for the MSBR fuel reprocessing scheme.

The mass transfer performance of this type of contactor is strongly dependent on cell geometry; therefore, tests were carried out with contactors having various dimensions: 5.25 in. in diameter and 7 in. high, 7.75 in. in diameter and 10.5 in. high, and 12 in. in diameter and 12.5 in. high. Agitators with diameters ranging from 3 to 7 in. were used; all agitator blades were four-vaned straight paddles. The rate of transfer of lead from dilute $Pb(NO_3)_2$ solution into a zinc-mercury amalgam was measured in the tests, and these measurements were compared with literature correlations.[12-14] Although the latter reproduced the aqueous-organic data fairly well, they did not correlate the mass transfer data from the water-mercury system.[15]

Using the Mayers correlation[14] as the best of the existing relationships, two additional terms were added to include the effects of the ratio of the densities of the two phases and the ratio of the heights of the phases.

A linear regression was performed on all the new water-mercury data and found to yield the following correlation:

$$60\frac{k_1 L_1}{\nu_1} = 0.2058(\mathrm{Re}_1\,\mathrm{Re}_2)^{1/2} \times\left(\frac{\eta_2}{\eta_1}\right)^{1.9}\left(0.6+\frac{\eta_2}{\eta_1}\right)^{-2.4} \times (\mathrm{Sc}_1)^{-1/6}\left(\frac{\rho_1}{\rho_2}\right)^{0.23}\left(\frac{L}{H}\right)^{0.45}, \quad (8)$$

where

k_1 = mass transfer coefficient, cm/sec,

L = stirrer length, cm,

9. J. A. Klein, in *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 14,* compiled by L. E. McNeese, ORNL-TM-4018 (in preparation).
10. J. A. Klein, in *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 15,* compiled by L. E. McNeese, ORNL-TM-4019 (in preparation).
11. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973,* ORNL-4883, pp. 25–27.
12. J. B. Lewis, *Chem. Eng. Sci.* **3,** 248–59 (1954).
13. W. J. McManamey, *Chem. Eng. Sci.* **18,** 123–32 (1961).
14. G. R. A. Mayers, *Chem. Eng. Sci.* **16,** 69–75 (1961).
15. C. D. Scott et al., *Experimental Engineering Semiannu. Progr. Rep. Sept. 1, 1973 to Feb. 28, 1974,* ORNL-TM-4602 (in preparation).

ν = kinematic viscosity = η/ρ, cm^2/sec,

η = viscosity, $g\ cm^{-1}\ sec^{-1}$,

ρ = density, g/cm^3,

Re = Reynolds number = $NL^2\rho/\eta$,

N = stirrer speed, rps,

Sc = Schmidt number = $\eta/\rho D$,

D = diffusion coefficient, cm^2/sec,

H = phase height, cm,

1, 2 = phase under consideration.

For the case in which the blades in each phase have identical dimensions and stirrer rate, Eq. (8) reduces to:

$$60\frac{k_1 L}{\nu_1} = 0.2058\mathrm{Re}_1\left(\frac{\eta_2}{\eta_1}\right)^{1.4}\left(0.6+\frac{\eta_2}{\eta_1}\right)^{-2.4} \times (\mathrm{Sc}_1)^{1/6}\left(\frac{\rho_2}{\rho_1}\right)^{0.27}\left(\frac{L}{H}\right)^{0.45} . \quad (9)$$

This correlation fits the experimental data with a standard deviation of 25% (see Fig. 12.2).

It was also considered necessary to investigate mass transfer rates in a fluoride-salt–bismuth contactor. Therefore, a 6-in.-diam mild steel contactor was installed in the flow-through reductive extraction facility for this purpose. Preliminary results from two experimental runs using ^{237}U as a tracer have indicated that mass transfer rates in the salt-bismuth system are somewhat higher than predicted by the modified correlation but are only 20% of the previously used Lewis correlation.[12]

12.4 RECOVERY OF TRITIUM BY SORPTION PROCESSES

One of the most promising methods for recovering tritium from liquid metal blankets or coolant fluids of fusion reactors appears to be sorption of tritium (from the potassium coolant or the lithium blanket) by using hydrogen-gettering metal sorbents such as yttrium,

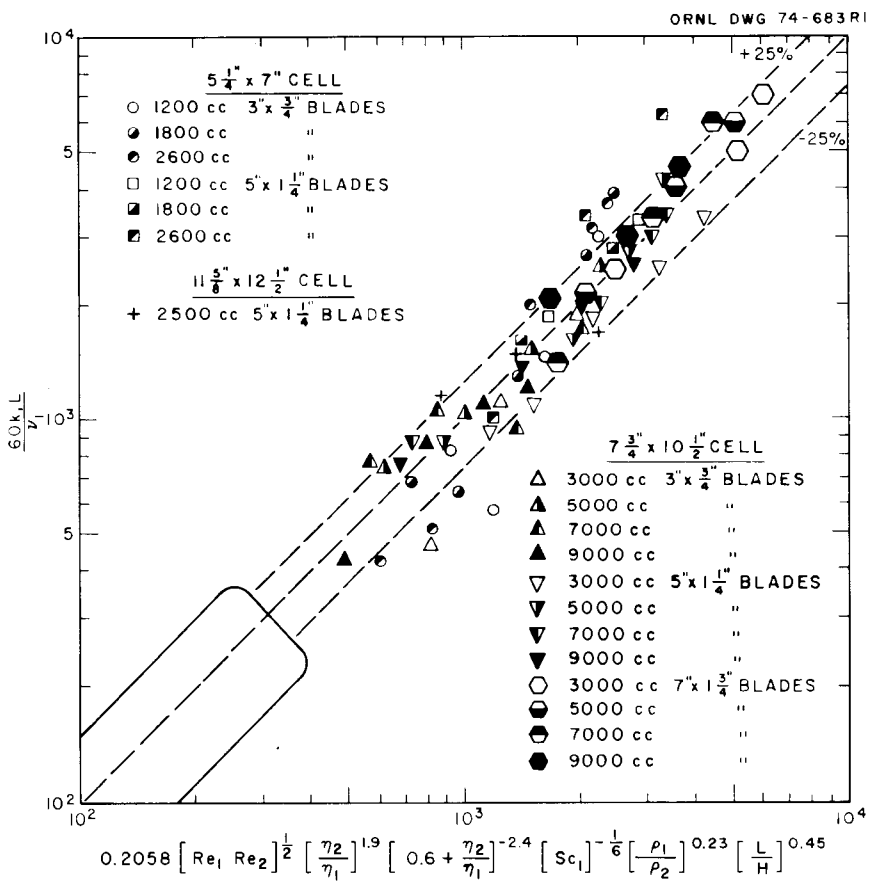

Fig. 12.2. New correlation for mass transfer rates in Lewis cells.

zirconium, or rare-earth metals. A study of tritium sorption from potassium is presently being conducted using selected metal sorbents (both coated and uncoated). Metals chosen for study include known hydride formers with large equilibrium tritium uptakes at low tritium pressures. These include yttrium, zirconium, and (to a much lesser extent) uranium and titanium.

Figure 12.3 shows the schematic of the liquid potassium purification and transfer system used in this study. It consists of a small sorption chamber, a potassium feed tank, and a drain tank which also serves as a bubbler. Research-grade argon (<0.0001% total impurities) is used to force the potassium from the feed tank to the drain tank through the adsorption chamber. To reduce the problems of oxygen contamination of the potassium, the entire process system is leak-tight and further enclosed in a glove box with a once-through dry argon atmosphere. The glove box serves as secondary tritium containment, operating at a slight negative pressure (0.5 in. H_2O) and exhausting to the hot off-gas system. The presence of an inert atmosphere around the potassium-containing vessels also gives an added measure of safety from fire hazards associated with alkali metals.

The concentration of tritium in the potassium is determined by dissolving the potassium in a toluene-ethanol mixture, which can be added to a liquid scintillator. An argon sweep gas carries the tritium released during this reaction through a CuO bed (600°C), and the evolved tritium is trapped by a water bubbler. (A small amount of hydrogen is added to the argon to flush tritium continuously from the CuO and from the walls of the tubing.) Aliquots of water bubbler and reactor vessel residue are taken for scintillation counting, and a portion of the residue is titrated with HCl for determining the mass of potassium in the sample. The toluene pool provides a heat sink for the heat of reaction between ethanol and potassium and dilutes the ethanol reactant. When added to potassium, pure ethanol reacts too vigorously for our purposes, resulting in considerable evolution of ethanol vapor.

Metallic sorbers are also periodically analyzed by dissolving them in acid medium and counting a neutralized, diluted aliquot of the resulting solutions. These reactions are carried out in a system which is continuously swept with argon-hydrogen, similar to that used in potassium analysis. A dilute caustic bubbler is used to protect the CuO bed from acid vapors.

Tests using yttrium metal sorbers were made first since yttrium appears to have the greatest capacity for hydrogen of all the hydride-forming metals. The metal did not sorb tritium in detectable quantities from potassium even after a contact period of four days. We believe that an impenetrable oxide barrier, which is formed on the metal surface, effectively closes the interior of the metal to hydrogen permeation.

A small quantity of natural uranium sheet was obtained from the Metals and Ceramics Division and tested. The metal was heavily oxidized; however, unlike the tenacious and impenetrable oxide films characteristic of yttrium and zirconium, the uranium oxide was flaky and broken. (It resembled the familiar iron oxides.) After being etched in dilute HCl, the samples of metal appeared to be clean and shiny. Sorption of tritium by the uranium was observed after short contact times; increasing contact time produced further sorption, although it was limited by equilibrium conditions.

Uncoated zirconium sorbents gave results similar to those observed for yttrium, that is, no measurable transfer of tritium from potassium to sorbent. This result seemed inconsistent with literature data describing zirconium affinity for hydrogen, and it was again our belief that a surface oxide film was acting as a barrier to mass transfer.

Results of experiments made using nickel-sputter-coated zirconium sorbers have been encouraging but inconclusive. Data obtained in several tests appear to demonstrate the existence of measurable tritium transport but thus far have shown considerable scatter. Therefore the objective of current experimental efforts is to determine whether thin permeable coatings of this type can be effective in permitting more rapid tritium uptake by zirconium (and/or yttrium).

12.5 REPRESENTATION OF GAS-LIQUID EQUILIBRIUM DATA FOR THE KALC PROCESS

For ease of calculation in computer models of the KALC[16] (krypton absorption in liquid CO_2) process, it was necessary to develop explicit algebraic representations of the gas-liquid equilibrium data for the major constituents in the process – CO_2, O_2, CO, and N_2. Data were available from the literature for the systems CO_2-O_2, CO_2-N_2, CO_2-CO, and CO_2-O_2-N_2. Some CO_2-O_2 data are presented in Fig. 12.4 (many of the data have been omitted for clarity) in the form y_iP/x_i, which is thermodynamically equal to $\gamma_i f^\circ_i/\theta_i$, vs P –

16. M. E. Whatley, *Calculations on the Performance of the KALC Process*, ORNL-4859 (May 1973), p. 11.

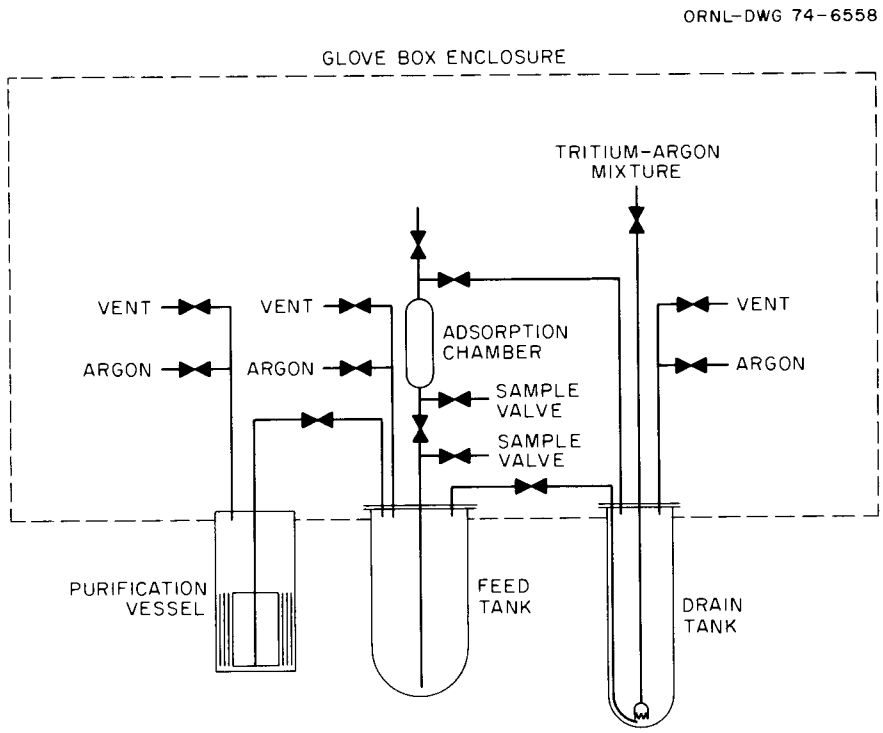

Fig. 12.3. Schematic diagram of the liquid potassium purification and transfer system.

$p^*_{CO_2}$, where

y_i = mole fraction of component i in the vapor phase,

P = total pressure, atm,

x_i = mole fraction of component i in the liquid phase,

γ_i = activity coefficient of component i,

f°_i = standard-state fugacity of component i, atm,

θ_i = fugacity coefficient of component i,

$p^*_{CO_2}$ = vapor pressure of pure CO_2, atm.

The ordinate would be constant for an ideal gas and an ideal liquid solution. At the critical point, $y_i = x_i$, the ordinate must equal the critical pressure, P_c. A function meeting these criteria and fitting the data reasonably well is as follows:

$$\left(\frac{y_1}{x_1}\right)P - P_c = K(P_c - P)^r , \qquad (10)$$

where k is an empirical coefficient and r is an empirical exponent.

The solid lines in Fig. 12.4 represent the best (least-squares) fits of *all* the CO_2-O_2 literature data to a function of the form of Eq. (10). For the systems CO_2-O_2 and CO_2-N_2, the optimum value of r was near 0.5 and k was an approximately linear function of temperature. In these cases, it was convenient to make k a linear function of temperature and force the exponent to the value 0.5. The best fit for the system CO_2-CO was found with a constant k and exponent r. The best-fit correlating equations are:

$$\left(\frac{y_{O_2}}{x_{O_2}}\right)P - P_c = (42.6 - 0.0677T)(P_c - P)^{0.5} ,$$

$$\left(\frac{y_{N_2}}{x_{N_2}}\right)P - P_c = (100.3 - 0.266T)(P_c - P)^{0.5} ,$$

$$\left(\frac{y_{CO}}{x_{CO}}\right)P - P_c = (28.06)(P_c - P)^{0.469} .$$

Although only binary-system data have been fitted, the limited amount of ternary data lies within the scatter of the binary data.

The following power-series representations of the critical pressures of binary systems with temperature

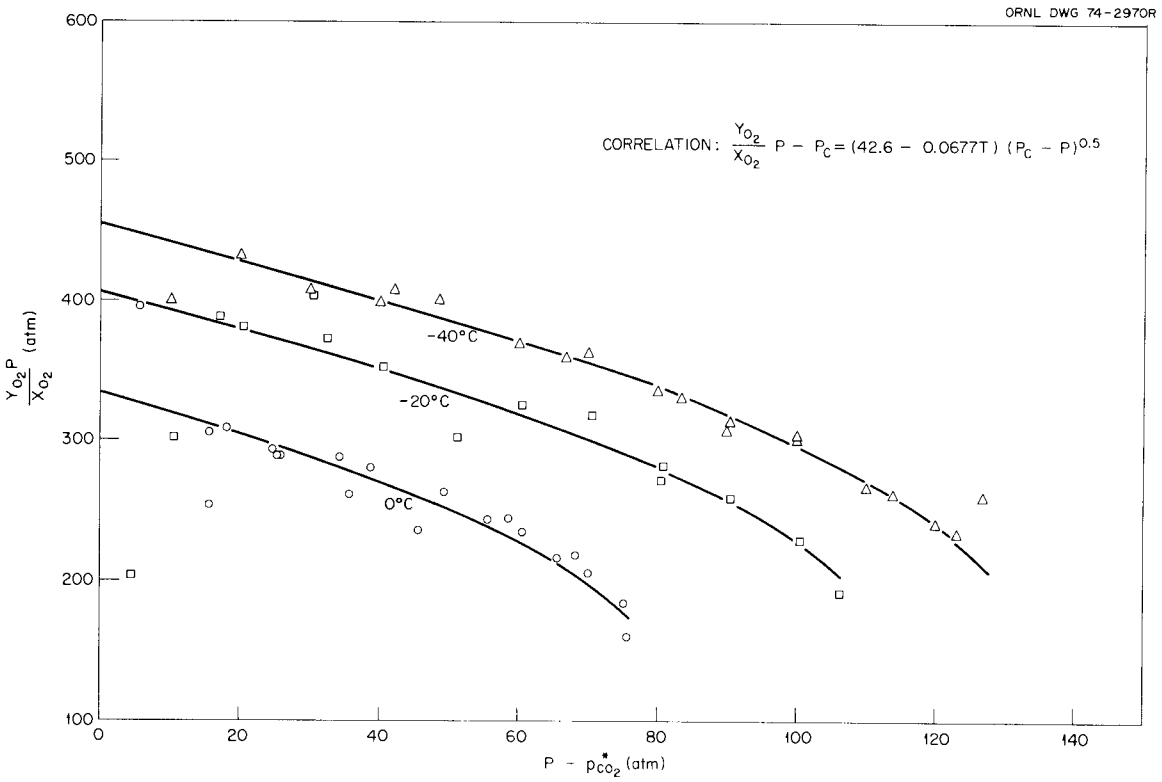

Fig. 12.4. Vapor-liquid equilibrium data for the CO_2-O_2 system.

were used to evaluate P_c:

$$\ln\left[\frac{P_c(CO_2\text{-}O_2)}{p^*_{CO_2}}\right] = 57.8 - 0.0935T - 1.26 \times 10^4/T + 1.23 \times 10^6/T^2 ,$$

$$\ln\left[\frac{P_c(CO_2\text{-}N_2)}{p^*_{CO_2}}\right] = 82.7 - 0.127T - 1.89 \times 10^4/T + 1.67 \times 10^6/T^2 ,$$

$$\ln\left[\frac{P_c(CO_2\text{-}CO)}{p^*_{CO_2}}\right] = 17.1 + 0.00194T + 6.82 \times 10^3/T - 5.41 \times 10^5/T^2 ,$$

where T = temperature, °K. An existing equation for the vapor pressure of carbon dioxide was used.[16]

13. Support for Controlled Thermonuclear Program

A controlled fusion reactor fueled with tritium and deuterium will face difficult problems in management, handling, and purification of its fuel inventory. Such a device must, with minimal release of tritium to the environment, recycle large quantities of tritium and deuterium from the unburned portion of the plasma and must recover bred tritium from its blanket system for subsequent fuel use. Its most difficult problem may be that of keeping tritium release to the environment to the desired low levels. The relatively new and growing program of support for the Controlled Thermonuclear Program in the Chemical Technology Division is concerned with implied problems in fusion reactor fuel cycles.

Recycle of deuterium and tritium from unburned plasma, which seems inherently less difficult than recovery of tritium from the blanket, is receiving priority attention at present since near-term plasma physics experiments will require us to recover and recycle the tritium. In addition, several experimental programs, largely funded by the USAEC Division of Physical Research, are directed to longer-term study of blanket chemistry and of tritium management and control. Since metallic lithium is still the most likely blanket material, a study of equilibria in the lithium–hydrogen-isotope systems continues as a prominent feature of the program. Recovery of tritium from metallic potassium (a possible secondary coolant) continues to be of interest, such studies are reported in Sect. 12.4. Rates and mechanisms of permeation of hydrogen isotopes through clean and oxided metals are of fundamental interest in assessment of tritium escape routes. Finally, we are attempting to determine whether molten salts are viable blanket materials and to establish whether our developed molten-salt technology can be of direct assistance in controlled thermonuclear reactor (CTR) development. These studies, with the exception noted above, are briefly described in the following sections.

13.1 TRITIUM RECOVERY AND HANDLING

During this reporting period, the study of tritium handling systems has concentrated on the problems of recovery of tritium (and deuterium) from the plasma exhaust. Although some attention has been paid to plasma recovery systems for ultimate reactors, our study has been directed primarily to a conceptual design of tritium handling facilities for a large experimental Tokamak (ORMAK F/BX) which may be constructed at ORNL during the late 1970s. As presently envisioned, the experimental program for that Tokamak would include "burning" experiments which would use mixtures of deuterium and tritium.

Three separate process steps seem to be required of any D-T plasma recovery system:

1. The partially burned gases (including D, T, H, He, and contaminant species) are removed from the plasma region.
2. Helium and all other species are removed from the mixture of hydrogen isotopes.
3. Hydrogen is removed from deuterium and tritium by isotope separation.

Such a system is shown schematically in Fig. 13.1.

In our proposed experimental Tokamak (ORMAK F/BX), the gases can simply be removed from the plasma region (the liner) by a suitable pump. The pumping system must provide high pumping rates at low pressure, must not add extraneous impurities to the gas, and must permit ready recovery of the pumped gases. This combination of requirements seems to be met most effectively by cryosorption pumps. Commercial pumps of this type are available at reasonable cost to meet the ORMAK F/BX requirements. Their major drawback lies in the necessarily cyclical nature of their operation. Continuous availability can be obtained

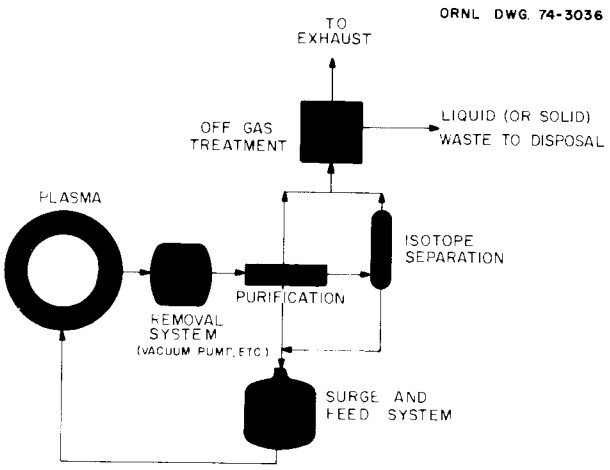

Fig. 13.1. Flow diagram of exhaust process system.

by use of dual pumps in parallel so that while one of them pumps, gas is desorbed from the other.

A similar pumping system of considerably larger size should suffice for much more ambitious experiments or even for full-scale reactors that do not incorporate diverters. One disadvantage of this pumping system is that it requires undesirably (but not prohibitively) large tritium inventories. Such a pumping system might also suffice for Tokamaks using some types of diverters; a diverter system that uses a high-Z gas to reduce the plasma temperature before it strikes a sacrificial metal wall might be amenable to pumping in this way. Diverter concepts are so speculative at present that we cannot be sure the simple pump concept will apply to all systems.

The second process step, removal of all impurities from the hydrogen isotopes, can be achieved by either of two rather simple single operations. Sorption and desorption of hydrogen isotopes on beds of uranium chips should be effective and economical for small systems such as ORMAK F/BX; for large systems, it may prove practicable to introduce compressors to increase the capacity of uranium beds and lower the uranium requirement. Separation of impurities by permeation of the hydrogen isotopes through palladium membranes should be given careful consideration for larger systems where continuous purification would be desirable.

Removal of hydrogen from the deuterium and tritium can be accomplished by any of several isotope separation methods already demonstrated and evaluated for H-D separation. ORMAK F/BX requires an isotope separation slightly different from that of an ultimate reactor. Present plans call for admitting a tritium-rich D-T mixture to the plasma region of ORMAK F/BX and feeding pure deuterium to the injectors to produce plasma heating. Accordingly, a separation of deuterium from tritium must be provided. At present, we are considering the use of existing separative capacity available at other AEC sites. Only if ORMAK F/BX proposes a long-term program of D-T studies would it become desirable to provide a local isotope separation capacity.

An experimental program has been devised and equipment is being assembled to test the effectiveness of cryosorption pumping and of the uranium bed purification system.

13.2 EQUILIBRIA IN THE HYDROGEN-ISOTOPE–LITHIUM SYSTEMS

The vapor-liquid equilibria for the hydrogen-isotope–lithium systems are being studied to aid in devising methods for tritium management in CTRs. The equilibrium pressures of the hydrogen isotopes in the Li-LiH-H_2, Li-LiD-D_2, and Li-LiT-T_2 systems are being measured using the modified Sieverts apparatus described previously.[1] Samples of lithium are sealed in metal capsules which have high permeation coefficients for the hydrogen isotopes, and the equilibrium hydrogen isotope pressure is established inside and outside the capsule. The equilibrium pressure is read externally relative to the capsule. The experimental data are considered in terms of the equilibrium

$$\mathrm{Li(d)} + \frac{1}{2}\mathrm{H_2(g)} = \mathrm{LiH(d)}\ ,$$

where (g) and (d) designate the gas and the liquid Li-LiH phases respectively. We have recently determined the equilibrium hydrogen and deuterium pressures as a function of the hydrogen and deuterium concentrations in the liquid phase at several temperatures between 800 and 1000°C. The maximum atom fraction of hydrogen or deuterium in the liquid phase was 0.15. All the data could be represented by the Sieverts relationship,[1]

$$\sqrt{P_{\mathrm{H_2(g)}}} = K_S C_{\mathrm{H}}\ ,$$

in which K_S is the Sieverts constant and C_{H} is the hydrogen concentration in the liquid. The preliminary

1. F. J. Smith and O. K. Tallent, *Chemical Development Sect. B Semiannu. Progr. Rep. Mar. 1, 1973 to Aug. 31, 1973, Part I*, ORNL-TM-4370, p. 412.

results for deuterium are shown in Fig. 13.2; the data for hydrogen and deuterium are summarized in Table 13.1. The data are well represented by

$$\log K_S = 4.360 - 2820/T(^\circ K)$$

for the Li-LiH-H_2 system and by

$$\log K_S = 3.980 - 2300/T(^\circ K)$$

for the Li-LiD-D_2 system.

The Sieverts apparatus gives information for only one vapor species, the molecular hydrogen isotope, in equilibrium with liquid lithium–lithium hydride solutions. A Bendix time-of-flight mass spectrometer is being used to study the species that volatilize from samples of Li-LiH over the temperature range 450 to 750°C. The equilibrium

$$2Li(g) + H_2(g) = 2LiH(g)$$

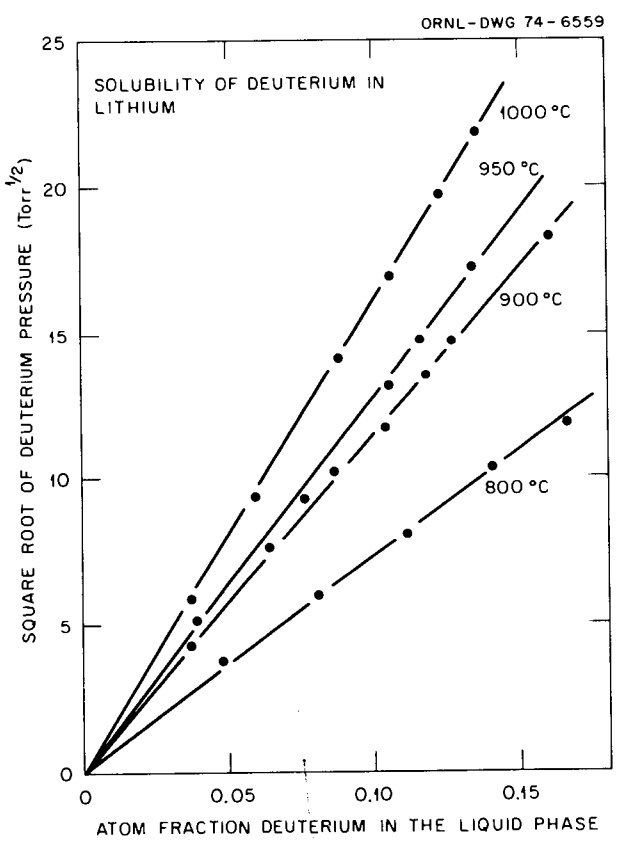

Fig. 13.2. The solubility of deuterium in liquid lithium determined with the Sieverts apparatus. Shown here are plots of the square root of deuterium pressure vs the atom fraction of deuterium dissolved in the Li-LiD phase.

Table 13.1. Experimentally determined Sieverts constants

Temperature (°C)	K_S [(torr$^{1/2}$)(atom fraction)$^{-1}$]	
	Hydrogen	Deuterium
1000	145	160
950	120	136
900	95	125
888	89	
800	60	74

is being studied by determining the equilibrium partial pressures of the volatile species effusing from a molybdenum effusion cell. The effusion beam source for mass-spectrometric techniques is limited to the 10^{-6} to 0.1 torr region. Therefore the Li-LiH sample must be prepared with a low LiH composition. Unambiguous ion peaks for the condensable species Li and LiH were easily obtained by using the molecular beam baffle. The H_2 species could not be detected because of residual H_2 in the instrumentation. The lithium partial pressure was determined to be 1.65×10^{-4} atm at the maximum temperature, 706°C, which agrees well with a literature value[2] of 6.3×10^{-4} atm. The measured variation of lithium partial pressure with temperature yielded a value of 39.7 kcal/mole for the enthalpy of sublimation of lithium. This value is in good agreement with a literature value[2] of 38.6 kcal/mole; such agreement indicates that steady-state conditions were attained inside the effusion cell. The partial pressures of LiH varied from 6.3×10^{-9} atm at 575°C to 2.8×10^{-7} atm at 706°C. These preliminary data indicate that a major tritium-containing species in the vapor of a CTR system may be LiT in addition to T_2. The mass spectrometer system is being modified to minimize the residual H_2 background and to measure the H_2 partial pressure.

13.3 PERMEATION OF MATERIALS BY HYDROGEN ISOTOPES

The present maximum permissible concentration of tritium in the liquid effluent from a fusion reactor's steam generator system having an area of about 8×10^7 cm^2, and with a dilution (cooling) flow of 6.5×10^5 gpm, is 5 nCi per liter of effluent. This means that the rate of tritium permeation through the walls of the steam generator must be less than 10^{-8} cm^3 (STP) hr^{-1}

2. R. Hultgren, *Selected Values of Thermodynamic Properties of Metals and Alloys*, p. 153, Wiley, New York, 1963.

cm^{-2}. Hydrogen permeation through metals with driving pressures greater than 1 torr is well documented. However, in most studies reported in the literature, the pressure dependence of hydrogen permeation through clean metals appeared to depart from the theoretically expected half-power relationship at low pressures. Extrapolation of the reported data to the very low pressures (about 10^{-8} torr) of interest in the processing of CTR blanket-coolants[3] obviously is quite risky. It is also recognized that at least one surface of the steam generator in a fusion reactor system will be coated with an oxide film. Consequently, we are investigating the permeation of hydrogen isotopes through both clean metals and metals coated with oxide films. A steady-state method has been used to determine the permeability to deuterium of selected clean and oxide-filmed metals and alloys, using mass spectrometry to analyze for deuterium over the pressure range 9×10^{-4} to 750 torr. A paper describing the results of these studies has been published in *Nuclear Technology*. The abstract follows:

"The Permeation of Hydrogen Isotopes through Structural Metals at Low Pressures and through Metals with Oxide Film Barriers," by R. A. Strehlow and H. C. Savage, *Nucl. Technol.* **22**, 127 (1974). *Abstract:* The permeation and the pressure dependence of the permeation of hydrogen isotopes through metals and oxidized metals were studied at temperatures from 300 to 800°C and at pressures of 10^{-3} Torr to 1 atm. Such knowledge is important to tritium management in both fusion and fission nuclear reactors. An adequate basis for predicting the permeation of hydrogen at very low pressures has not previously been established; therefore, the two complementary objectives of this study were (a) to determine the pressure dependence of hydrogen permeation through materials of which steam generators might be built, and (b) to determine whether an oxide film might serve as a tritium permeation barrier.

The metals studied included nickel, Type-304L stainless steel, Hastelloy N, Incoloy 800, Croloy T9, Croloy T22, and Type-406 stainless steel. Deuterium, rather than normal hydrogen, was used as the permeating gas in order to achieve high sensitivity in the mass spectrometric analyses. At a given temperature, the permeation rate of deuterium through metals that are substantially free of oxide films was found to proceed with a half-power pressure dependence in accordance with the relationship

$$J = K(P_1^{1/2} - P_1^{1/2}) ,$$

where J is the permeation flow rate, K is a constant, and P_1 and P_2 are the upstream and downstream gas pressures, respectively.

The rates of the permeation of deuterium through oxidized metals were usually lower than through unoxidized metals and the observed pressure dependence was frequently greater than the half-power. For some alloys, a reduction in permeation rate by a factor of a hundred or more at 1-atm pressure was observed; the reduction at low pressures was even greater. The observations made are consistent with considerations of the chemical stability of the oxide and of the presence of cracks or other imperfections in the oxide film.

The effects of oxide films on the outgassing of metals were considered in conjunction with the permeation studies. These considerations are presented in a paper that will be published in the *Journal of Nuclear Materials.* The abstract follows:

"Formation and Use of Oxide Films to Impede Outgassing of Metals," by R. A. Strehlow and H. C. Savage, *Journal of Nuclear Materials,* in press. *Abstract*: Phenomena associated with the outgassing of metals are generally interpreted by using models based either on desorption of compounds from the surface or on diffusion of dissolved gases from the interior of the metal. It is generally recognized that surface oxide films can serve to decrease outgassing rates of metals. However, the processes associated with the outgassing of oxidized or oxide-coated metals are not well understood. Outgassing of oxidized metals is considered in light of the results of recent studies of hydrogen permeation through metals with well-characterized oxide films. The chemical stabilities of the oxides, as well as the physical imperfections of the film, are considered. A model is suggested for the expected outgassing behavior of oxidized steels at temperatures which are of interest in the design of controlled thermonuclear research experiments and reactors. The role of impurities and the usefulness of specialized oxidation treatments are discussed.

13.4 MOLTEN SALTS AS BLANKET MATERIALS

The functions of the blanket in a fusion reactor are to absorb and to moderate energetic fusion reaction products (predominantly 14-MeV neutrons) in order to produce fuel (tritium) and to transport energy to the electrical power-generating system of the reactor. Lithium-containing molten salts (e.g., Li_2BeF_4) can fulfill these requirements for the blanket.[4] Furthermore, the magnetohydrodynamic (MHD) effects on molten salts are less severe than those on liquid metals because of the lower electrical conductivities of the salts.[4] Magnetohydrodynamic effects that probably will not be too significant for molten salts are (1) pressure head losses[5] and, therefore, thermal stresses on struc-

3. J. S. Watson, *An Evaluation of Methods for Recovering Tritium from the Blankets or Coolant Systems of Fusion Reactors,* ORNL-TM-3794 (July 1972).

4. W. R. Grimes and Stanley Cantor, p. 161 in *The Chemistry of Fusion Technology,* ed. by D. M. Gruen, Plenum Publishing Corp., New York, 1972.

5. J. C. R. Hunt and R. Hancox, *The Use of Liquid Lithium as Coolant in a Toroidal Fusion Reactor. Part 1. Calculation of Pumping Power,* UKAEA report CLM-R115, Culham Laboratory, England (October 1971).

tural metals[6] and (2) degraded heat transfer because of suppressed turbulence when flowing through the magnetic field.[7]

Harmful chemical reactions in molten salts may arise from the induced electromotive force associated with any electrical conductor traversing magnetic fields. To provide insight into this problem and to plan an experimental program with molten salt coolants, we have studied[8] the induced emfs of aqueous electrolyte solutions flowing across a magnetic field as high as 21,000 G. Voltages have been measured at metal electrodes positioned perpendicular to the direction of flow and to the magnetic flux density vector. The observed voltages agreed with Faraday's law of electromagnetic induction for solutions whose electrical conductivities were as high as 34 mhos/m passing through the magnetic field in glass pipes; typical results are presented in Fig. 13.3. These data suggest that the induced emf in molten Li_2BeF_4, with even higher electrical conductivity (~250 mhos/m at 650°C), will be quantitatively consistent with Faraday's law. However, the extent of corrosion caused by the electric field cannot be predicted since it is not yet known how much electric current will be shorted out through metal conduit carrying the salt.

Initial corrosion experiments have been carried out with short sections of aluminum tubing through which a mildly basic solution (0.2 wt % K_2CO_3) was pumped at rates that could generate an induced emf of 0.2 V. Our first results indicated that the corrosion of aluminum in the magnetic field was no greater than the

6. R. Hancox and J. A. Booth, *The Use of Liquid Lithium as Coolant in a Toroidal Fusion Reactor. Part 2. Stress Limitations,* UKAEA report CLM-R116, Culham Laboratory, England (November 1971).

7. M. A. Hoffman, *Magnetic Field Effects on the Heat Transfer of Potential Fusion Reactor Coolants,* UCRL-73993, Lawrence Livermore Laboratory (1972).

8. S. Cantor and W. R. Grimes, *Nucl. Technol.* 22, 121 (1974).

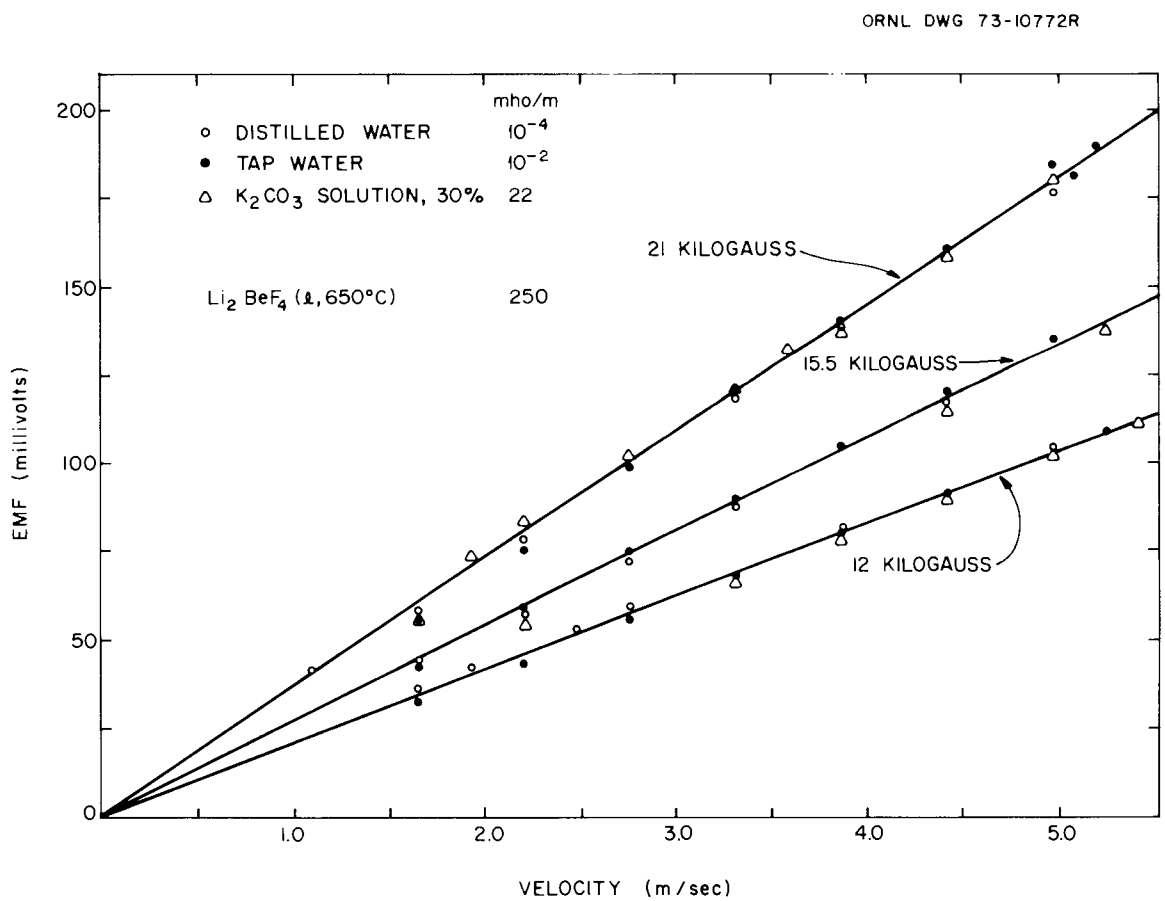

Fig. 13.3. Potential induced in H_2O and aqueous solutions flowing through magnetic fields. The solid lines are calculated from Faraday's law of electromagnetic induction.

corrosion of samples in other parts of the loop where the magnetic flux density was negligible.

The magnetic retarding effect on fluid flow of highly conducting aqueous solutions has also been investigated. No increased resistance to flow caused by the magnetic field was detected for liquids flowing with turbulence (Reynolds number of 10^5) at velocities as high as 5.5 m/sec. Also for laminar flow, we did not observe any increased resistance to flow of aqueous solutions caused by a flux of 21 kG. By contrast, liquid mercury flowed about 40% slower through the magnetic field.

14. Iodine Sorption on Charcoal

14.1 CHARCOAL IGNITION AND IODINE DESORPTION

The primary method used in nuclear reactor installations for cleanup of radioactive iodine during normal operation is adsorption on activated charcoal impregnated with an additive such as KI_3. Although modern power reactors rely primarily upon chemically treated water sprays to scavenge iodine during postulated accidents, there is a remote possibility that charcoal adsorbers could become loaded heavily with radioactive iodine in the postulated accidents for some reactor installations.[1] Our experimental program is being conducted to determine what effect, if any, such loading (as simulated in the laboratory) would have on the retention of the iodine at high temperatures and whether the resulting decay heat would ultimately lead to ignition of the charcoal.

Our experimental method is to load highly radioactive $^{130}I_2$ (half-life, 12.3 hr) on a well-insulated charcoal bed 1 in. in diameter and 2 in. deep. Normal dry air flow (30 fpm at 25°C) provides adequate cooling, while iodine movement within the bed is observed by means of a collimated radiation detector and desorption from the end of the bed is measured by means of sequentially operated collection traps. After 2 hr or more, the air

1. R. P. Shields, "Ignition of Charcoal Adsorbers by Fission Product Decay Heat," *Proceedings of the 11th AEC Air Cleaning Conference, Richland, Washington, August 31–September 4, 1970.*

Table 14.1. Summary of experiments with highly radioactive ^{130}I adsorbed on charcoal

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Charcoal type[a]	MSA-85851	MSA-85851	MSA-85851	MSA-85851	BC-727	Witco-42
Curies of ^{130}I[b]	0.2	8	150	1100	1100	550
Duration of air flow, hr	7	7	30	4	4	8
Velocity at ignition, fpm at 25°C				4	4	0.75
Maximum temperature,[c] °C	150	150	100	575	533	507
Fraction desorbed, ppm						
Elemental iodine	~0.2	~0.2	~0.3	~2	5.5	~10,000
Particulate iodine	~0.02	~0.02	1.0	17	2.0	15
Penetrating iodine	64	5.6	1.8	3.4	8.9	6.4
Total	64	5.8	3.0	22	16.4	~10,000

[a]MSA-85851 and BC-727 are KI_3-impregnated coconut-base charcoals; Witco-42 is a KI-impregnated petroleum-based charcoal.

[b]One curie of ^{130}I produces a maximum beta radiation intensity of $\sim 5 \times 10^5$ rads/hr in the first $^1/_8$-in. bed segment and an essentially uniform gamma radiation intensity of 1.3×10^4 rads/hr.

[c]The inlet air temperature was controlled at 100 to 150°C in runs 1 and 2, 100°C in runs 3, 4, and 5, and 70°C in run 6.

flow rate is descreased to 4 fpm (25°C) in simulation of an abnormal condition that would allow the charcoal temperature to rise. If the amount of ^{130}I on the charcoal bed equals or exceeds 400 Ci, ignition of the bed can occur in our apparatus.

Table 14.1 summarizes the experiments performed during this report period and the amounts of the different forms of radioiodine released from the bed. Particulate iodine was released early in each run. Penetrating iodine, probably methyl iodide, was released continuously at a slightly decreasing rate with time. The low total release from the bed demonstrates that desorption of radioiodine cannot be relied upon to prevent ignition of the charcoal.

Figure 14.1 shows the distribution of iodine throughout the bed during run 6. A computer program was written to calculate the partial pressure of iodine in equilibrium with the charcoal that corresponded to the observed rate of movement within the bed. We assumed a linear adsorption isotherm so that the partial pressure of iodine was directly proportional to the mass concentration on the charcoal:

$$P = x/k ,$$

where

P = partial pressure of iodine, atm,

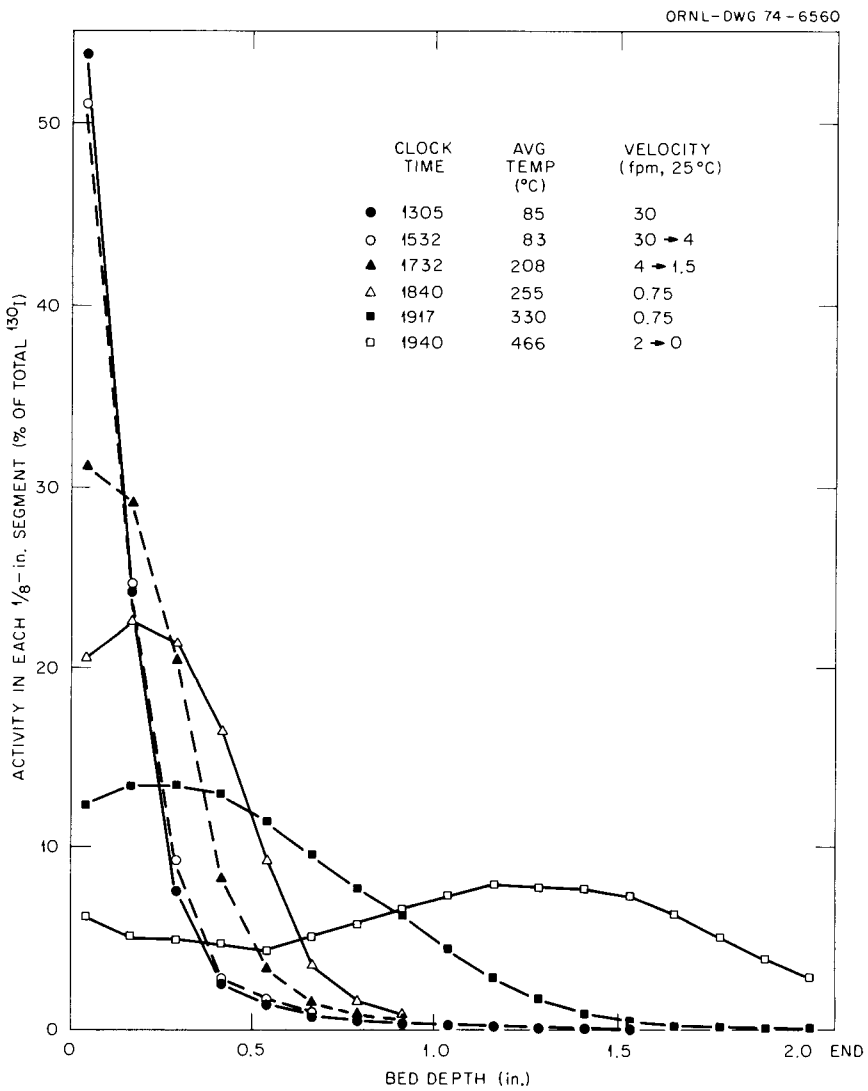

Fig. 14.1. Distribution of ^{130}I during run 6.

x = total concentration of iodine on the charcoal, 0.03 to 0.1 g per gram of charcoal,

k = adsorption isotherm constant.

For elemental iodine there is an essentially continuous equilibrium between the charcoal and the vapor phase so that the movement of iodine is directly proportional to the air flow velocity within the bed, and the value of k changes rapidly with temperature.

For each type of charcoal we could express the value of k satisfactorily with the Arrhenius formula

$$k = k_0 e^{-A/RT},$$

where

A = activation energy, cal/mole,

R = gas constant, 1.987,

T = absolute temperature, °K,

k_0 = constant for type of charcoal, (g I) (g charcoal)$^{-1}$ (atom I)$^{-1}$.

For MSA-85851 charcoal, $A = -19{,}000$ cal/mole and $k_0 = 3.3 \times 10^{-6}$. No radiation effect on k was detected in the range 2 to 1100 Ci of ^{130}I. The Witco-42 charcoal had the lowest value of k – a factor of 5 lower at 100°C but becoming equal to the other k values at 300°C. The much larger total release of iodine from the Witco-42 charcoal during run 6 was primarily a result of much longer operation at high temperatures. We have observed that the relative concentrations of potassium and iodine in the charcoal affect the value of k, with an excess of potassium resulting in more effective retention of elemental iodine.

Heat balance calculations for the three ignition experiments (runs 4–6) revealed the rate of heat release from the slow oxidation of charcoal as the temperature rose above 200°C. A typical result was obtained for run 5, in which the heat release rate is given by:

$$H = H_0 e^{-A/RT},$$

where

$H_0 = 1.65 \times 10^8$ cal min^{-1} (g charcoal)$^{-1}$,

A = 19,000 cal/mole,

R = 1.987 cal mole^{-1} (°K)$^{-1}$,

H = the heat released by oxidation, cal min^{-1} (g charcoal)$^{-1}$.

In each of these experiments the rate of heat release reached a maximum that was controlled by the supply of oxygen in the flowing air. As the size and depth of a charcoal bed increase, the rate of oxidation at lower temperatures becomes more important.[2]

One objective of our program is to determine the accuracy of methods for calculating charcoal bed temperatures. We tested the CHART computer program[3] after modifying it slightly to include the heat contribution from oxidation of charcoal. As input to CHART we used the parameters for run 4, including air flow rate changes; charcoal density, heat capacity, and thermal conductivity; air-to-charcoal heat transfer coefficient; amount and decay rate for 1100 Ci of ^{130}I, along with distribution differences for elemental iodine and methyl iodide; and the experimentally observed oxidation rate. The CHART-calculated temperatures agree quite well with the observed temperatures.

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2. K. Bratzler, "Die Selbstentzundung des Kohlenstoffs als verfahrenstechnisches Problem," Chem.-Ing.-Tech. **28**(8/9), 569–76 (1956); *The Spontaneous Ignition of Carbon as a Process Problem,* ORNL-tr-2568 (December 1972).

3. R. P. Shields and M. Siman-Tov, *The Effect of Iodine Decay Heat on Charcoal Adsorbers,* ORNL-4602 (January 1971).

15. Chemical Applications of Nuclear Explosives

We have participated in the Plowshare Program for several years by studying the potential behavior of radionuclides in underground applications of nuclear explosives. During the past year, our studies have been concerned with tritium behavior in the recovery of oil from oil shale. In the proposed recovery process, the shale formation would be fractured by detonating a nuclear explosive, and the oil would be recovered by subsequent in-situ retorting. The results of our bench-scale tests indicate that, while some tritium contamination of the oil can be expected, the level of contamination can be minimized by washing the shale before retorting and by introducing water vapor to the system during retorting.

The 1500-g shale samples (in pieces in the size range 0.2 to 1 in.) are contaminated with tritium by sealing the shale in a vessel which contains about 100 μCi of tritium in 0.25 ml of water, and maintaining the vessel at 85°C for periods between 30 and 50 days. At the end of the treatment period, the contaminated shale is transferred to a 2-in.-ID retort, where it forms a 30-in. bed. About 200 ml of oil is then produced by heating the outside of the glass column with a clamshell heater while a nitrogen–carbon dioxide mixture is passed through the bed; the furnace is lowered mechanically along the column to generate a moving temperature front. The effect of temperature on tritium behavior is determined by making a series of runs with a single shale sample, lowering the furnace at each desired temperature. The retort tube and furnace are enclosed in an insulated box that is equipped with a small heater. The heater maintains the shale temperature (with the furnace off) at 52°C at the top of the shale bed and at 60°C at the bottom.

Reducing the retorting rate from 6 in./hr, which had been used in all previous tests,[1] to 2.3 in./hr did not change the tritium contamination of the retorted oil (Fig. 15.1). The oil produced at either rate contained an average tritium concentration of 0.11 μCi/ml. In a second test at a rate of 2.3 in./hr, addition of water vapor to the gas stream entering the retort reduced the tritium concentration of the oil by about half (to 0.061 μCi/ml). The oil recovered at a rate of 0.77 in./hr, with water vapor added during retorting, contained 0.043 μCi of tritium per milliliter. In these tests, the gas stream was sparged through water at 50°C before it entered the retort. This introduced about 30 g of water vapor to the retort in each of the four runs at 2.3 in./hr (at shale temperatures of 130, 245, 350, and 485°C respectively). In the first two runs, the water that was collected prior to any oil production contained about 65% of the tritium found in the retort products. An additional 14% of the tritium was present in the water produced with the oil. About 80 g of water vapor was added to the system in each of the four retorting runs

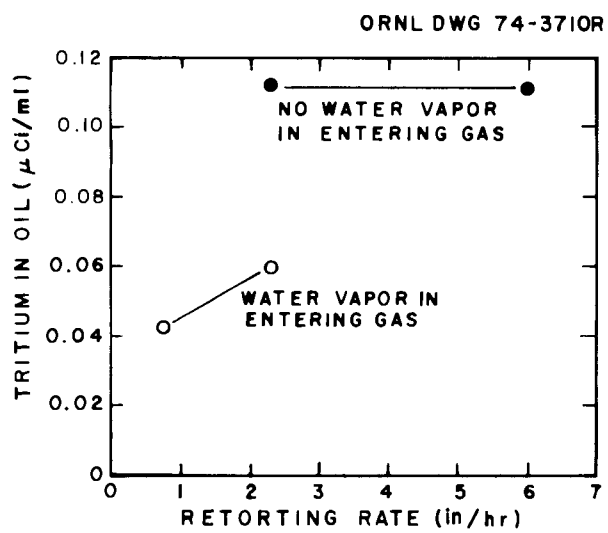

Fig. 15.1. Effect of retorting rate on tritium contamination of shale oil. Procedure: Shale samples were contaminated by exposure to tritiated water at 85°C. Oil was recovered from the contaminated shale in a bench-scale retort. Water vapor was added to the gas stream entering the retort by sparging through water at 50°C.

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1973,* ORNL-4883, p. 63.

at 0.77 in./hr. The shale temperatures in these runs were 160, 300, 430, and 515°C respectively.

The extent of tritium contamination was reduced by extended washing of the shale before retorting. After a 100-ml sample of water had been circulated through a bed of contaminated shale for 20 days at 1 ml/min, the oil recovered in subsequent retorting tests contained only 0.0354 μCi of tritium per milliliter. The tritium concentration in the circulating wash solution increased from 0.32 μCi/ml after 1 day to 0.42 μCi/ml after 5 days, to 0.49 μCi/ml after 9 days, and to 0.52 μCi/ml after 20 days. The shale surfaces appeared to be uniformly wet after about 5 days. About 36 ml of the water was drained at the end of the washing test, and an additional 103 ml was recovered in a retorting test at 230°C. The oil was recovered in a second retorting run at 435°C. Water vapor was added to the system during the runs, and a retorting rate of 2.3 in./hr was used.

In a washing test carried out at a higher shale temperature, tritium removal from the shale was more efficient, and the tritium content of the oil subsequently recovered was lower. The temperature in the shale bed during this test was increased by heating the bottom 4 in. of the bed with the retort furnace. At a furnace temperature of 250°C, the shale temperature was 56°C at the top of the bed, 68°C at the middle, and 110°C at the bottom. A 150-ml water inventory was required during the test in order to maintain sufficient volume at the pump intake. At the end of an 18-day wash, the water contained 54 μCi of tritium. A total of 180 ml of water was removed from the system on conclusion of the washing test and in the first retorting run, which was made at a retorting rate of 2.3 in./hr and a shale temperature of 230°C. The oil recovered at 430°C contained 0.0314 μCi of tritium per milliliter.

The tritium concentration and the volume of water used in the shale exposure tests affected the tritium contamination of the oil recovered from the shale. When the tritium concentration in the water during a shale exposure test was increased from 390 μCi/ml to 4120 μCi/ml, the tritium concentration in the oil increased proportionally, from 0.0354 μCi/ml to 0.360 μCi/ml. In each test, the shale was washed with water for 20 days before oil recovery, and water vapor was added to the system during oil recovery. The tritium buildup rates in the circulating wash solutions were almost identical, with the tritium concentration being proportional to that in the tritiated water used in the shale exposure. Increasing the volume of water (containing the 100 μCi of tritiated water) from 0.25 ml to 0.75 ml during an exposure test caused a reduction in the tritium concentration of the oil from 0.0354 μCi/ml to 0.0285 μCi/ml. Both shale samples were washed with water for 20 days before retorting, and water vapor was added to the system in each case during the retorting tests at 2.3 in./hr.

16. Thermal Generation of Hydrogen

The concept of a hydrogen economy, that is, the use of hydrogen as a major energy source, is currently receiving increased attention. Hydrogen as a fuel has a number of compelling advantages, including: (1) it can be used as a means of storing or transporting energy, (2) it has applicability in mobile transportation, and (3) its combustion product causes minimal environmental degradation. Considerable research is being done at a number of laboratories to define an economic route for the large-scale production of hydrogen from water by electrolysis or by chemical reaction cycles. In either case, nuclear reactors would be the primary source of thermal energy.

Preliminary thermodynamic analyses suggest that the direct use of thermal energy to produce hydrogen from water could be more efficient and more economical than the intermediate generation of electricity followed by electrolysis of water. Since any chemical scheme is limited by the Carnot cycle, the operating temperature of the nuclear reactor establishes the upper temperature limit, and thus the efficiencies, for the chemical reactions. The maximum temperature limit of reactors such as the HTGR is not completely defined; however, we have selected 1000°C as the practical maximum temperature to be considered in various reactions. Indeed, compatibility of the chemicals used in the thermal cycles with the materials of construction of the heat exchangers may be more of a limiting factor than the maximum reactor temperature.

Several criteria have been established to aid in defining potentially useful chemical reactions. Obviously, the series or sequence of oxidation-reduction reactions must have the net overall effect of simply decomposing water to yield hydrogen and oxygen. Only compounds of elements of relative abundance are being considered. It is desirable to avoid difficult physical separations of reaction products. The number of reactions involved in the cycle should be minimized; certainly 5 would be a maximum. Low-temperature waste heat from power plants, either nuclear or coal, would be essentially free, and as many steps as possible will be designed to take advantage of this.

The present program to study various candidate reactions initially involved the calculation of equilibrium constants from thermochemical data, when available, followed by experimental confirmation of the reaction in a dynamic system. To date, two three-reaction cycles have been identified and shown to be technically feasible. These, along with a hybrid cycle using thermal energy and electricity, are under investigation.

Additional experiments are planned in an attempt to confirm other potential cycles. The cycles showing the most promise, as evaluated by the above criteria, will be studied in detail with respect to equilibria and kinetics. It is anticipated that basic thermochemical data will also be obtained from some of these experiments.

17. Miscellaneous Programs

17.1 QUALITY ASSURANCE PROGRAM

The Quality Assurance (QA) program at ORNL now includes all AEC-funded projects, and quality assurance coordinators have been appointed for all divisions. During the past year, the Chemical Technology Division continued to strengthen and implement its QA program through the use of 19 Division QA procedures and 43 Laboratory QA procedures. These procedures, which cover such topics as planning, design, fabrication, operation, and maintenance, provide guidance to project management.

As programs leave the research and bench-scale experiment stage, more formalized QA actions are required. For example, large prototype equipment and process development projects are guided by a QA program plan. There are now 23 projects using this higher level of assurance. Six plans were written this year for such projects as fuel reprocessing, off-gas decontamination, and Iodox system demonstration. Twenty-two nonconformance reports, which dealt mostly with minor dimensional discrepancies during equipment fabrication, were issued.

The control of quality can be evaluated effectively by holding a QA audit. This audit allows management to judge whether the requirements set forth in the planning and design stages are being met. During this reporting period, four formal audits were held on projects within the division. Two were initiated by the ORNL QA Director's Office, and two by USAEC–Oak Ridge Operations. Appropriate corrective actions resulted from recommendations made through these audits.

17.2 RESOURCE STUDIES

The Chemical Technology Division continued to contribute to the Laboratory's interdivisional efforts on resource and energy analyses. The major effort now in progress is the preparation (by H. E. Goeller and W. L. Carter) of a book, *World Energy Conference Survey of Energy Resources, 1974.* This effort, which is being coordinated through the AEC Office of Planning and Analysis, is nearing completion. The document will summarize the results of an energy resource survey currently under way in the 69 World Energy Conference (WEC) nations, and in a number of additional nations which are members of the UN but not of WEC. The statistical summaries on fossil fuels (including bituminous sands and oil shales), hydraulic resources, uranium, and thorium and semiquantitative data on solar, geothermal, tidal, and wind energy will be reported in a series of appendixes preceded by a nine-chapter text on the various resources. The book will also contain a significant number of maps and other illustrative material needed to give full coverage to the subject. It is scheduled to be issued at the Ninth General Meeting of the World Energy Conference to be held in Detroit, Michigan, September 22–27, 1974.

As indicated in ORNL-4794,[1] H. E. Goeller was a member of Panel II of the Committee on the Study of Materials Science and Technology (COSMAT) sponsored jointly by NAS-NAE. In this capacity, he contributed information on material resources, as well as on opportunities for substitution and recycle. The COSMAT summary report has recently been issued (1974) as *Materials and Man's Needs;* more detailed reports will be issued in the future.

Goeller also presented a talk entitled "An Optimistic Outlook for Mineral Resources" at several seminars.

17.3 ENVIRONMENTAL IMPACT OF THE NUCLEAR FUEL CYCLE FOR LIGHT WATER REACTORS

Development of "As Low as Practicable" (ALAP) Guides

Engineering survey studies were carried out to provide the Directorate of Regulatory Standards (DRS)–

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1972,* ORNL-4794, p. 100.

USAEC with the technical information required to formulate appropriate ALAP guidelines for the release of radioactive materials from all segments of the nuclear fuel cycle. Four draft reports were submitted to the USAEC 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, Part 1. Nuclear Fuel Reprocessing; Part 2. Fabrication of Light Water Reactor Fuel from Enriched Uranium Dioxide; Part 3. Milling of Uranium Ores;* and *Part 4. Fabrication of Light-Water Reactor Fuels Containing Plutonium.* The DRS has prepared environmental statements which present the impact of any proposed new ALAP guidelines. The engineering survey and environmental reports are expected to be issued to the nuclear industry, the public, and governmental agencies for comment in mid-1974. 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.

Studies were initiated on surveys which will cover conversion of "yellow cake" to UF_6, milling of thorium, preparation and fabrication of fuels from thorium and ^{233}U, reprocessing of reactor fuels containing ^{233}U and thorium, and the permanent disposal of waste in commercial burial grounds.

A Critical Review of Solid Radioactive Waste Practices at Nuclear Power Plants[2]

A survey was made of solid radioactive waste (radwaste) practices at light-water-cooled nuclear power plants. Plant operating reports maintained from initial criticality through December 31, 1972, were the main sources of information. A comparison of the data for boiling water reactors (BWRs) and pressurized water reactors (PWRs) shows that BWRs consistently shipped a larger total volume of solid radwaste per thermal megawatt-hour than PWRs. At the end of 1972, the cumulative thermal megawatt-hour output was 2.2×10^8 for BWRs and 2.5×10^8 for PWRs included in this survey. The corresponding cumulative volumes of solid radwaste shipped were approximately 3.3×10^5 ft^3 and 1.4×10^5 ft^3, or 1.5×10^{-3} and 0.6×10^{-3} ft^3/MWhr(t) for BWRs and PWRs respectively. The cumulative total curie (uncorrected for decay) contents of these wastes were 6.7×10^3 Ci for the BWRs and 7.7×10^3 Ci for the PWRs, which give average specific activities of 2×10^{-2} and 5.5×10^{-2} Ci/ft^3 for the BWR and PWR wastes respectively. The average number of curies shipped offsite to licensed burial grounds per thermal megawatt-hour through the end of 1972 was the same for both types of reactors – 3×10^{-5} Ci for each. The PWRs made fewer radwaste shipments of higher specific activity per thermal megawatt-hour output. Shipments per 1,000,000 MWhr(t) averaged about 3 for BWRs and $1\frac{1}{3}$ for PWRs.

17.4 DISPOSAL OF ORNL WASTE BY HYDRAULIC FRACTURING

Environmental Impact Statement for the Shale Fracturing Facility

The shale fracturing process is being used at Oak Ridge National Laboratory for the permanent disposal of radioactive waste solutions. In this process, the waste solution is mixed with cement and injected into an impermeable shale formation at a depth of about 800 ft. Here the waste grout sets, fixing the radionuclides in the cement matrix. Since 1966, over 1,000,000 gal of waste solution containing nearly 500,000 Ci of ^{137}Cs and 30,000 Ci of ^{90}Sr have been injected successfully. A new disposal facility, as presently proposed, will have the capability for handling sludges and wastes with a higher specific activity than the 2 Ci/gal that can be handled in the existing facility. An environmental impact statement has been written for the new facility.

The overall environmental impact of the new shale fracturing facility is expected to be beneficial. The facility will remove large volumes of potentially hazardous radioactive wastes from existing surface storage facilities and fix these wastes in impermeable shale formations well removed from the biosphere. The probable consequences of accidental escape of activity from the disposal facility have been analyzed for several possible means of release. Most of these are regarded as quite improbable; and, in each case studied, the ultimate release of radionuclides to the environment is estimated to be small.

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

Two processes have been considered as alternatives to the shale fracturing facility. These are indefinite storage in tanks and solidification of the waste solution followed by storage of the solids in a vault. The shale fracturing process appears to offer a smaller environmental impact than either tank storage or solidification, less need for long-term monitoring, and a much lower cost.

Environmental Impact Statement for the Waste System Modifications

A recent change in emphasis in the waste handling programs has led to a postponement of the funding for the new shale fracturing facility. Instead, several modifications to the existing ORNL intermediate-level liquid waste system have been proposed. An environmental impact statement for these modifications has been written.

The proposed modifications include a second waste evaporator facility, evaporator feed and hold tanks, a new waste pipeline, and two large waste storage tanks. The second waste evaporator will ensure continuity of Laboratory operations in the event that the existing evaporator should fail. The new waste collection and storage tanks will permit operation of the waste handling system without use of the Gunite waste tanks – the first step toward eventual retirement of these tanks.

The overall environmental impact of the new facilities is expected to be beneficial. The new waste evaporator would ensure continuity of the Laboratory's operation in the event of a major malfunction of the existing unit. New storage tanks would provide safe storage for concentrated intermediate-level waste solution. The possibly adverse environmental effects attributable to these facility modifications are limited to those of any construction project and thus are not considered to be major.

The probable consequences of accidental escape of activity from the proposed new facilities have been analyzed for several possible means of release. Most of these are regarded as quite improbable; consequently, the ultimate release of radionuclides to the environment is estimated to be small.

The most viable alternative to construction of the proposed new facilities is continued use of the existing facilities and acceptance of the consequent risks. Solidification of the waste solution is not an alternative to the present mode of operation since facilities essentially equivalent to those proposed would be required even if a workable solidification facility were available.

Site Proof Test

A site located about 800 ft south of the existing facility has been proposed for the new shale fracturing plant. It is believed that the geologic formations underlying the new site are essentially identical to those underlying the present site and that similar fractures will be formed when waste is injected. To be certain that this is the case, however, a "site proof" test will be made. An injection well and four observation wells will be installed for the test. Then an injection of 100,000 gal of grout will be made from the injection well, and the horizontal orientation of the fractures will be verified from a determination of the depth at which the grout sheet intercepts the observation wells.

Drilling and cementing of the new injection well and the four new observation wells are complete. The inclination of all five wells has been determined. Cores of the shale formations were obtained during the drilling of one of the observation wells; these cores indicate that the formations underlying the new site are very similar to those underlying the present site, except they are about 100 ft deeper. Procurement of equipment for the site proof injection is in progress.

Sludge Removal Studies

A total of approximately 300,000 gal of sludge has been accumulated in the six Gunite waste tanks during the 30 years they have been in service. Before these tanks can be phased out of service, the sludge (which contains up to 500,000 Ci of ^{90}Sr) must be removed and disposed of. The sludge in each of the six tanks has been sampled and analyzed. Results show that the solids content of the sludge varies between 30 and 65 wt %. Between 45 and 95% of the solids consists of fines with a particle diameter of about 1 to 5 μ; the remaining solids are friable agglomerates with a diameter of up to 1 mm. A slurry of the fines will settle fairly quickly to a quasi-stable suspension with a volume from 1.5 to 4 times that originally observed. Further settling is quite slow; a period of several weeks is required for any significant change. The uranium and thorium contents of some of the samples were quite high – up to 188 and 167 mg/g respectively. These concentrations are in fair agreement with the quantities known to be in the tanks from accountability records.

Leaching of Cement Grouts

A series of leach tests is currently in progress to determine how effectively cementitious grouts retain radionuclides. In these tests, grouts comprised of the

standard dry mix used in the hydrofracture experiments and simulated waste solution traced with either ^{137}Cs, ^{85}Sr, ^{239}Pu, or ^{244}Cm are leached with tap water. In general, the method of leach testing proposed by the International Atomic Energy Agency[3] has been followed. The results obtained thus far show generally that (1) the amount leached from a product decreases with curing time (the length of time a product dries in air before being exposed to leachant); (2) the leach rate decreases with increasing leaching time; and (3) after approximately two to three weeks of leaching, the amount leached becomes linear and almost constant with time. Representative results for cesium and plutonium are given in Table 17.1. To explain these results, theoretical expressions based on mass transport phenomena that relate the amount of a nuclide escaping from the grout to several mechanisms (diffusion, dissolution, and curing of the cement) were applied to the data. For most of the products, the measured amount leached and that predicted by the model agree within a few percent. Such a fit of the data based on a theoretical model may be extrapolated with a greater degree of confidence than a fit of the data to an empirical relationship. Typical data are shown in Table 17.1. These studies will be summarized in ref. 4.

17.5 STUDIES OF SPECIFICATION CONTAINERS

As design burnups are achieved, large quantities of plutonium will be produced in light water reactors. This

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

4. J. G. 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-TM-4640 (in preparation).

Table 17.1. Experimental results for the leaching of cesium and plutonium from cement grout[a]

Leaching time (days)		Fraction leached[b]	
Incremental	Cumulative	Incremental	Cumulative
		Cesium	
1	1	7.96×10^{-4}	0.796×10^{-4}
1	2	3.18×10^{-4}	1.114×10^{-3}
5	7	5.02×10^{-4}	1.616×10^{-3}
7	14	3.93×10^{-4}	2.009×10^{-3}
7	21	4.41×10^{-4}	2.450×10^{-3}
7	28	4.44×10^{-4}	2.894×10^{-3}
7	35	6.21×10^{-4}	3.515×10^{-3}
7	42	4.48×10^{-4}	3.963×10^{-3}
7	49	3.20×10^{-4}	4.283×10^{-3}
7	56	3.28×10^{-4}	4.611×10^{-3}
21	77	6.57×10^{-4}	5.268×10^{-3}
28	105	6.48×10^{-4}	5.916×10^{-3}
28	133	6.22×10^{-4}	6.538×10^{-3}
28	161	3.20×10^{-4}	6.858×10^{-3}
22	183	4.67×10^{-4}	7.325×10^{-3}
69	252	6.28×10^{-4}	7.953×10^{-3}
		Plutonium	
1	1	0.14×10^{-6}	0.14×10^{-6}
6	7	1.67×10^{-6}	1.81×10^{-6}
27	34	1.02×10^{-6}	2.83×10^{-6}
28	62	0.65×10^{-6}	3.48×10^{-6}
28	90	1.12×10^{-6}	4.60×10^{-6}

[a]Contains 6 lb of dry mix (type I cement, 38.5 wt %; fly ash, 38.5 wt %; attapulgite, 15.4 wt %; Grundite, 7.6 wt %) per gallon of simulated ORNL intermediate-level waste.

[b]Leach samples have an exposed-surface-to-volume ratio of 0.2 cm^{-1}.

plutonium, after recovery in reprocessing plants, will be shipped to some repository or a fuel fabrication plant. Recently, there has been much concern over the form of the plutonium in such shipments.

We have completed the design of a container which is capable of transporting 10 liters of plutonium nitrate. The design features double containment of the product, seals that can be checked in place, a gas space expected to reduce the chance of violent recombination of radiolytic decomposition products, and shielding which will be adequate for plutonium that is produced in power reactors in the future. The design will be maintained on file, pending an expression of interest from the USAEC in fabricating and testing the container.

17.6 STUDIES INVOLVING TESTS OF OBSOLETE CASKS

Type B shipping containers for radioactive materials are frequently quite expensive; therefore, a detailed analysis of their behavior under normal and hypothetical accident conditions is required of all such containers before they are approved by the competent authority. Some rather sophisticated methods of analysis, based primarily on either component or model testing, have been developed within the past few years. It has generally not been possible, primarily because of the cost involved, to test massive prototype casks to determine whether their actual behavior was in agreement with calculated behavior and, consequently, to determine whether the evaluation was adequate.

Small casks, weighing 6000 lb, will be dropped initially. These casks have been analyzed to determine the effect of an end drop. Each cask will be instrumented, and detailed measurements will be made in order to compare predicted behavior with actual behavior.

We expect to extend this effort to include casks weighing up to 30 tons. The HWCTR cask has been requested from the Savannah River Operations Office for this purpose.

A safety analysis of the Tower Shielding Facility has been initiated to permit its use in dropping casks weighing up to 30 tons from a height of 30 ft.

17.7 ^{233}U STORAGE, PURIFICATION, AND DISTRIBUTION

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. Also, a shielded interim storage vault (located in cell 3) can hold up to 70 kg of ^{233}U or ^{239}Pu in shipping containers. The latter vault is to be replaced by a permanent facility (Building 3100), which is ready for occupancy. The Building 3100 vault is designed for storage of unirradiated fissile materials according to the latest AEC specifications.[5]

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 that is 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 per week, has been placed in operation to provide several hundred kilograms of UO_2 to Bettis Atomic Power Laboratory[6] (see Sect. 7).

Receipts during this report period consisted of 62.1 kg of uranium as $^{233}UO_2$, $^{233}UO_2$-ThO_2 scrap pellets, and a small amount of other scrap in a total of 13 shipments. Disbursements consisted of 182.4 kg of uranium as $^{233}UO_2$ in a total of 13 shipments.

An inventory made on March 31, 1974, showed that the facility contained a total of 960.1 kg of ^{233}U and 800.2 kg of ^{235}U. Of these quantities, 101.6 kg of ^{233}U and 800.2 kg of ^{235}U as uranyl nitrate solution are stored in the TRUST (Thorium Reactor Uranium Storage Tank) facility,[7] where the concentrations of uranium and soluble neutron poison, gadolinium, have been found to remain constant for a period of five years. On the other hand, the concentration of cadmium, another soluble neutron poison, apparently decreased to about two-thirds of the required concentration during the past year; thus additional quantities of this poison had to be added. The hydrogen concentration in the off-gas from the storage tank was found to be 0.04% by volume. Studies of the system off-gas

5. 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).

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

7. J. R. Parrott, R. G. Nicol, and J. P. Nichols, *Receipt and Analysis of the Consolidated Edison Uranium Product Solution and Subsequent Storage Using Soluble Neutron Absorbers,* ORNL-TM-3348 (June 1971).

activity during the current report period showed that high radiation in the off-gas system could be reduced by providing a charcoal bed on which to sorb the thoron gas being emitted. This arrangement would allow the high-energy daughters to be collected on a filter.

17.8 LICENSING OF OPERATING PERSONNEL FOR FUEL REPROCESSING PLANTS

The Chemical Technology Division is assisting the USAEC Directorate of Licensing in licensing the personnel who operate nuclear fuel reprocessing plants. To obtain an operator license, an individual is required to pass both a written and an oral examination based on the equipment, operating procedures, etc., used at the specific plant at which he will be working. During this report period, we have assisted in licensing personnel for the Midwest Fuel Recovery Plant (MFRP) at Morris, Illinois. Four types of licenses are being issued at MFRP: Senior, Remote Process, Mechanical Cell, and Fuel Receipt and Storage. Chemical Technology Division personnel have assisted in preparing and grading the written examinations as well as in administering the oral examinations.

17.9 PREPARATION OF TRAINING GUIDES FOR NUCLEAR FACILITY PERSONNEL

A *Training Guide,* consisting of 11 chapters, is being prepared for use by nuclear fuel reprocessing facility licensees and by the USAEC branch organizations responsible for safety and licensing actions in this private sector of the reactor fuel cycle.

The purpose of the *Guide* is to provide private industry with information that is useful in the preparation of training manuals and in the planning of training programs for operating personnel who must demonstrate, through AEC-supervised testing procedures, that their knowledge and understanding of the facility operations and administration are satisfactory and sufficient to allow them to operate the controls of an AEC-licensed nuclear fuel refabrication plant.

Members of the Chemical Technology Division have been utilized by the USAEC Directorate of Licensing in these operator certification actions.

This task was started during 1973 when 17 ORNL employees and 2 individuals employed by other AEC contractors, all specialists in various fuel reprocessing operations, agreed to make written contributions to the *Guide.* Financing totaled $20,000 in FY 1973 and $30,000 in FY 1974.

By March 1974, all authors had begun their write-ups, and 50% of the document had been prepared in draft form. By July 1974, an edited first draft is scheduled to be ready for distribution to the USAEC Safety Branch and to others in private industry for review and comment prior to issuance for general use.

17.10 STUDY OF OPTIONS FOR CONTROLLING SO_2 EMISSIONS FROM COAL-FIRED POWER STATIONS

A study was conducted in 1973 by the Oak Ridge National Laboratory, the Ohio Valley Electric Corporation, and the American Electric Power Service Corporation to evaluate the alternatives that might be applied at the Clifty Creek Station of the Ohio Valley Electric Corporation for control of SO_2 emissions.[8] Clifty Creek is a 1300-MW station located at Madison, Indiana, on the Ohio River. It furnishes a large portion of the power used at the AEC's gaseous diffusion plant at Portsmouth, Ohio. The fuel used at Clifty Creek is a bituminous coal, typical of that found in the eastern interior region, with an average sulfur content of about 3.5%. Sulfur dioxide emissions are about 6.4 lb per million Btu; the proposed 1975 standard for Indiana is 1.2 lb per million Btu.

It was concluded that stack gas treating did not yet have the necessary operating reliability so that satisfactory installation and operation by 1977 could be guaranteed. Accordingly, the only technologically feasible alternatives that could be applied by 1977 are based on the use of low-sulfur fuel oil, low-sulfur coal, or natural gas. Longer-term alternatives include the use of low-Btu gas, solvent-refined coal, or synthetic fuel oils made from coal by catalytic hydrodesulfurization.

Natural Gas and Low-Sulfur Fuel Oil

Converting to the use of natural gas was judged not to be a feasible alternative for coal-burning plants. Natural gas is in very short supply, and the scarcity is expected to grow more acute. Projected importation of liquefied natural gas will not be sufficient to alleviate the shortage appreciably.

Low-sulfur fuel oil made from petroleum is also in very short supply. In early 1973 the use of low-sulfur fuel oil appeared feasible but risky. It was clear that incremental supplies would have to come from the Middle East and that security and reliability of supply could not be guaranteed.

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8. C. L. Bazelmans et al., *Study of Options for Control of Emissions from an Existing Coal-Fired Power Station,* ORNL-TM-4298 (September 1973).

Low-Sulfur Coal

Ample supplies of low-sulfur coal are available in the western United States. Cost in early 1973 was about $2.50 per ton at the mine mouth. Transportation cost to Clifty Creek was estimated at about $8.50 per ton, giving a total delivered cost of about $11 per ton. However, there are many problems associated with the burning of Western coal in boilers designed for Eastern bituminous coals. Before committing a plant to a changeover to Western coal, it is essential to make a test run to find out what difficulties are encountered and to determine how much derating is necessary.

Flue Gas Treating

Four flue gas treating processes were considered: wet lime or limestone scrubbing, catalytic oxidation (the Cat-Ox process), magnesia scrubbing, and sodium sulfite scrubbing (the Wellman-Lord process). These four were selected as representative of processes in a fairly advanced stage of development, with large-scale trial installations built or planned.

Estimated costs for the four stack gas treating processes are shown in Table 17.2. Capital costs are about $50 to $70 per kilowatt; the total amount added to the cost of power is about 2.5 mills/kWhr, using an annual fixed charge rate of 16.7% on capital investment. This does not include any penalty for derating or forced outage; the effect of this penalty is shown later.

Low-Btu Gas

Low-Btu gas is made by gasifying coal with air and steam. The raw gas is treated to remove particulates, tars, and H_2S. The purified gas typically has a heating value of 120 to 180 Btu/scf and can be burned in utility boilers with some derating. The recovered H_2S can be converted to sulfur in a Claus plant. A very high degree of sulfur removal is possible. Instead of burning the low-Btu gas under a boiler, it could be burned in a gas turbine, and the hot exhaust gases from the turbine could be used to generate steam which would be used in a steam turbine. This combined cycle could have a higher efficiency than that of typical steam-electric plants.

Coal Liquefaction

The Pittsburg-Midway solvent-refined coal (SRC) process produces a low-sulfur, ash-free solid product with a heating value of 16,000 Btu/lb. A pilot plant demonstrating this process is operating at Wilsonville, Alabama, and another will soon start up near Tacoma, Washington. The SRC process appears to have great potential for utility fuel. The coal is slurried with a process-derived solvent and treated with hydrogen at about 1000 psi. Partial liquefaction takes place during this step. The residual solids are then separated, and the liquid is vacuum flashed to produce recycle solvent. The vacuum bottoms are the solvent-refined coal product.

Several other liquefaction processes such as H-Coal, COED, Consol, and Synthoil are being developed. In this study, however, only two processes were considered: SRC and H-Coal. SRC is representative of processes which produce only heavy fuel oil, while H-Coal is representative of processes that use more severe hydrogenation to produce motor fuels as well as fuel oil.

Cost Comparisons

The costs of flue gas treating shown in Table 17.2 were based on capital and operating costs only. For a

Table 17.2. Estimated costs of flue gas treatment[a]

	Wet limestone scrubbing	Wet magnesia scrubbing	Sodium sulfite solution scrubbing (Wellman-Lord)	Cat-Ox process
Capital investment, millions of dollars	83.6	78.6	86.4	61–95
Annual charges, millions of dollars per year				
Annual capital charges	14.0	13.1	14.4	10.2–15.9
Operating and maintenance costs	10.3	12.7	10.8	7.6–8.2
Total annual cost	24.3	25.8	25.2	17.8–24.1
Added power cost, mills/kWhr	2.4	2.6	2.5	1.8–2.4

[a]Not including derating and forced outage costs.

more complete comparison, a cost model that includes derating and forced outage costs was used. The amount added to the cost of power by the addition of the emission-control facilities consisted of five components: (1) annual charges on capital; (2) additional fuel cost (above the base cost of 35¢ per million Btu); (3) other operating and maintenance costs, depending on the process; (4) derating cost; and (5) forced outage cost. The last two items were based on purchasing electricity at an estimated 11 mills/kWhr to replace electricity lost by derating or outage. The net cost of purchased power, taking into account reduced fuel usage, was estimated at 8 mills/kWhr.

The costs of the near-term options (low-sulfur fuel oil and low-sulfur coal) are shown in Table 17.3. For low-sulfur fuel oil, the added cost of power was 3.5 to 4.5 mills/kWhr; for low-sulfur coal, it was 4.1 to 5.2 mills/kWhr. In the case of low-sulfur fuel oil, there are no derating or forced outage costs. For low-sulfur coal, the cost was based on an estimated derating of 5 to 15%. It might be noted that the costs of both of these fuels have escalated considerably since the study was made.

Table 17.4 shows the estimated added power cost for the longer-term options. The flue gas treating process shown here is the wet limestone slurry process; this is for the sake of illustration only and in no way implies preferability over the other processes considered. Derating and forced outage costs were based on estimated ranges of 2.4 to 5% for derating and 10 to 65% for forced outage rate. The lower end of the cost range assumes that 90% reliability has been achieved. The upper end represents 35% reliability, based on operating experience at Commonwealth Edison's Will County plant.

Low-Btu gas costs amounted to about 6 mills/kWhr based on a derating of 5% and a forced outage of 10%.

Solvent-refined coal and low-sulfur fuel oil made from coal were treated as purchased fuels with no penalties for derating or unreliability. Estimated costs were 4 to 6 mills/kWhr.

Table 17.3. Costs of near-term options

	Low-sulfur fuel oil	Low-sulfur coal
Capital investment, millions of dollars	23	10
Annual charges, millions of dollars per year		
Annual capital charges	3.8	1.7
Additional fuel costs	32.9–42.4	32.9
Operating and maintenance costs	(1.0)	1.0
Derating cost	0	5.5–16.6[a]
Forced outage cost	0	0
Total annual cost	35.7–45.2	41.1–52.2
Added power cost, mills/kWhr	3.5–4.5	4.1–5.2

[a]Based on an estimated derating of 5 to 15%.

Table 17.4. Costs of long-term options

	Flue gas treating	Low-Btu gas	Solvent-refined coal	Low-sulfur fuel oil from coal
Capital investment, millions of dollars	84–65	150	5	23
Annual charges, millions of dollars per year				
Annual capital charges	14.0–10.9	25.1	0.8	3.8
Additional fuel costs	0	10.0	37.6–51.5	48.6–59.8
Operating and maintenance costs	7.8–11.5	10.0	(0.5)	(1.0)
Derating cost	2.5–5.5	5.5	0	0
Forced outage cost	9.0–58.4	9.0	0	0
Total annual cost	33.3–86.3	59.6	37.9–51.8	51.4–62.6
Added power cost, mills/kWhr	3.3–8.5	5.9	3.8–5.1	5.1–6.2

Publications, Speeches, and Seminars

BIOCHEMICAL TECHNOLOGY

Anderson, N. G.,[1] and C. A. Burtis,[1] "GeMSAEC Fast Clinical Analyzers," in *Clinical Biochemistry – Principles and Methods,* Walter de Gruyter and Co., Berlin, West Germany, 1974.

Anderson, N. G.,[1] C. A. Burtis,[1] and T. O. Tiffany,[1] "Enzymology, Clinical Chemistry, and the Development of Fast Analyzers," in *Enzymology in Medicine,* P. Blume, ed., Academic, New York, 1974.

Burtis, C. A.,[1] "Applications of a GeMSAEC Fast Analyzer," presented at the Department of Pharmacology, University of California at San Francisco, San Francisco, Calif., July 5, 1973.

Burtis, C. A.,[1] "Automated Clinical and Serological Analysis for Large-Scale Processing," presented at the Annual Meeting of the Tennessee Public Health Workers, Gatlinburg, Tenn., Mar. 28, 1973.

Burtis, C. A.,[1] "Automated Pharmaceutical Analysis Using a Fast Analyzer," presented at the Federation Internationale Pharmaceutique, The 33rd International Congress of Pharmaceutical Sciences, Stockholm, Sweden, Sept. 3–7, 1973.

Burtis, C. A.,[1] "Bioanalytical Applications of Centrifugal Fast Analyzers," presented at Merck, Sharp and Dohme, Rahway, N.J., Feb. 8, 1974.

Burtis, C. A.,[1] "Bioanalytical Applications of Fast Analyzers," presented at Boehringer Mannheim GmbH, Tutzing, West Germany, Sept. 12, 1973.

Burtis, C. A.,[1] "Development of an Analytical System Based around a Miniature Fast Analyzer," presented at the 17th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 23–25, 1973.

Burtis, C. A.,[1] "Development of a Miniature Fast Analyzer," presented at Ernst Leitz GmbH, Wetzlar, West Germany, Sept. 10, 1973.

Burtis, C. A.,[1] "Introduction and History of the GeMSAEC Fast Analyzer," presented at the Centrifugal Fast Analyzer Workshop, Fall Meeting of the American Society of Clinical Pathologists, Chicago, Ill., Oct. 20, 1973.

Burtis, C. A.,[1] "Miniature Laboratory System for Space Flights and Health Care Delivery," presented at the Eighth Annual Meeting of the Association for the Advancement of Medical Instrumentation, Washington, D.C., Mar. 23, 1973.

Burtis, C. A.,[1] "The Centrifugal Fast Analyzer," presented at the Annual Convention for Medical Technology and American Medical Technologists, Little Rock, Ark., Apr. 12, 1973.

Burtis, C. A.,[1] W. F. Johnson,[2] J. C. Mailen, J. B. Overton, T. O. Tiffany,[1] and M. B. Watsky,[3] "Development of an Analytical System Based around a Miniature Fast Analyzer," presented at the Fifth Annual Symposium on Advanced Concepts for the Clinical Laboratory, ORNL, Mar. 15–16, 1973.

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1. MAN Program.
2. Instrumentation and Controls Division.
3. Presidential intern.

Burtis, C. A.,[1] W. F. Johnson,[2] J. C. Mailen, J. B. Overton, T. O. Tiffany,[1] and M. B. Watsky,[3] "Development of an Analytical System Based around a Miniature Fast Analyzer," *Clin. Chem.* **19**, 895 (1973).

Burtis, C. A.,[1] W. F. Johnson,[2] J. B. Overton, T. O. Tiffany,[1] and J. C. Mailen, "Parametric Optimization and Analytical Applications of the Technique of Dynamic Introduction of Liquids into Centrifugal Fast Analyzers," presented at the Sixth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, ORNL, Mar. 14–15, 1974.

Burtis, C. A.,[1] W. F. Johnson,[2] and C. D. Scott, "Microchemical Analysis with a Miniature Fast Analyzer," presented at the 25th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, Mar. 4–8, 1974.

Chilcote, D. D., "A Mathematical Analysis of Normalization Techniques Used in Chromatography," presented at the Eighth International Symposium on Advances in Chromatography, Toronto, Ontario, Canada, Apr. 16–19, 1973.

Chilcote, D. D., "Computer Assisted Chromatographic Analysis of Body Fluid Samples," presented at the 75th National Meeting of the American Institute of Chemical Engineers: Symposium on Engineering Methods in Medical Diagnostic Techniques, Detroit, Mich., June 3–6, 1973.

Chilcote, D. D., "Computer Technique for Identification of Chromatographic Peaks," *Clin. Chem.* **19**, 826–31 (1973).

Chilcote, D. D., "The Indole Analyzer: A Simple, Sensitive Liquid Chromatographic Analyzer for Naturally Occurring Indoles in Body Fluids," presented at the 165th American Chemical Society National Meeting, Dallas, Tex., Apr. 8–13, 1973.

Chilcote, D. D., and J. E. Mrochek, "An Engineering Approach to the Analysis of Indole Compounds in Physiologic Fluids," presented at the 75th National Meeting of the American Institute of Chemical Engineers, Detroit, Mich., June 3–6, 1973.

Chilcote, D. D., and J. E. Mrochek, "Rapid Chromatographic Analysis of Nucleosides and N-Bases in Physiologic Fluids," *Anal. Lett.* **6**, 531–38 (1973).

Chilcote, D. D., and C. D. Scott, "A Theoretical Derivation of the Axial Diffusion Coefficient in Chromatography," *J. Chromatogr.* **87**, 315 (1973).

Chilcote, D. D., and C. D. Scott, "Mathematical Analysis of Normalization Techniques Used in Chromatography," *Anal. Chem.* **45**, 721 (1973).

Egan, B. Z., "Separation of Oligodeoxynucleotides by Reversed-Phase Chromatography," *Anal. Biochem.* **56**, 616–17 (1973).

Egan, B. Z., and A. D. Kelmers, "Improved Separation of Oligonucleotides by Reversed-Phase Chromatography," p. 469 in *Methods in Enzymology,* vol. XXIX, ed. by L. Grossman and K. Moldave, Academic, New York, 1974.

Egan, B. Z., J. F. Weiss, and A. D. Kelmers, "Separation and Comparison of Primary Structures of Three Formylmethionine tRNAs from *E. coli* K-12 MO," *Biochem. Biophys. Res. Commun.* **55**, 320–27 (1973).

Hancher, C. W., R. L. Pearson, and A. D. Kelmers, "Preparation of Crude tRNA and Aminoacyl-tRNA Synthetase from Calf Liver," p. 510 in *Methods in Enzymology,* vol. XXIX, ed. by L. Grossman and K. Moldave, Academic, New York, 1974.

Hancher, C. W., and A. D. Ryon, "Evaluation of Ultrafiltration Membranes with Biological Macromolecules," *Biotechnol. Bioeng.* **15**, 677–92 (1973).

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

Jolley, R. L., "Determination of Chlorination Effects on Organic Constituents in Sewage Treatment Plant Effluents: A Coupled ^{36}Cl Tracer–High-Radiation Chromatographic Technique," presented at the 167th American Chemical Society National Meeting, Los Angeles, Calif., Mar. 31–Apr. 5, 1974.

Jolley, R. L., W. W. Pitt, Jr., C. D. Scott, and M. D. McBride, "Determination of Trace Organic Contaminants in Natural Waters by High-Resolution Liquid Chromatography," presented at the First Annual NSF Trace Contaminants Conference, ORNL, Aug. 8–10, 1973.

Katz, S., W. W. Pitt, Jr., and G. Jones, Jr., "Sensitive Fluorescence Monitoring of Aromatic Acids after Anion-Exchange Chromatography of Body Fluids," *Clin. Chem.* **19**, 817 (1973).

Kelmers, A. D., D. E. Heatherly, and B. Z. Egan, "Miniature Reversed-Phase Chromatography Systems for the Rapid Resolution of Transfer RNA's and Ribosomal RNA's," p. 483 in *Methods in Enzymology,* vol. XXIX, ed. by L. Grossman and K. Moldave, Academic, New York, 1974.

Mailen, J. C., "The Development of a Miniature Fast Analyzer," presented at the 75th National Meeting of the American Society of Chemical Engineers: Symposium of Engineering Methods in Medical Diagnostic Techniques, Detroit, Mich., June 3–6, 1973.

Mailen, J. C., C. A. Burtis,[1] W. F. Johnson,[2] C. D. Scott, and T. O. Tiffany,[1] "The Miniature Fast Analyzer; A Portable System for the Analysis of Human Serum," presented at the National Meeting of the American Institute of Chemical Engineers, Detroit, Mich., June 3–6, 1973.

Mrochek, J. E., "Application of Integrated Gas Chromatographic and Mass Spectrometric Methods in the Identification of Urinary Constituents Isolated by Liquid Chromatography," presented at the Symposium of Gas Chromatography–Mass Spectrometry: A New Analytical Technology, Houston, Tex., Jan. 29, 1974.

Mrochek, J. E., "High-Resolution Liquid Chromatography – A New Analytical Tool for the Clinical Chemist," presented at the Fifth Annual Central Regional Meeting of the American Chemical Society, Cleveland, Ohio, May 13–15, 1973.

Mrochek, J. E., "Liquid Chromatographic Analysis of Urinary Nucleosides in Normal and Malignant States," presented at the American Chemical Society Symposium on Analytical Advances in Clinical and Medicinal Chemistry, Chicago, Ill., Aug. 30, 1973.

Mrochek, J. E., "The Use of Electrolytic Hydrogen for Ammonia Synthesis," in *Ammonia,* a Fertilizer Technology Monograph, ed. by A. V. Slack and G. R. James, Marcel Dekker, New York, 1973.

Mrochek, J. E., S. R. Dinsmore, and D. W. Ohrt, "Monitoring Phenylalanine-Tyrosine Metabolism by High-Resolution Liquid Chromatography of Urine," *Clin. Chem.* **19**, 927 (1973).

Mrochek, J. E., S. Katz, W. H. Christie, and S. R. Dinsmore, "The Metabolism of Acetaminophen in Man as Determined by High-Resolution Liquid Chromatography," presented at the Sixth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, ORNL, Mar. 14–15, 1974.

Mrochek, J. E., and W. T. Rainey, Jr., "Gas Chromatography and Mass Spectrometry of Some Trimethylsilyl Derivatives of Urinary Glucuronides," *Anal. Biochem.* **57**, 173–89 (1974).

Pearson, R. L., C. W. Hancher, J. F. Weiss, D. W. Holladay, and A. D. Kelmers, "Preparation of Crude Transfer RNA and Chromatographic Purification of Transfer RNA's from Calf Liver," *Biochim. Biophys. Acta* **294**, 236–49 (1973).

Pearson, R. L., J. F. Weiss, D. W. Holladay, and A. D. Kelmers, "Purification of Calf Liver tRNA's," p. 514 in *Methods in Enzymology,* vol. XXIX, ed. by L. Grossman and K. Moldave, Academic, New York, 1974.

Pitt, W. W., Jr., "Analysis for Trace Organic Contaminants in Polluted Water by High-Resolution Ion Exchange Chromatography," presented at the Gordon Conference on Ion Exchange, Wolfeboro, N.H., Aug. 7, 1973.

Pitt, W. W., Jr., S. Katz, and L. H. Thacker,[2] "A Rapid, Sensitive Method for the Determination of the Chemical Oxygen Demand of Polluted Waters," pp. 1–5 in *Water – 1972,* American Institute of Chemical Engineers Symposium Series, vol. 69, No. 129, 1973.

Pitt, W. W., Jr., C. D. Scott, and M. D. McBride, "Determination of Trace Organic Contaminants by High-Resolution Liquid Chromatography," presented at the Seventh Annual Conference on Trace Substances in Environmental Health, University of Missouri, Columbia, Mo., June 12–14, 1973.

Scott, C. D., "Fast Analyzer Systems," presented at the American Society for Pharmacology and Experimental Therapeutics, East Lansing, Mich., Aug. 23, 1973.

Scott, C. D., "Health-Care Delivery and Advanced Technology," *Science* **180**, 1339 (1973).

Scott, C. D., "High Pressure Liquid Chromatography as Applied to the Clinical Laboratory Sciences," presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Inc., Cleveland, Ohio, Mar. 4, 1974.

Scott, C. D., "High Resolution Liquid Chromatography," presented at the University of Salford, Salford, England, May 8, 1973.

Scott, C. D., "High Resolution Liquid Chromatography as Applied to the Separation of Complex Biochemical Mixtures," presented at Iowa State University, Ames, Iowa, Apr. 9, 1973.

Scott, C. D., "High Resolution Liquid Chromatography as Applied to the Separation of Complex Biochemical Mixtures," presented at the 3-M Company, St. Paul, Minn., Apr. 11, 1973.

Scott, C. D., "High Resolution Liquid Chromatography as Applied to the Study of Drug Metabolism," presented at the Pharmaceutical Analysis Session of the Fifteenth Eastern Analytical Symposium, New York, N.Y., Nov. 14–16, 1973.

Scott, C. D., "Recent Developments in Fast Analyzer Systems," presented at the University of Birmingham, Birmingham, England, May 7, 1973.

Scott, C. D., "The Miniature Centrifugal Fast Analyzer," presented at ATOMEDIC '73, USAEC Seminar for Newsmen and Science Writers, Argonne National Laboratory, Argonne, Ill., Sept. 26, 1973.

Scott, C. D., W. F. Johnson,[2] L. H. Thacker,[2] and C. A. Burtis,[1] "A Small Battery-Operated Centrifugal Fast Analyzer System," presented at the Sixth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, ORNL, Mar. 14–15, 1974.

Scott, C. D., and N. E. Lee, "Use of Sequential Columns of Microreticular and Pellicular Ion Exchange Resins in the High-Resolution Separation of Complex Biochemical Mixtures," presented at the First International Symposium on Column Liquid Chromatography, Interlaken, Switzerland, May 2–4, 1973; proceedings in *J. Chromatogr.* **83**, 383 (1973).

Scott, C. D., and R. S. Melville,[4] "Introduction. Fifth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory," *Clin. Chem.* **19**, 806 (1973).

Scott, C. D., and W. W. Pitt, Jr., "Advances in the Development of High Resolution Liquid Chromatography as Applied to Analyses of Physiologic Fluids," presented at the 75th National Meeting of the American Institute of Chemical Engineers, Symposium of Engineering Methods in Medical Diagnostic Techniques, Detroit, Mich., June 3–6, 1973.

Tiffany, T. O.,[1] "Recent Developments in Fast Analyzers," presented at the Joint Spring Meeting of the Canadian Society of Clinical Chemists and the American Association of Clinical Chemists (Upstate New York Section), Hamilton, Ontario, Canada, May 3–4, 1973.

Tiffany, T. O.,[1] "The Fluorescent Fast Analyzer," presented at the Spring Meeting, Southeast Section of the American Association of Clinical Chemists, Gatlinburg, Tenn., Apr. 5–6, 1973.

Tiffany, T. O.,[1] C. A. Burtis,[1] and N. G. Anderson,[1] "Fast Analyzers for Biochemical Analysis," in *Methods in Enzymology,* vol. 31, Academic, New York, 1974.

Tiffany, T. O.,[1] C. A. Burtis,[1] J. C. Mailen, and L. H. Thacker,[2] "A Dynamic Multicuvette Fluorometer-Spectrophotometer Based on the GeMSAEC Fast Analyzer Principle," *Anal. Chem.* **45**, 1716 (1973).

Tiffany, T. O.,[1] C. A. Burtis,[1] and M. B. Watsky,[3] "The Use of the Fluorometric Fast Analyzer for Measuring Enzyme Activity (A Discussion of Direct Referencing of Fluorescence Assays)," presented at the 25th National Meeting of the American Association of Clinical Chemists, New York, N.Y., July 15–20, 1973.

4. National Institute of General Medical Sciences, Bethesda, Md.

Tiffany, T. O.,[1] D. D. Chilcote, and C. A. Burtis,[1] "Evaluation of Kinetic Enzyme Parameters by Use of a Small-Computer Interfaced 'Fast Analyzer' – An Addition to Automated Clinical Enzymology," *Clin. Chem.* **19**, 908–18 (1973).

Tiffany, T. O.,[1] W. F. Johnson,[2] C. A. Burtis,[1] R. C. Lovelace, and C. D. Scott, "Blood Grouping and Specific Protein Determination with a Miniature Fast Analyzer," presented at the Sixth Annual Symposium on Advanced Concepts for the Clinical Laboratory, ORNL, Mar. 14–15, 1974.

Tiffany, T. O.,[1] M. B. Watsky,[3] C. A. Burtis,[1] and L. H. Thacker,[2] "Fluorometric Fast Analyzer: Some Applications to Fluorescence Measurements in Clinical Chemistry," *Clin. Chem.* **19**, 871–82 (1973).

Veening, H. W.,[5] W. W. Pitt, Jr., and G. Jones, Jr., "Ion-Exchange Chromatographic Separation and Detection of Urinary Polyamines Using Fluorescamine," *J. Chromatogr.* **90**, 129–39 (1974).

Veening, H. W.,[5] W. W. Pitt, Jr., and G. Jones, Jr., "Ion Exchange Chromatographic Separation and Detection of Urinary Polyamines Using Fluorescamine," presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Inc., Cleveland, Ohio, March 1974.

Waalkes, T. P.,[6] S. R. Dinsmore, and J. E. Mrochek, "Urinary Excretion by Cancer Patients of the Nucleosides, N^2,N^2-Dimethylguanosine, 1-Methylinosine, and Pseudouridine," *J. Nat. Cancer Inst.* **51**, 271 (1973).

DEVELOPMENT OF THE THORIUM FUEL CYCLE

de Nordwall, H. J., J. O. Kolb,[7] F. F. Dyer,[8] and W. J. Martin, "An Interim Report of Fission-Product Release during Operation of the Second Peach Bottom Core," presented at the International Conference on Nuclear Fuel Performance, London, England, Oct. 15–19, 1973.

Lindemer, T. B., and H. J. de Nordwall, *An Analysis of Chemical Failure of Coated UO_2 and Other Oxide Fuels in the High-Temperature Gas-Cooled Reactor,* ORNL-4926 (January 1974).

North, E. D.,[9] and R. L. Booth,[9] *Fission Product Gas Retention Study – Final Report,* ORNL-TM-4409 (August 1973).

Notz, K. J., and P. A. Haas, "Uranium Loading of Ion Exchange Resins for HTGRs," presented at the 75th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 1973; abstract published in *Ceram. Bull.* **52**(4), 400 (1973).

Notz, K. J., A. B. Meservey, and R. D. Ackley, "The Solubility of Krypton and Xenon in Liquid CO_2," presented at the 1974 Winter Meeting of the American Nuclear Society, San Francisco, Calif., Nov. 11–16, 1973; published in *Trans. Amer. Nucl. Soc.* **17**, 318–19 (November 1973).

Notz, K. J., and G. B. Pollock,[10] "Nuclear Fuel Microspheres Derived from Ion Exchange Resin Beads," presented at the Joint Nuclear Division and Pacific Coast Regional Meeting of the American Ceramic Society, San Francisco, Calif., Oct. 26, 1973; abstract published in *Ceram. Bull.* **52**(9), 721 (1973).

Whatley, M. E., *Calculations on the Performance of the KALC Process,* ORNL-4859 (May 1973).

Wymer, R. G., "Elements of High Temperature Gas-Cooled Reactor Fuel Recycle," presented at the University of Tennessee, Knoxville, Sept. 11, 1973.

---

5. Department of Chemistry, Bucknell University, Lewisburg, Pa.
6. National Cancer Institute, Bethesda, Md.
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9. Nuclear Fuel Services, Inc., Rockville, Md.
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MISCELLANEOUS

Annis, B. K.,[11] A. P. Malinauskas, and E. Z. Mason,[12] "Theory of Diffusiophoresis of Spherical Aerosol Particles and of Drag in a Gas Mixture," *Aerosol Sci.* **4**, 271–81 (1973).

Arnold, W. D., R. Salmon, K. H. Lin, and W. de Laguna, "Evaluation of Methods for the Disposal of Tritiated Water from Nuclearly Stimulated Gas Wells," *Waste Management Research Abstracts,* No. 8, p. 105, International Atomic Energy Agency, Vienna, Austria (1973).

Arnold, W. D., R. Salmon, K. H. Lin, and W. de Laguna, *Preliminary Evaluation of Methods for the Disposal of Tritiated Water from Nuclearly Stimulated Natural Gas Wells,* ORNL-TM-4024 (April 1973).

Bacarella, A. L.,[11] and J. C. Griess, Jr., "The Anodic Dissolution of Copper in Flowing Sodium Chloride Solutions between 25° and 175°C," *J. Electrochem. Soc.* **120**, 459–65 (1973).

Bamberger, C. E., D. M. Richardson, and W. R. Grimes, "Thermochemical Cyclic Processes for Hydrogen Production at Oak Ridge National Laboratory," presented at Los Alamos Scientific Laboratory, Los Alamos, N.M., Jan. 17–18, 1974.

Bazelmans, C. L.,[13] F. T. Binford,[14] R. D. Dunlevy,[13] P. A. Haas, J. R. Hightower, J. M. Holmes, E. B. Morris,[15] J. P. Nichols, S. Ruggeri,[15] and R. Salmon, *Study of Options for Control of Emissions from an Existing Coal-Fired Electric Power Station,* ORNL-TM-4298 (September 1973).

Bell, M. J.,[16] *ORIGEN – The ORNL Isotope Generation and Depletion Code,* ORNL-4628 (May 1973).

Brooksbank, R. E., "The Nuclear Fuel Cycle," presented to Radiological Health Personnel, Oak Ridge Associated Universities, Mar. 28, 1973.

Brooksbank, R. E., "The Nuclear Fuel Cycle," presented at the "Energy Sources for the Future" Symposium, Oak Ridge Associated Universities, Aug. 10, 1973.

Clark, W. E., *Survey of Mercury Usage by Agencies of the United States Government during 1971,* ORNL-NSF-EATC-4 (January 1974).

Davis, L. P.,[17] and J. J. Perona,[17] "Development of Free Axial Flow through a Tube Bundle," *Int. J. Heat Mass Transfer* **16**, 1425–38 (1973).

DeCarlo, V. A., *Design of a System for the Nondestructive Assay of* ^{233}U *in Waste Drums,* ORNL-TM-4249 (August 1973).

DiStefano, J. R.,[10] and K. H. Lin, "Compatibility of Refractory Metals with $^{244}Cm_2O_3$," *Nucl. Technol.* **19**(7), 34–45 (July 1973).

Dresner, L.,[7] V. R. Cain,[7] and W. Davis, Jr., *INTAKE: A Numerical Program to Calculate Fluid Velocity Profiles near a Rectangular Inlet in a Stream with Cross Flow,* ORNL-TM-4185 (July 1973).

Endelman, F. J., M. L. Northup,[18] R. R. Hughes,[19] D. R. Keeley,[19] and J. R. Boyle,[20] "The Mathematical Modeling of Soil Nitrogen Transformations," pp. 83–90 in *Water – 1973,* American Institute of Chemical Engineers Symposium Series, vol. 70, No. 136, 1974.

---

11. Chemistry Division.
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19. University of Wisconsin, Madison.
20. University of Michigan, Ann Arbor.

Endelman, F. J., and R. Prober,[21] "A Series of Problems on Industrial Water Processes for Use by Chemical Engineers," pp. 465–69 in *Water – 1972,* American Institute of Chemical Engineers Symposium Series, vol. 69, No. 129, 1973.

Gambill, W. R., "Estimate of Effect of Localized Flow Blockages on PWR Clad Temperatures during Reflood," *National Topical Meeting on Water-Reactor Safety, Salt Lake City, Utah, Mar. 26–28, 1973,* USAEC CONF-730304, pp. 222–40, June 1973.

Gambill, W. R., "Fluid Flow and Heat Transfer in Water-Cooled Reactors," presented at Nuclear Power Safety Short Course, Georgia Institute of Technology, Atlanta, Ga., Feb. 25–Mar. 1, 1974.

Gambill, W. R., "Prediction and Correlation of Physical Properties," pp. 3-226–3-250 in *Chemical Engineers' Handbook,* 5th ed., ed. by R. H. Perry and C. H. Chilton, McGraw-Hill, New York, 1973.

Gambill, W. R., J. J. Keyes,[22] T. S. Kress,[7] and C. G. Lawson,[7] *Comments on the Application of PWR-FLECHT Experimental Results to a LOCA,* ORNL-TM-4205 (April 1973).

"Fossil Fuels for Central-Station Electric Power Generation," pp. A.2-1–A.2-105 in *LMFBR Program Draft Environmental Statement,* vol. IV, Sect. A.2, WASH-1535, March 1974. (W. R. Gambill, contributor.)

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

Godbee, H. W., and D. S. Joy, *Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment. Part I: Background and Theory,* ORNL-TM-4333 (February 1974).

Goeller, H. E., "An Optimistic Outlook for Mineral Resources," presented at the Joint American Institute of Chemical Engineers–American Society for Metals Meeting, Oak Ridge, Tenn., December 1973.

Goeller, H. E., "An Optimistic Outlook for Mineral Resources," presented at the Mechanical Engineering Colloquium, Worcester Polytechnic Institute, Worcester, Mass., Sept. 25, 1973.

Griess, J. C. Jr., *The Hydrolysis of Lanthanide and Actinide Carbides – A Survey of Recent Literature,* ORNL-TM-4489 (February 1974).

Griess, J. C., Jr., A. L. Bacarella,[11] and E. G. Bohlmann,[11] *Water Research Program Final Report March 15, 1966 to October 31, 1972,* ORNL-TM-4340 (October 1973).

Holmes, J. M., "Coal Liquefaction and Carbonization: Sources of Fuels and Chemical Feedstocks," presented at the American Production and Inventory Control Society, Knoxville, Tenn., Feb. 13, 1974.

Holmes, J. M., "Coal Liquefaction and Carbonization: Sources of Fuels and Chemical Feedstocks," presented at the American Institute of Plant Engineers, Knoxville, Tenn., Mar. 26, 1974.

Holmes, J. M., and J. R. Hightower, Jr., "Coal Utilization," presented at "Energy Sources for the Future" Symposium, Oak Ridge Associated Universities, Aug. 13, 1973.

Horner, D. E., and W. H. Baldwin,[11] *Reactions of Sodium with Dowtherm,* ORNL-TM-4186 (May 1973).

Jaffe, H.,[23] F. J. Endelman, J. R. Hightower, Jr., B. Berger,[24] W. Crothers,[24] A. Pasternak,[24] and R. Carter,[25] "Methanol from Coal for the Automotive Market," AEC Study for Project Independence (Feb. 1, 1974).

Joy, D. S., "Applications of Modular Optimal Generation Expansion Model," presented at the Nuclear Utilities Planning Methods Symposium, Chattanooga, Tenn., Jan. 16–18, 1974; included in ORNL-TM-3549 (January 1974).

---

21. Case Western Reserve University, Cleveland, Ohio.
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Joy, D. S., and R. T. Jenkins,[26] "A Probabilistic Model for Estimating the Operating Cost of an Electric Power Generating System," presented at the Nuclear Utilities Planning Methods Symposium, Chattanooga, Tenn., Jan. 16–18, 1974; included in ORNL-TM-3549 (January 1974).

Joy, D. S., and R. T. Jenkins,[26] "WASP/SAGE: A Modular Generation Expansion Model Utilizing Dynamic Programming and Probabilistic Production Costing," presented at the Nuclear Utilities Planning Methods Symposium, Chattanooga, Tenn., Jan. 16–18, 1974; included in ORNL-TM-3549 (January 1974).

Lin, K. H., "Application of Chemical Engineering Principles in the Nuclear Industry," presented at the Institute of Nuclear Energy Research, Taiwan, Republic of China, Jan. 15, 1974.

Lin, K. H., "Reaction Kinetics and Reactor Design," Sect. 4 in *Chemical Engineers' Handbook,* 5th ed., ed. by R. H. Perry and C. H. Chilton, McGraw-Hill, New York, 1973.

Lin, K. H., "Role of Chemical Engineering Operations in Nuclear Power Plants," presented at the University of Toledo, Toledo, Ohio, May 2, 1973.

Lin, K. H., "Separation of Trace Radionuclides by Ion Exchange in the Presence of Competing Ions," presented at the 76th National Meeting of the American Institute of Chemical Engineers, Tulsa, Okla., Mar. 10–13, 1974.

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

Lin, K. H., and D. N. Braski,[10] *Anomalous Behavior in the Kinetics of Phase Transformation in CsCl-KCl System,* ORNL-4872 (May 1973).

McClain, W. C., *Rock Deformations Resulting from Project Salt Vault,* ORNL-TM-4381 (November 1973).

Morgan, M. T., R. L. Towns, and L. L. Fairchild, "Fission Product Release from Coated Fuel Particles," *Ceram. Bull.* **52**(4), 397 (1973.)

Parrott, J. R., and L. B. Shappert, "The ORNL Foamglas Shipping Container," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Nov. 11–15, 1973; to be published in the *Proceedings.*

Shappert, L. B., "Radioactive Material Shipping Packages: Their Design and Safety Analysis," presented at the Southern Interstate Nuclear Board Meeting, Oak Ridge, Tenn., May 16, 1973.

Shappert, L. B., "Shipping Cask Design and Testing," presented at the Association of American Railroads and American Industrial Forum Joint Meeting on Railroad Transportation of Irradiated Fuel, Washington, D.C., May 22, 1973.

Shappert, L. B., "The Shipping Container Program at ORNL," presented at the Quality Assurance Program Quarterly Meeting, ORNL, Feb. 20, 1974.

Shappert, L. B., W. A. Brobst,[16] J. W. Langhaar,[27] and J. A. Sisler,[16] "Probability and Consequences of Accidents in the Nuclear Fuel Cycle," presented at the American Society of Mechanical Engineers Winter Meeting, Detroit, Mich., Nov. 11–15, 1973.

Shappert, L. B., W. A. Brobst,[16] J. W. Langhaar,[27] and J. A. Sisler,[16] "Probability and Consequences of Transportation Accidents Involving Radioactive-Material Shipments in the Nuclear Fuel Cycle," *Nucl. Safety* **14**(6), 597 (1973).

Stephenson, M. J.,[28] D. I. Dunthorn,[28] and F. E. Harrington, *System Design Description of the ORGDP Fuel Reprocessing Off-Gas Decontamination Pilot Plant,* K-GD-873 (September 1973).

Turnage, J. C.,[7] L. L. Bennett,[7] D. S. Joy, and B. E. Prince,[7] "Power System Simulation and Optimization Models for Planning Nuclear Refueling Cycles," presented at Operation Research Society of America, San Diego, Calif., Nov. 12, 1973.

---

26. Division of Power Resource Planning, TVA, Chattanooga, Tenn.
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28. Gaseous Diffusion Development Division, ORGDP.

Turnage, J. C.,[7] L. L. Bennett,[7] D. S. Joy, and B. E. Prince,[7] "Probabilistic Simulation and Optimization Models for Nuclear and Fossil Plant Generation Planning," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Calif., November 1973.

MOLTEN-SALT REACTOR PROGRAM

Bamberger, C. E., "Applicatión de los Diagramas de Pourbaix a Sistemos de Fluoruros Fundidos, Detalles de Construcción," *Energ. Nucl. (Madrid)* **17**(82), 133 (1973).

Bamberger, C. E., B. F. Hitch, and C. F. Baes, Jr.,[11] "Determination of the Free Energies of Formation of $NaNiF_3$ and $NaFeF_3$," *J. Inorg. Nucl. Chem.* **36**, 543–45 (1974).

Cantor, S., *Density and Viscosity of Several Molten Fluoride Mixtures,* ORNL-TM-4308 (September 1973).

Cantor, S., "Lattice Energies of Cubic Alkaline-Earth Oxides. Affinity of Oxygen for Two Electrons," *J. Chem. Phys.* **59**, 5189 (1973).

Cantor, S., "Molar Volumes in New Methods for Estimating Entropy of Ionic Compounds," *Inorg. Nucl. Chem. Lett.* **9**, 1275 (1973).

Cantor, S., "Solubility of BF_3 in Salts of Molten-Salt Reactor Interest," *J. Nucl. Mater.* **47**, 177 (1973).

Ferris, L. M., and M. A. Bredig, "Solubility and Dimerization of Lithium Metal in Molten Lithium Chloride Equilibrated with Liquid Lithium-Lead Alloys at 650°C," presented to the Division of Nuclear Chemistry and Technology, 167th National American Chemical Society Meeting, Los Angeles, Calif., Mar. 31–Apr. 5, 1974.

Ferris, L. M., M. A. Bredig, and F. J. Smith, "Equilibrium Distribution of Lithium and Bismuth between Liquid Lithium-Bismuth Alloys and Molten Lithium Chloride at 650 to 800°C," *J. Phys. Chem.* **77**, 2351 (1973).

Hightower, J. R., Jr., and L. E. McNeese, "Low-Pressure Distillation of Molten Mixtures of LiF, BeF_2, and ZrF_4 for Removal of Rare-Earth Fission Products," *Ind. Eng. Chem., Process Des. Develop.* **12**, 232 (1973).

Ross, R. G., C. E. Bamberger, and C. F. Baes, Jr.,[11] "The Oxide Chemistry of Protactinium in Molten Fluorides," *J. Inorg. Nucl. Chem.* **35**, 433 (1973).

PATENTS

Baes, C. F., Jr.,[11] C. E. Bamberger, and R. G. Ross, "Recovery of Protactinium from Molten Fluoride Nuclear Fuel Compositions," U.S. Patent 3,781,403 (Dec. 25, 1973).

Cathers, G. I., and C. J. Shipman, "Removal of Iodine from Nitric Acid Solutions," U.S. Patent 3,792,154 (Feb. 12, 1974).

Ferris, L. M., and J. C. Mailen, "Separation of Californium from Other Actinides," U.S. Patent 3,761,564 (Sept. 25, 1973).

Godbee, H. W., and R. C. Lovelace, "Method for Storing Radioactive Combustible Waste," U.S. Patent 3,764,552 (Oct. 9, 1973).

Haas, P. A., "Conversion of Fuel-Metal Nitrate Solutions to Oxides," U.S. Patent 3,725,293 (Apr. 3, 1973).

Haas, P. A., "Loading a Cation Exchange Resin with Uranyl Ions," U.S. Patent 3,800,023 (Mar. 26, 1974).

Haas, P. A., D. E. Ferguson, and R. E. Leuze, "Quantitative Recovery of Krypton from Gas Mixtures Mainly Comprising Carbon Dioxide," U.S. Patent 3,742,720 (July 3, 1973).

Harrington, F. E., and J. D. Sease,[10] "Nuclear Fuel Element with Axial Aligned Fuel Pellets and Fuel Microspheres Therein," U.S. Patent 3,778,348 (Dec. 11, 1973).

Lloyd, M. H., "Solvent Extraction Process for Producing Low-Nitrate and Large-Crystal-Size PuO_2 Sols," U.S. Patent 3,794,715 (Feb. 26, 1974).

Mailen, J. C., "Rotor for Fast Analyzer of Rotary Cuvette Type," U.S. Patent 3,795,451 (Mar. 5, 1974).

Mailen, J. C., "Rotor for Multistation Photometric Analyzer," U.S. Patent 3,744,975 (July 10, 1973).

Mailen, J. C., N. G. Anderson,[1] C. A. Burtis,[1] W. F. Johnson,[2] and C. D. Scott, "Compact Dynamic Multistation Photometer Utilizing Disposable Cuvette Rotor," U.S. Patent 3,798,459 (Mar. 19, 1974).

Mailen, J. C., L. H. Thacker,[2] and T. O. Tiffany,[1] "Dynamic Multistation Photometer-Fluorometer," U.S. Patent 3,763,374 (Oct. 2, 1973).

McCorkle, K. H.,[29] W. L. Pattison, and J. P. McBride, "Production of Predominantly Crystalline Sols," U.S. Patent 3,758,670 (Sept. 11, 1973).

Scott, C. D., and E. L. Collins,[30] "Portable Dynamic Multistation Photometer-Fluorometer," U.S. Patent 3,800,161 (Mar. 26, 1974).

Seeley, F. G., and W. H. Baldwin,[11] "Extraction of Lithium from Neutral Brines Using a Beta Diketone and Trioctylphosphine Oxide," U.S. Patent 3,793,433 (Feb. 19, 1974).

Shockley, W. E., and G. I. Cathers, "Removal of Organic and Inorganic Iodine from a Gaseous Atmosphere," U.S. Patent 3,752,876 (Aug. 14, 1973).

Strehlow, R. A., R. L. Hamner,[10] E. W. Stooksbury,[31] and J. M. Napier,[31] "Composition for Preparing Graphite Bodies," U.S. Patent 3,798,161 (Mar. 19, 1974).

POWER REACTOR FUEL PROCESSING

Ackley, R. D., and Z. Combs,[32] *Applicability of Inorganic Sorbents for Trapping Radioiodine from LMFBR Fuel Reprocessing Off-Gas,* ORNL-TM-4227 (May 1973).

Bell, M. J.,[16] "Radiation Properties of Spent Plutonium Fuels," *Nucl. Technol.* **18**(1), 5–14 (April 1973).

Cox, R. L., *A Computer Program for Calculating Temperatures Attained by LMFBR Fuels from Decay Heat Emission,* ORNL-TM-3773 (June 1973).

Crouse, D. J., and J. M. Schmitt, "Scrubbing Radioiodine from Reprocessing Plant Off-Gases with Mercuric Nitrate Solutions," presented at the American Nuclear Society Meeting, Nov. 11–16, 1973, San Francisco, Calif.; summary published in *Trans. Amer. Nucl. Soc.* **17**, 319 (1973).

Ferguson, D. E., "Chemical Reprocessing of Nuclear Fuel," presented at the XXIVth International Congress of Pure and Applied Chemistry, Hamburg, Germany, Sept. 3–8, 1973; to be published in *Pure and Applied Chemistry.*

Goode, J. H., C. L. Fitzgerald, and V. C. A. Vaughen, "Effects of Fabrication and Irradiation on the Dissolution of $(U,Pu)O_2$ Reactor Fuels," presented at the American Ceramic Society Meeting, San Francisco, Calif., Oct. 30–Nov. 2, 1973.

Groenier, W. S., *An Engineering Evaluation of the Iodex Process: Removal of Iodine from Air Using a Nitric Acid Scrub in a Packed Column,* ORNL-TM-4125 (August 1973).

Groenier, W. S., *The Application of Modern Solvent Extraction Techniques to the Removal of Trace Quantities of Toxic Substances from Industrial Effluents,* ORNL-TM-4209 (July 1973).

Irvine, A. R., and B. B. Klima, *LMFBR Spent Fuel Transport: Dowtherm A Heat Transport Test,* ORNL-TM-4262 (June 1973).

29. General Atomic Co., San Diego, Calif.
30. Magnavox Corp., Jefferson City, Tenn.
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32. Information Division.

Irvine, A. R., and L. B. Shappert, *LMFBR Spent Fuel Transport: A LiOH-NaOH Neutron-Thermal Shield for Spent Fuel Shipping Casks,* ORNL-TM-4357 (October 1973).

Yarbro, O. O., F. E. Harrington, and D. S. Joy, *Effluent Control in Fuel Reprocessing Plants,* ORNL-TM-3899 (March 1974).

PROGRESS REPORTS

Burtis, C. A.,[1] W. F. Johnson,[2] J. C. Mailen, C. D. Scott, T. O. Tiffany, and M. B. Watsky,[3] *Gravity Zero (GØ) Analytical Clinical Laboratory System Annual Progress Report for the Period April 15, 1972, to May 1, 1973,* ORNL-TM-4225 (July 1973).

Burtis, C. A.,[1] W. F. Johnson,[2] J. C. Mailen, C. D. Scott, and T. O. Tiffany,[1] *Gravity Zero (GØ) Analytical Clinical Laboratory System Semiannual Progress Report for the Period June 1, 1973, to November 30, 1973,* ORNL-TM-4434 (January 1974).

King, L. J., J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1972,* ORNL-4884 (August 1973).

King, L. J., J. E. Bigelow, and E. D. Collins, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June 30, 1973,* ORNL-4921 (March 1974).

McNeese, L. E., *Engineering Development Studies for Molten-Salt Breeder Reactor Processing No. 9,* ORNL-TM-3259 (September 1973).

Scott, C. D., C. A. Burtis,[1] D. J. Crouse, L. M. Ferris, J. C. Mailen, and W. W. Pitt, *Chemical Development Section B Semiannual Progress Report, March 1, 1973 to August 31, 1973; Part I,* ORNL-TM-4370 (February 1974).

Scott, C. D., C. A. Burtis,[1] D. J. Crouse, L. M. Ferris, J. C. Mailen, and W. W. Pitt, *Chemical Development Section B Semiannual Progress Report, March 1, 1973 to August 31, 1973; Part II,* ORNL-TM-4370 (February 1974).

Unger, W. E., R. E. Blanco, D. J. Crouse, A. R. Irvine, and C. D. Watson, *Aqueous Fuel Reprocessing Quarterly Report for Period Ending March 31, 1973,* ORNL-TM-4240 (June 1973).

Unger, W. E., R. E. Blanco, D. J. Crouse, A. R. Irvine, and C. D. Watson, *Aqueous Fuel Reprocessing Quarterly Report for Period Ending June 30, 1973,* ORNL-TM-4301 (August 1973).

Unger, W. E., J. C. Mailen, A. R. Irvine, and C. D. Watson, *Aqueous Fuel Reprocessing Quarterly Report for Period Ending September 30, 1973,* ORNL-TM-4394 (February 1974).

SEPARATIONS CHEMISTRY

Campbell, D. O., "Isotopic Enrichment of the Product of a Neutron Capture (n,γ) Reaction in Lanthanide and Actinide Exchanged Zeolites," presented at the Third International Conference on Molecular Sieves, Zurich, Switzerland, Sept. 3–7, 1973; published in *Advan. Chem. Ser.* **121**, 281–90 (1973).

Campbell, D. O., "Rapid Lanthanide and Actinide Separations with Pressurized Ion Exchange Chromatography," presented at the 10th Rare Earth Research Conference, Carefree, Ariz., Apr. 30–May 3, 1973.

Campbell, D. O., "Rapid Rare Earth Separations by Pressurized Ion Exchange Chromatography," *J. Inorg. Nucl. Chem.* **35**, 3911-19 (1973).

Hurst, F. J., and D. J. Crouse, "Recovery of Uranium from Wet-Process Phosphoric Acid by Extraction with Octylphenylphosphoric Acid," presented at the American Chemical Society Meeting, Chicago, Ill., Aug. 27, 1973.

McDowell, W. J., *A Correlation of Available Lithium Chloride and Hydrochloric Acid Activity Coefficient Data,* ORNL-TM-4220 (June 1973).

McDowell, W. J., and C. F. Coleman, "Some Methods of Controlling Quenching in Extractive Scintillators for Liquid Scintillation Counting of Alpha-Emitting Nuclides," *Anal. Lett.* **6**, 795–99 (1973).

Roddy, J. W., "Americium Hydride and Metallides," presented at the American Chemical Society National Meeting, Los Angeles, Calif., Mar. 31–Apr. 5, 1974.

Roddy, J. W., and C. F. Coleman, "Investigation of Intermolecular Association of 4-*sec*-Butyl-2-(α-methylbenzyl)phenol (BAMBP) by Use of Dielectric and Isopiestic Measurements," *J. Inorg. Nucl. Chem.* **35**, 4271–78 (1973).

Roddy, J. W., and C. F. Coleman, "Reference Solutes for Isopiestic and Dynamic Vapor Pressure Osmometry in Organic Solvents: Tri-*n*-octylamine in *n*-Hexane and Benzophenone in Carbon Tetrachloride," *J. Inorg. Nucl. Chem.* **35**, 4317–19 (1973).

Seeley, F. G., and D. J. Crouse, "Purification of Beryllium by Solvent Extraction from Carbonate Solutions with Quaternary Alkylammonium Carbonate," *Nucl. Technol.* **19**, 140–47 (1973).

Silva, R. J.,[11] W. J. McDowell, O. L. Keller,[11] and J. R. Tarrant,[11] "Oxidation State and Ionic Radius of Nobelium," presented at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1974.

Weaver, B. S., "Solvent Extraction in the Separation of Rare Earths and Trivalent Actinides," chap. 4 in *Ion Exchange and Solvent Extraction,* vol. 6, ed. by J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1974.

SOL-GEL PROCESSES

Haas, P. A., and W. J. Lackey,[10] *Improved Size Uniformity of Sol-Gel Spheres by Imposing a Vibration on the Sol in Dispersion Nozzles,* ORNL-TM-4094 (May 1973).

Lloyd, M. H., and R. G. Haire, "Studies on the Chemical and Colloidal Nature of Pu(IV) Polymer," presented at the 24th International Congress of Pure and Applied Chemistry, Hamburg, West Germany, September 1973.

Lloyd, M. H., and O. K. Tallent, "A New Solvent Extraction Process for Preparing PuO_2 Sols," *Nucl. Technol.* **18**, 205–15 (1973).

Wymer, R. G., "Sol-Gel Processes at Oak Ridge National Laboratory: Development, Demonstration and Irradiation Tests," presented at the International Atomic Energy Agency Panel on Sol-Gel Processes for Fuel Fabrication, Vienna, Austria, May 21–24, 1973; to be published in the *Proceedings.*

Wymer, R. G., "Status Report from the United States of America: Sol-Gel Processes for Fuel Fabrication," presented at the International Atomic Energy Agency Panel on Sol-Gel Processes for Fuel Fabrication, Vienna, Austria, May 21–24, 1973; to be published in the *Proceedings.*

SUPPORT FOR CONTROLLED THERMONUCLEAR PROGRAM

Cantor, S., and W. R. Grimes, "Fused-Salt Corrosion and Its Control in Fusion Reactors," *Nucl. Technol.* **22**, 120–26 (1974).

Cantor, S., and W. R. Grimes, "Fused-Salt Corrosion and Its Prevention in Fusion Reactors," presented at the American Nuclear Society Meeting, San Francisco, Calif., Nov. 11–16, 1973; abstract published in *Trans. Amer. Nucl. Soc.* **17**, 150 (1973).

Cantor, S., and W. R. Grimes, "Molten Salts as Blankets for Controlled Thermonuclear Reactors," presented at the Gordon Conference, Brewster Academy, Wolfeboro, N.H., Aug. 27–31, 1973.

Savage, H. C., and R. A. Strehlow, "The Permeation of Hydrogen through Structural Metals at Low Pressures and Metals with Oxide Film Barriers," presented at the American Nuclear Society Meeting, San Francisco, Calif., November 1973; abstract published in *Trans. Amer. Nucl. Soc.* **17**, 152 (1974).

Smith, F. J., "The Limits of Miscibility in the Lithium-Potassium System," *J. Less-Common Metals* **35**, 147–51 (1974).

Strehlow, R. A., "Tritium Permeation at Low Pressures – The Controlled Thermonuclear Problem," presented at Sandia Livermore Laboratory, Albuquerque, N.M., Nov. 16, 1973.

Strehlow, R. A., and H. C. Savage, "Formation and Use of Oxide Films to Impede Outgassing of Metals," presented at the Conference on Surface Effects in Controlled Thermonuclear Fusion Devices and Reactors, Argonne National Laboratory, Argonne, Ill., Jan. 10–12, 1974.

Strehlow, R. A., and H. C. Savage, "The Permeation of Hydrogen Isotopes through Structural Metals at Low Pressures and through Metals with Oxide Film Barriers," *Nucl. Technol.* **22**, 127 (1974).

Watson, J. S., "Section for Tritium Control Technology Report," in *Tritium Control Technology,* WASH-1269 (December 1973).

Watson, J. S., and R. C. Forrester III, "Tritium Handling in Fusion Reactors," presented at the 75th National American Institute of Chemical Engineers Meeting, Detroit, Mich., June 4–6, 1973.

Wymer, R. G., "Fusion Reactors and Their Fuel Cycle: A Primer," presented at Lowell Technological Institute, Lowell, Mass., Nov. 30, 1973.

THESES

Endelman, F. J., "A Systems Study of the Transport and Transfermutations of Soil Nitrogen," Ph.D. dissertation, University of Wisconsin, Madison, December 1973.

Jolley, R. L., "Chlorination Effects on Organic Constituents in Effluents from Domestic Sanitary Sewage Treatment Plants," Ph.D. dissertation, University of Tennessee, Knoxville, August 1973; also published as ORNL-TM-4290 (October 1973).

TRANSURANIUM ELEMENT PROCESSING

Asprey, L. B.,[33] and R. G. Haire, "On the Actinide Tetrafluoride Lattice Parameters," *Inorg. Nucl. Chem. Lett.* **9**, 1121 (1973).

Baybarz, R. D.,[34] "Californium," pp. 124–25 in the *1973 McGraw-Hill Yearbook of Science and Technology,* McGraw-Hill, New York, 1973.

Baybarz, R. D.,[34] "High-Temperature Phases, Crystal Structures, and the Melting Points for Several of the Transplutonium Sesquioxides," *J. Inorg. Nucl. Chem.* **35**, 4149 (1973).

Baybarz, R. D.,[34] R. G. Haire, J. H. Ward,[33] and W. Muller,[35] "Preparation of ^{249}Cf Metal, and the Determination of Some of Its Physical and Chemical Properties," presented at the 24th International Congress of Pure and Applied Chemistry, Hamburg, West Germany, September 1973.

Baybarz, R. D.,[34] and J. B. Knauer, Jr., "The Separation of Pure ^{248}Cm from ^{252}Cf by Extraction Chromatography," *Radiochim. Acta* **19**, 30–34 (1973).

Bigelow, J. E., J. E. Van Cleve, Jr.,[10] J. B. Knauer, Jr., and L. C. Williams,[10] "Preparation and Calibration of ^{252}Cf Neutron Sources at the Oak Ridge National Laboratory," presented at the Latin American Seminar on the Use and Calibration of Intense Sources of Radiation, Santiago, Chile, June 18–23, 1973; CONF-730641-1.

Burns, J. H.,[11] J. R. Peterson,[36] and R. D. Baybarz,[34] "Hexagonal and Orthorhombic Crystal Structures of Californium Trichloride," *J. Inorg. Nucl. Chem.* **35**(4), 1171 (1973).

Delle Site, A.,[37] and F. A. Kappelmann, "Complexation Behavior of the Lanthanide–Iminodiacetic Acid System and Its Possible Application to the Separation of Light Rare Earths from Transplutonium Elements by Ion Exchange," *Inorg. Nucl. Chem. Lett.* **10**, 81–86 (1974).

---

33. Los Alamos Scientific Laboratory.
34. Deceased.
35. European Institute for Transuranium Elements.
36. Department of Chemistry, University of Tennessee, Knoxville.
37. Industrial Chemistry Laboratory, C.N.E.N., Cassaccia, Rome, Italy.

Haire, R. G., and R. D. Baybarz,[34] "Crystal Structure and Melting Point of Californium Metal," *J. Inorg. Nucl. Chem.* **36**, 1295–1302 (1974).

Haire, R. G., and L. B. Asprey,[33] "The Preparation and Lattice Parameters of CfF_4," *Inorg. Nucl. Chem. Lett.* **9**, 869 (1973).

Haire, R. G., "The Thermal Decomposition of Berkelium Compounds," *Proceedings of the Tenth Rare Earth Research Conference, Carefree, Ariz., Apr. 30–May 3, 1973,* vol. II, p. 882 (1973).

Nugent, L. J.,[11] R. D. Baybarz,[34] J. L. Burnett,[16] and J. L. Ryon,[38] "Electron-Transfer and f→d Absorption Bands of Some Lanthanide and Actinide Complexes and the Standard (II-III) Oxidation Potentials for Each Member of the Lanthanide and Actinide Series," *J. Phys. Chem.* **77**(12), 1528–39 (1973).

Peishel, F. L., W. W. Evans,[39] and J. L. Matherne, "Remote Maintenance Experience in the Transuranium Processing Plant at ORNL," presented at the Winter Meeting of the American Nuclear Society, San Francisco, Calif., Nov. 11–15, 1973 [abstract published in *Trans. Amer. Nucl. Soc.* **17**, 512–13 (1973)]; *Proceedings of 21st Conference on Remote Systems Technology,* pp. 70–77 (1973).

Roddy, J. W., "The Actinide Hydrides: The Americium-Hydrogen System," *J. Inorg. Nucl. Chem.* **35**, 4141 (1973).

WASTE TREATMENT AND DISPOSAL

Blomeke, J. O., "Disposal of Radioactive Wastes," presented at the American Physical Society Energy Study Planning Committee, Los Alamos, N.M., Aug. 14, 1973.

Blomeke, J. O., "Nuclear Fuel Waste Disposal," presented at the Workshop on Electrical Power Generation, Madison, Wis., Aug. 9, 1973.

Blomeke, J. O., and C. W. Kee, "Projections of Radioactive Wastes from the Nuclear Fuel Cycle," presented at the American Nuclear Society Winter Meeting, San Francisco, Calif., Nov. 11–16, 1973; published in *Trans. Amer. Nucl. Soc.* **17**, 324–25 (1973).

Blomeke, J. O., C. W. Kee, and J. P. Nichols, *Projections of Radioactive Wastes to Be Generated by the U.S. Nuclear Power Industry,* ORNL-TM-3965 (February 1974).

Blomeke, J. O., and J. P. Nichols, *Commercial High-Level Waste Projections,* ORNL-TM-4224 (May 1973).

Blomeke, J. O., J. P Nichols, and W. C. McClain, "Managing Radioactive Wastes," *Phys. Today* **26**(8), 36–42 (August 1973).

Burch, W. D., "Nuclear Waste Disposal," presented at the Fourth Annual Environmental Pollution Symposium of the American Ordnance Association, Edgewood Arsenal, Md., Apr. 4–5, 1973; to be published in the *Proceedings.*

Cheverton, R. D., and W. D. Turner,[40] "Thermal Considerations and Analysis for a Radioactive Waste Repository," *Nucl. Technol.* **19**, 21–33 (1973).

Clark, W. E., and W. C. Ulrich, *Pressurized Aqueous Combustion of Alpha-Contaminated Waste Final Program Status Report,* ORNL-TM-4366 (November 1973).

Jenks, G. H., and C. D. Bopp, *Storage and Release of Radiation Energy in Salt in Radioactive-Waste Repositories,* ORNL-TM-4449 (January 1974).

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

Lin, K. H., "Engineering Evaluation of Processes for Treatment of Tritiated Aqueous Effluents from Various Nuclear Installations," presented at the meeting on Tritium Separation Requirements and Development, sponsored by USAEC Division of Waste Management and Transportation, Las Vegas, Nev., Sept. 27, 1973.

---

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Lin, K. H., "Processes for Treatment and Control of Tritiated Liquid Effluents," presented at the Institute of Nuclear Energy Research, Taiwan, Republic of China, Jan. 17, 1974.

Lomenick, T. F., "Management and Disposal of Wastes from the Nuclear Power Industry," presented at the Oak Ridge Summer Lecture Program, Oak Ridge Associated Universities–Oak Ridge National Laboratory, July 11, 1973.

Lomenick, T. F., "Radioactive Waste Disposal," presented at the "Energy Sources for the Future" Symposium, Oak Ridge Associated Universities, Aug. 10, 1973.

Lomenick, T. F., "An Ultimate Disposal Scheme for Radioactive Waste," presented at the Summer Institute on Applied Ecology, Oak Ridge Associated Universities, Aug. 1, 1973.

Lomenick, T. F., and A. L. Boch, "Site Investigations for a Bedded Salt Pilot Plant in the Permian Basin," presented at the Second Annual Symposium on Underground Waste Management and Artificial Recharge, New Orleans, La., September 1973; published in the *Proceedings* (September 1973).

McClain, W. C., "Status of AEC Project to Establish a Salt Mine Radioactive Waste Repository," presented at the Fourth Symposium on Salt, Astroworld Hotel, Houston, Tex., Apr. 15–18, 1973; published in the *Proceedings* (December 1973).

McClain, W. C., "Disposal of High-Level Radioactive Waste," presented at Oak Ridge Associated Universities, July 19, 1973.

McClain, W. C., and R. L. Bradshaw,[34] "Underground Waste Disposal Systems," in *Society of Mining Engineers Mining Engineering Handbook,* vol. 2, I. A. Given, ed., American Institute of Mining, Metallurgical and Petroleum Engineers, Baltimore, Md., 1973.

Moore, J. G., *Low-Level Waste Treatment Laboratory Studies: Evaporation of Simulated Ion-Exchange Eluates,* ORNL-TM-4454 (February 1974).

Starfield, A. M.,[41] and W. C. McClain, "Project Salt Vault: A Case Study in Rock Mechanics," *Int. J. Rock Mech. Mining Sci.* **10**(6), 641–57 (1973).

SEMINARS

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May 16	Tritium Separation Techniques for Controlled Thermonuclear Reactors	J. S. Watson F. J. Smith R. C. Forrester

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May 23	Thoughts Concerning Design Basis Accident Impact Resistance; Experience and Capability	A. R. Irvine J. H. Evans, General Engineering Division
	Fire Resistance Capability	L. B. Shappert
	Dowtherm Heat Transport and Chemical Compatibility	L. B. Shappert
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