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Annual Progress Report

PERIOD ENDING MARCH 31, 1972

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for Plutonium and Uranium

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CHEMICAL TECHNOLOGY DIVISION
ANNUAL PROGRESS REPORT
for Period Ending March 31, 1972

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AUGUST 1972

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1. Molten-Salt Reactor Processing

Oak Ridge National Laboratory is developing a molten-salt breeder reactor (MSBR) which would operate on the ^{232}Th-^{233}U fuel cycle to produce low-cost power while producing more fissile material than is consumed. The reactor would use a molten fluoride salt as the fuel and graphite as the moderator. If the reactor is 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. The Chemical Technology Division is responsible for developing an on-site processing plant to economically effect these operations. Processes that employ liquid-liquid extraction of the reactor salt with a bismuth phase containing reductant appear to offer the best means to this end and have been the major subjects of our studies.

The reference processing plant flowsheet (Fig. 1.1) uses fluorination for removal of uranium from the fuel salt, reductive extraction for isolation of protactinium, and the metal transfer process for the removal of rare earths. For a 1000-MW(e) MSBR, fuel salt is removed from the reactor at the rate of 0.88 gpm, which results in a processing cycle time of 10 days. The fuel salt has the composition 71.67-16-12-0.33 mole % LiF-BeF_2-ThF_4-UF_4 and contains $^{233}PaF_4$ and rare-earth fluorides at concentrations of about 100 wt ppm. The salt is first fed to a fluorinator, where 99% of the uranium is removed as UF_6. The salt stream leaving the fluorinator

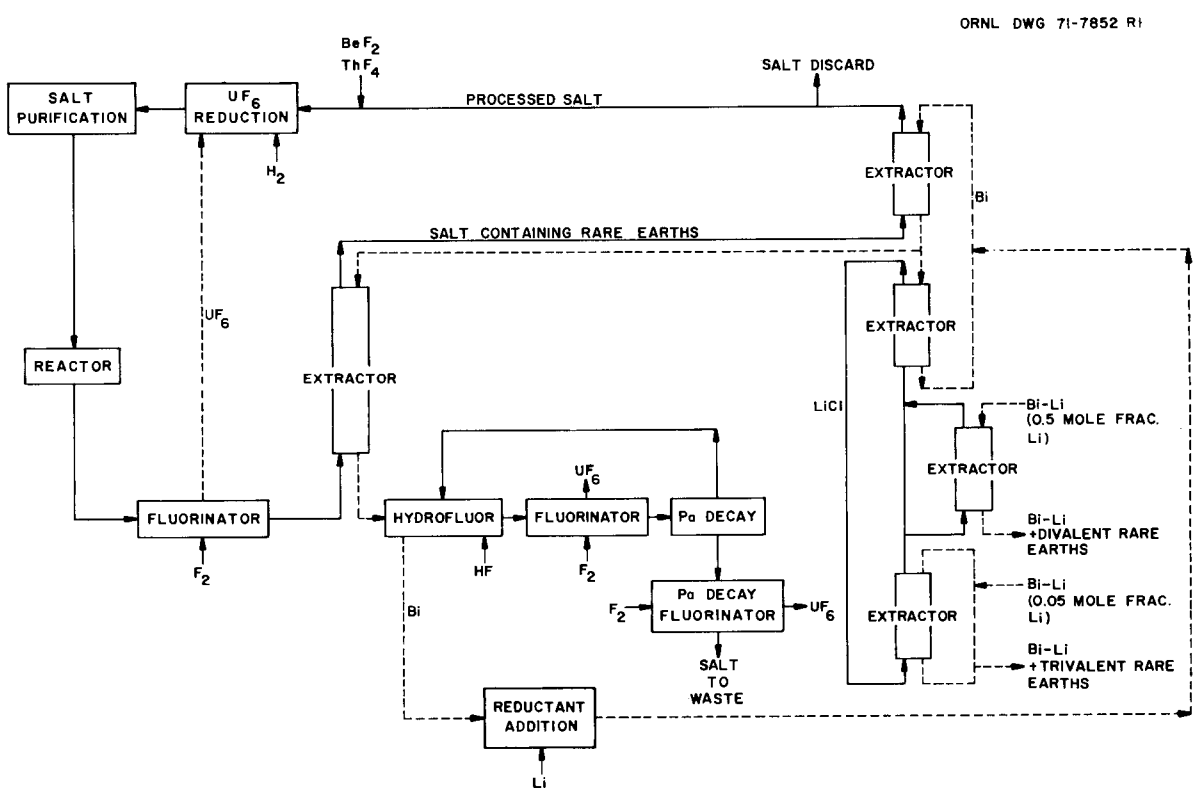

Fig. 1.1. Fluorination–reductive extraction–metal transfer flowsheet for processing a single-fluid MSBR.

is countercurrently contacted with a 0.13-gpm bismuth stream that contains reductant in order to extract protactinium and the remaining uranium. The bismuth stream leaving the extractor is hydrofluorinated in the presence of a secondary fluoride salt in order to transfer the extracted materials from the bismuth to the salt. The secondary salt flows through a fluorinator, where 90% of the uranium is removed, and through a 160-ft^3 tank in which the protactinium is held for decay to ^{233}U. Lithium reductant is added to the bismuth stream leaving the hydrofluorinator, and the resulting stream is returned to the protactinium extractor after passing through a captive bismuth phase in the rare-earth removal system.

The salt stream leaving the protactinium extraction column is essentially free of uranium and protactinium but contains the rare earths at essentially the concentration present in the reactor. The salt stream is countercurrently contacted with a 12.5-gpm bismuth stream containing reductant in order to extract 20 to 50% of the rare earths. The bismuth stream leaving the extractor is then countercurrently contacted with a 33-gpm stream of molten lithium chloride into which the rare earths transfer selectively. The lithium chloride is countercurrently contacted with a 5-95 at. % Li-Bi stream in order to remove the trivalent rare earths. About 2% of the LiCl is contacted with a 50-50 at. % Li-Bi solution for removal of the divalent rare earths. The processed fuel carrier salt leaving the rare-earth extractor is combined with the required quantity of UF_6 resulting from fluorination in order to reconstitute the fuel salt. In this operation, the UF_6 is absorbed into salt containing UF_4 in order to form UF_5, which is subsequently reduced to UF_4 by contact with hydrogen. The resulting salt stream is then purified for removal of bismuth and other potentially harmful materials before it is returned to the reactor.

1.1 MOLTEN-SALT REACTOR FLOWSHEET ANALYSIS

The treatment of molten-salt reactor fuel by the fluorination–reductive extraction–metal transfer process (shown in Fig. 1.1) has been described previously.[1,2] A continuing study of the flowsheet revealed that a significant improvement could be made in the method for treating the H_2-HF gas streams produced in the UF_6-to-UF_4 reduction step, the hydrofluorination steps, and several salt sparging operations. In earlier versions of the flowsheet, most of the gas was recycled and the HF in the remaining gas was converted to a solid waste for disposal. All fluorine used by the process was purchased.

We have observed that a significant economic advantage results from operation with complete gas recycle using distillation to separate the interhalogen compounds from the HF, and electrolysis of HF for regeneration of fluorine and hydrogen. This allows recovery of 95% of the hydrogen and greater than 98% of the hydrogen fluoride. For a 1000-MW(e) MSBR, the partial fuel cycle cost[3] with this mode of operation is 0.02 mill/kWhr as compared with 0.11 mill/kWhr for the case in which no recycle occurs. The savings result primarily from the lower costs for waste disposal and purchased fluorine.

We completed a design and a cost study[3] of a plant utilizing the fluorination–reductive extraction–metal transfer flowsheet to process the fuel salt from a 1000-MW(e) MSBR. The plant processed the reactor fuel salt (volume, 1683 ft^3) on a 10-day cycle. The estimated direct cost was $21 million, and the indirect cost was $15 million; the total investment was $36 million. Allowances for site, site preparation, and buildings, plus facilities shared with the reactor, were not included since these were accounted for in the overall cost of the power station.[4] The net fuel cycle cost was estimated to be 1.1 mills/kWhr, which includes credit for a fissile yield of 3.3% of the reactor fissile inventory per year. The required capital investment was not strongly influenced by the processing rate. A plant for processing the same reactor on a 3.3-day cycle was estimated to cost $48 million.

Calculations were carried out to determine the heat generation rates in an MSBR processing plant that will result from decay of the noble metal and halogen fission products. The noble metals were assumed to be transferred from the fuel salt, on a 50-sec cycle, into a holdup volume having a residence time ranging from 1 sec to 1 year. Noble metal fission products that form stable volatile fluorides (As, Se, Nb, Mo, Tc, Ru, Sb, and Te) were assumed to be completely removed from the salt in the primary fluorinator, and noble metals

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, pp. 2–4.

2. L. E. McNeese, *MSR Program Semiannu. Progr. Rep. Feb. 28, 1970*, ORNL-4548, pp. 282–88.

3. W. L. Carter and E. L. Nicholson, *Design and Cost Study of a Fluorination–Reductive Extraction–Metal Transfer Processing Plant for the MSBR*, ORNL-TM-3579 (May 1972), p. 74.

4. R. C. Robertson (ed.), *Conceptual Design Study of a Single-Fluid Molten-Salt Breeder Reactor*, ORNL-4541 (June 1971).

that do not form stable volatile fluorides (Rh, Pd, and Ag) were assumed to be extracted into bismuth in the protactinium isolation system. If the residence time in the holdup volume is 1 min and if 1% of the noble metals are transferred to the processing plant, the heat generation rate in the processing plant will be increased by 200 kW, with the bulk of the heat being generated in the UF_6 recovery system. About the same heat generation rate would result if 10% of the noble metals reached the processing plant after a 1-day holdup or if 20% reached the plant after a 10-day holdup. The heat generated by the halogens (bromine and iodine) will depend upon both the halogen removal time and the noble metal removal time since halogens are produced by the decay of some noble metals. If the noble metal removal time is assumed to be 0.1 day, heat generation rates of 210 and 520 kW resulting from decay of the halogens would be observed with halogen removal times of 10 and 3 days, respectively.

A study was made using published data on the availability of, and future demand for, natural resources of special importance to the MSBR program.[5] Materials considered in the survey included the constituents of the coolant and fuel salts, Hastelloy N, and materials required for constructing and operating a chemical processing plant. The known world reserves of beryllium, fluorine, and bismuth are being rapidly depleted by non-MSR uses and are expected to be exhausted before the end of the century. Ample beryllium resources (in the form of bertrandite) and fluorine (in the form of phosphate rock) exist; however, an improved mining technology will be required to make recovery of these materials economical. Bismuth resources are limited by the demand for lead, copper, and zinc ores from which bismuth is recovered as a by-product. In order to satisfy the cumulative world demand through the year 2000, it is necessary that new base metal ores be developed and that the technology for recovering bismuth during the refining of copper and zinc ores be improved. Ores from which thoria can be recovered for $10/lb will be available well into the next century. Large reserves of higher-priced thoria are also available. MSR demands for all materials, with the exception of thorium and hafnium, comprise only a small fraction of the world demand for these materials and will not require the development of new industries for the sole purpose of sustaining an MSBR economy.

A computer program has been developed for calculating steady-state concentrations and heat generation rates in an MSBR processing plant. This program represents the behavior of a total of 687 nuclides in 56 regions that are used to represent the processing system. Consideration of this number of nuclides is necessary because many important heat sources result from the decay of nuclides having short half-lives, while nuclides that are present in significant concentrations are normally long-lived or stable. The program can be easily expanded to include as many as 250 regions if needed. Each region can consist of two phases that are in equilibrium, and a given region can communicate with any other region either by flow of one of the phases between the regions or by rate-limited transfer of material from one of the phases. The performance of the reference molten-salt breeder reactor is simulated by the computer code MATADOR.[6]

Approximately 38,000 simultaneous algebraic equations result from consideration of 687 nuclides in 56 regions. The simultaneous solution of these equations, plus those required for representing the behavior of nuclides in the reactor, would normally be a formidable task. However, if the processing plant is considered separately from the reactor, and if the concentrations of each nuclide throughout the processing plant are calculated before the concentrations of daughters of the nuclide are calculated, the set of 38,000 equations can be divided into 687 subsets, each of which consists of 56 equations. Direct solutions can then be obtained for each of the subsets, and, in this manner, the concentrations of all nuclides in all regions of the processing plant can be calculated directly for a specified set of concentrations in the reactor. The results of this calculation are then used with MATADOR for obtaining an improved estimate for the concentrations of nuclides in the reactor. Through repetitive calculations, rapid convergence (18 iterations or less; 7 min or less of CPU time on an IBM 360/91 computer) is obtained in both the reactor and the processing plant; the resulting concentrations are then used to calculate heat generation rates in each of the regions.

The code has been used for calculating heat generation rates and concentrations of all materials in a processing plant whose operation is based on the fluorination–reductive extraction–metal transfer flowsheet. Present work on the code is aimed at improving the representation of process steps. In the immediate

5. M. J. Bell, *The Availability of Natural Resources for Molten-Salt Breeder Reactors,* ORNL-TM-3563 (November 1971).

6. *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971,* ORNL-4728, pp. 178–83.

future, attention will be given to parametric studies of the fluorination–reductive extraction–metal transfer flowsheet, to a more complete representation of the flowsheet, and to comparative studies of flowsheets based on other processing methods such as oxide precipitation.

1.2 DISTRIBUTION OF LITHIUM AND BISMUTH BETWEEN LIQUID Li-Bi ALLOYS AND MOLTEN LiCl

In the metal transfer process (see Fig. 1.1), rare earths and the attendant small amount of thorium would be stripped from the LiCl acceptor salt into Li-Bi solutions having lithium concentrations of 5 to 50 at. %. We have measured the distribution of lithium and bismuth between liquid Li-Bi alloys and molten LiCl at several temperatures between 650 and 800°C.[7,8] The extent of distribution to the LiCl at each temperature increased with increasing lithium concentration in the alloy. The ratio of "free" lithium to bismuth in the salt phase was 3, suggesting that the data could be interpreted in terms of the distribution of the saltlike species Li_3Bi between the two phases. ("Free" lithium is considered to be metallic lithium that is present in the LiCl.)

Bredig[9] has proposed a model for describing the distribution of Li_3Bi between a liquid Li-Bi alloy and molten LiCl. In this model, the activity of Li_3Bi dissolved in LiCl is defined as:

$$a_{Li_3Bi(d)} = N_{Bi(d)}\,\gamma_{Li_3Bi(d)} = [N_{Li(d)}/3]\,\gamma_{Li_3Bi(d)}\,, \quad (1)$$

in which $N_{Bi(d)}$ and $N_{Li(d)}$ are the measured mole fractions of bismuth and "free" lithium in the LiCl, and γ is an activity coefficient. Concentrations in the alloy phase are defined by assuming that the following reaction occurs when lithium is added to bismuth:

$$3Li^0 + Bi^0 \rightarrow 3\,Li^+ + Bi^{3-}\,. \quad (2)$$

The ion fractions of Li^+ and Bi^{3-} are defined as:

$$X_{Li^+} = \frac{n_{Li^+}}{n_{Li^+} + n_{Bi^0}}\,, \quad (3)$$

and

$$X_{Bi^{3-}} = \frac{n_{Bi^{3-}}}{n_{Bi^{3-}} + n_{Bi^0}}\,, \quad (4)$$

in which n denotes number of moles. It should be noted that n_{Bi^0} is the number of moles of Bi^0 present in the alloy after reaction (2) has occurred. The activity of Li_3Bi in the alloy phase is defined as:

$$a_{Li_3Bi(m)} = [X_{Li^+}{}^3]\,[X_{Bi^{3-}}]\,[\gamma_{Li_3Bi(m)}]\,, \quad (5)$$

in which (m) denotes species dissolved in the alloy. Since the activity of Li_3Bi is the same in each phase at equilibrium at a given temperature, Eqs. (1) and (5) can be equated. After appropriate substitutions and rearrangements, we can obtain in logarithmic form,

$$\log N_{Bi(d)} = \log\,[N_{Li(d)}/3] = \log\left[\frac{N_{Li}{}^4}{(3-N_{Li})^3\,(3-3N_{Li})}\right] + \log\Gamma\,, \quad (6)$$

in which N_{Li} is the mole fraction of lithium in the alloy. At a given temperature, a plot of $\log N_{Bi(d)}$ or $\log\,[N_{Li(d)}/3]$ vs the logarithm of the bracketed term on the right-hand side of Eq. (6) should give a line of unit slope if the ratio of the activity coefficients is constant.

Equilibrium data obtained at each of four temperatures (650, 700, 750, and 800°C) obeyed the relationship represented by Eq. (6); N_{Li} was varied from about 0.1 to 0.5. Values of Γ were obtained from the respective isotherms. From these values, we derived the following expression which correlates the data over the temperature range 650 to 800°C:

$$\log N_{Bi(d)} = \log\,[N_{Li(d)}/3] = \log\left[\frac{N_{Li}{}^4}{(3-N_{Li})^3\,(3-3N_{Li})}\right] + 1.421 - 1785/T(^\circ K)\,.$$

The estimated uncertainty in $\log N_{Bi(d)}$ is ±0.05.

1.3 MUTUAL SOLUBILITIES OF RARE EARTHS AND THORIUM IN LIQUID BISMUTH

In support of development of the metal transfer process (Fig. 1.1), we have continued an investigation

7. L. M. Ferris and J. F. Land, *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, p. 191.

8. L. M. Ferris and J. F. Land, *MSR Program Semiannu. Progr. Rep. Feb. 29, 1972*, ORNL-4782 (in press).

9. M. A. Bredig, ORNL, personal communications.

of solubilities, both individual and mutual, of thorium and selected rare earths in Li-Bi solutions. Previously,[10] we determined the individual solubilities of neodymium and thorium in Li-Bi solutions. During the past year, we measured the mutual solubilities of thorium and lanthanum, neodymium, or europium in bismuth solution throughout the approximate temperature range of 450 to 750°C.[11,12] Thorium and each lanthanide (Ln), when dissolved in liquid bismuth, were found to interact to produce a solid compound with the apparent composition $ThLnBi_y$ according to the reaction

$$Th_{(Bi)} + Ln_{(Bi)} + yBi_{(liq)} = ThLnBi_{y(solid)} \cdot \quad (1)$$

In several experiments conducted at different temperatures, the change in thorium concentration in the liquid phase was determined as a function of the lanthanide concentration. Data from these experiments could be expressed in terms of a mole fraction solubility product

$$K_{sp} = N_{Th} N_{Ln} N_{Bi}{}^{y} , \quad (2)$$

in which N denotes mole fraction. Since the mole fraction of bismuth was very close to unity in each case, the data could be adequately represented by

$$K_{sp} = N_{Th} N_{Ln} \cdot \quad (3)$$

The variation of the solubility products with temperature followed the usual relationship:

$$\log K_{sp} = \log [N_{Th} N_{Ln}] = A + B/T . \quad (4)$$

Data obtained for $ThLaBi_y$ could be expressed as $\log K_{sp} = 2.410 - 6480/T(°K)$, whereas the expression for $ThNdBi_y$ was $3.233 - 7285/T(°K)$.

The solubility of europium in bismuth was determined over the temperature range 350 to 550°C. The data can be represented by the expression: $\log S_{Eu}$ (wt %) $= 4.4823 - 2973/T(°K)$.

The solubilities, individual and mutual, of thorium and rare earths in liquid Li-Bi solutions are sufficiently high to satisfy metal transfer process conditions.

10. F. J. Smith, *J. Less-Common Metals* 27, 195 (1972).

11. F. J. Smith, "Mutual Interactions of Thorium, Lanthanides, and Bismuth in Th-Ln-Bi Solutions: Evidence for the Formation of $ThLnBi_y$ Compounds," *J. Less-Common Metals* (in press).

12. F. J. Smith, C. T. Thompson, and J. F. Land, *MSR Program Semiannu. Progr. Rep. Aug. 31. 1971*, ORNL-4728, p. 193.

1.4 PROTACTINIUM OXIDE PRECIPITATION STUDIES

It has been shown previously[13,14] that protactinium can be selectively precipitated as Pa_2O_5 from LiF-BeF_2-ThF_4-UF_4 salts at 550 to 750°C. Consequently, oxide precipitation processes for isolating protactinium from MSBR fuel salt are being evaluated.[15] The method we are investigating involves sparging of the salt with HF-H_2O-Ar gas mixtures.[16] The data obtained are being considered in terms of the equilibrium

$$PaF_{5(d)} + \tfrac{5}{2} H_2O_{(g)} = \tfrac{1}{2} Pa_2O_{5(s)} + 5HF_{(g)} , \quad (1)$$

for which the equilibrium quotient at a given temperature can be written as:

$$Q_1 = \frac{p_{HF}{}^5}{p_{H_2O}{}^{5/2} N_{PaF_5}} . \quad (2)$$

In the above expressions, (d), (g), (s), N, and p denote dissolved species, gas, solid, mole fraction, and partial pressure, respectively. If the ratio p_{H_2O}/p_{HF} is fixed at some value A, Eq. (2) can be written, in logarithmic form, as:

$$\log N_{PaF_5} = 2.5 \log (p_{HF}/A) - \log Q_1 . \quad (3)$$

At a given temperature, log-log plots of protactinium concentration in the salt vs p_{HF}/A should be linear with a slope of 2.5 and an intercept of $-\log Q_1$.

Experiments have been conducted at several temperatures in the range 530 to 650°C using LiF-BeF_2-ThF_4 (72-16-12 mole %) containing up to 0.25 mole % UF_4; the initial protactinium concentration in each case was about 100 wt ppm. The salt was sparged with various HF-H_2O-Ar mixtures, and equilibrium protactinium concentrations were determined as a function of p_{HF}/A. The data obtained at each temperature obeyed Eq. (3). The values of Q_1 derived from the data can be expressed as: $\log Q_1 = 16.78 - 14220/T(°K)$.

13. R. G. Ross, C. E. Bamberger, and C. F. Baes, Jr., *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, p. 64.

14. O. K. Tallent and F. J. Smith, *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, p. 196.

15. M. J. Bell and L. E. McNeese, *MSR Program Semiannu. Progr. Rep. Feb. 28, 1971*, ORNL-4676, p. 237.

16. O. K. Tallent and L. M. Ferris, *MSR Program Semiannu. Progr. Rep. Feb. 29, 1972*, ORNL-4782 (in press).

In each experiment, the uranium concentration in the salt remained constant at its initial value while the protactinium concentration decreased with decreasing p_{HF}/A as a result of the precipitation of Pa_2O_5 until a point was finally reached where the uranium concentration in the salt also began to decrease. We assume that, at this point, the salt became saturated with both Pa_2O_5 and a UO_2-ThO_2 solid solution. Thus, we were able to estimate values for the equilibrium quotient for the reaction

$$\tfrac{1}{2}Pa_2O_{5(s)} + \tfrac{5}{4}UF_{4(d)} = PaF_{5(d)} + \tfrac{5}{4}UO_{2(ss)}\,, \qquad (4)$$

for which

$$Q_2 = \frac{N_{PaF_5} N_{UO_2}{}^{5/4}}{N_{UF_4}{}^{5/4}}. \qquad (5)$$

The mole fraction of UO_2 in the UO_2-ThO_2 solid solution, $N_{UO_{2(ss)}}$, was calculated from the analytical uranium concentration in the salt and the equilibrium quotient for the reaction

$$ThF_{4(d)} + UO_{2(ss)} = UF_{4(d)} + ThO_{2(ss)} \qquad (6)$$

reported by Bamberger and Baes.[17] The values of Q_2 obtained, 0.022 ± 0.01 at 600°C and 0.033 ± 0.01 at 650°C, are in reasonable agreement with those reported by Ross, Bamberger, and Baes.[13]

1.5 CHEMISTRY OF FUEL RECONSTITUTION

In the current flowsheet for the processing of MSBR fuel (Fig. 1.1), the fuel reconstitution method involves, first, absorbing the UF_6 evolved in the fluorination step in salt containing dissolved UF_4 and, then, reducing the resultant higher-valent uranium species to UF_4 with gaseous hydrogen. Experiments conducted with molten LiF-BeF_2-ThF_4 (72-16-12 mole %) at 600°C indicate that the stoichiometry of the absorption reaction is:

$$UF_{6(g)} + UF_{4(d)} = 2UF_{5(d)}\,, \qquad (1)$$

in which (g) denotes gas and (d) denotes species dissolved in the salt. It was also shown that gaseous hydrogen reacts with dissolved UF_5 as follows:

$$2UF_{5(d)} + H_{2(g)} = 2UF_{4(d)} + 2HF_{(g)}\,. \qquad (2)$$

Since both UF_6 and UF_5 are strong oxidants, our initial studies[18,19] were conducted primarily to find a container that was inert to these species. These studies showed that, at 600°C, nickel, copper, and graphite were not sufficiently inert, but that gold was stable both to gaseous UF_6 and to salt containing up to at least 6 wt % UF_5. Consequently, our latest experiments[19] were conducted in gold apparatus.

In each experiment, a predetermined amount of UF_6 was bubbled into LiF-BeF_2-ThF_4 (72-16-12 mole %) containing 1 to 2 wt % uranium as UF_4. The amount of UF_6 admitted to the system generally was insufficient to convert all of the uranium in the salt to UF_5. The salt was sampled immediately after addition of the UF_6, and the samples were analyzed for both total uranium and U^{5+}. The results of the analyses showed that the UF_6 had reacted quantitatively according to reaction (1). After the addition of UF_6 was complete, the system was usually left under a slight argon pressure and samples of the salt were removed periodically. Results from several experiments showed that UF_5 slowly disproportionated [the reverse of reaction (1)] when its initial concentration in the salt was less than about 2 wt %. The rate of disproportionation was second order with respect to UF_5 concentration.

In one experiment at 600°C, excess UF_6 was bubbled into LiF-BeF_2-ThF_4 (72-16-12 mole %) that contained about 5 wt % uranium; about 91% of the uranium was present as UF_5. Analyses of salt samples taken immediately after the addition of UF_6 showed that both the total uranium and UF_5 concentrations had not changed significantly. Since the apparent oxidation state of the uranium in the salt was not increased above 5+, we conclude that the solubility of UF_6 in the salt is low.

Preliminary experiments relating to the reduction of dissolved UF_5 with gaseous hydrogen have been conducted. The results show that UF_5 is easily reduced to UF_4 according to reaction (2), although this reaction appears to be slower than reaction (1).

1.6 REDUCTIVE EXTRACTION ENGINEERING STUDIES

We have completed a series of six mass transfer experiments in which the rate of transfer of ^{97}Zr was measured by adding ^{97}Zr tracer to MSBR fuel carrier salt (72-16-12 mole % LiF-BeF_2-ThF_4) prior to con-

17. C. E. Bamberger and C. F. Baes, Jr., *J. Nucl. Mater.* **35**, 177 (1970).
18. M. R. Bennett, *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, p. 199.
19. M. R. Bennett and L. M. Ferris, *MSR Program Semiannu. Progr. Rep. Feb. 29, 1972*, ORNL-4782 (in press).

tacting the salt with bismuth containing reductant in the 0.82-in.-diam packed column. In the runs, 18 to 46% of the ^{97}Zr tracer was observed to transfer to the bismuth. The resulting HTU values ranged from about 2 to 4.7 ft, with the average value being about 4.4 ft.

Prior to carrying out the ^{97}Zr tracer experiments, the new salt feed tank and recently installed lines were treated with hydrogen at 600°C to remove surface oxides. Thorium reductant was added to the bismuth in the treatment vessel, and the bismuth and salt were circulated through the system to complete the removal of oxides. Following a 20-hr treatment with a 30-70 mole % $HF-H_2$ mixture, the bismuth and salt were sparged with argon for 20 hr. Reductant totaling 1 g-equiv was added to the treatment vessel before the bismuth and salt were separated, and about 8 mCi of $^{97}ZrO_2$ was added to the salt. In the ensuing experiment, ZTR-1, no measurable transfer of ^{97}Zr occurred because of an unexpectedly low distribution coefficient for zirconium; postrun samples from the treatment vessel showed that D_{Zr} was only 0.023 rather than the expected value of 1.0. The low D_{Zr} value was attributed to the consumption of reductant by a side reaction in the treatment vessel. Subsequent experiments showed that the loss of reductant was greatest immediately following the treatment of the bismuth and salt with an $HF-H_2$ mixture (as before ZTR-1), and likely results from reaction of the reductant with HF that is released slowly by the graphite crucible and with FeF_2 present in the salt phase. Some consumption of reductant may also have occurred due to accumulation of trace oxides in the flow circuit between experiments; the effect of such an accumulation was minimized by circulating bismuth and salt through the system immediately prior to adding tracer to the salt before each mass transfer experiment.

Halfway through the series of ^{97}Zr tracer experiments, several changes were made to reduce the scatter in the ^{97}Zr counting data for flowing stream samples. The principal change was a modification of the sampler housing to maintain a leak-tight seal on the sampler capillary tubing in order to prevent the entry of air into the housing. In order to buffer the system with respect to trace oxidants in the argon cover gas and possible release of HF from the graphite crucible, the uranium inventory of the system was increased from 0.135 to 0.315 g-mole. Subsequent experiments (ZTR-7, -9, -10) confirmed the effectiveness of these measures in improving the quality of flowing stream counting data; all of the individual samples fell within 8% of the respective average for a set of six bismuth and six salt samples. The ^{97}Zr tracer balance for these experiments, for both flowing stream samples and for tank samples, generally ranged from 90 to 105%.

The tracer method for measuring mass transfer performance was extended to include uranium by the simultaneous use of 5 to 10 mCi each of ^{237}U and ^{97}Zr. In the first experiment of this type, UZTR-1, the measured HTU value for uranium was 4.6 ft and the value for zirconium was 3.6 ft. Because of unexpected peaks in the gamma emission energies near the 0.208-MeV value used for counting ^{237}U, a purification treatment was carried out to remove this interference. Beryllium reductant was added to the system electrolytically and the bismuth was treated with HF in H_2 in order to oxidize the impurities, plus uranium and zirconium, into a small salt volume which was subsequently discarded. Uranium and zirconium metal were added to the system, and run UZTR-2 was carried out. The HTU for uranium transfer was 4.4 ft based on tank samples (^{237}U balance, 94%) and 5.2 ft based on flowing stream samples (^{237}U balance, 37%). The calculated HTU value for zirconium was 4.7 ft based on tank samples (^{97}Zr balance, 110%) and 5.4 ft based on flowing stream samples (^{97}Zr balance, 82%).

1.7 DEVELOPMENT OF THE METAL TRANSFER PROCESS FOR REMOVING RARE EARTHS

The metal transfer process is being developed for the removal of rare earths from molten-salt breeder reactor fuel salt (see Fig. 1.1). The results of two engineering-scale experiments (MTE-1 and MTE-2) that demonstrated the basic steps of the metal transfer process were reported previously.[20] In experiment MTE-2, lanthanum and neodymium (typical trivalent rare earths) were extracted from the fuel carrier salt (72-16-12 mole % $LiF-BeF_2-ThF_4$) and were accumulated in a Li-Bi solution at 650°C. This experiment proceeded as expected, with the exception that the decrease in the lithium concentration in the Li-Bi solution (from 35 to 18 mole %) was greater than could be accounted for by the lithium displaced by rare earths. This decrease was thought to have resulted from the transfer of metallic lithium by the molten LiCl circulated through the Li-Bi container. Recently, a correlation (see Sect. 1.2) has been developed for the concentration of metallic lithium and bismuth (as Li_3Bi) in LiCl in equilibrium with Li-Bi solutions, using data obtained in the range of 10 to 50 mole % lithium in the Li-Bi phase. Comparison of the decrease in

20. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, pp. 24–29.

lithium concentration in the Li-Bi solution during MTE-2 with values calculated using the correlation showed the calculated and observed data to be in good agreement.[21] In addition, a separate experiment (MTE-2B) similar to MTE-2 was carried out to measure the rate of transfer of metallic lithium by LiCl in contact with Li-Bi solutions having lithium concentrations ranging from 3.7 to 16 at. %. The rate of transfer of lithium was determined from (1) the change in lithium concentration in the bismuth phases, (2) voltage measurements, and (3) the change in distribution of thorium and neodymium in the system. In the first 4 months of operation, during which 2307 liters of LiCl was circulated, the lithium concentration in the Li-Bi solution was maintained in the range 3.7 to 6 at. %. During this period, the lithium concentration in the Li-Bi solution decreased at a rate equivalent to a lithium concentration in the LiCl of 0.2 ppm. This is higher than the equilibrium value (0.02 ppm); however, there are indications that most of the decrease in the Li-Bi concentration was caused by reaction with impurities rather than by transfer via circulation of the LiCl. After 2307 liters of LiCl had been circulated, the lithium concentration in the Li-Bi solution was increased to 15.6 at. %. At this concentration, the rate of transfer of metallic lithium was determined to be equivalent to a lithium concentration in the LiCl of about 0.8 ppm. This value compares reasonably well with the equilibrium value of 1.6 ppm. Experiment MTE-2B adequately explains the behavior of lithium in experiment MTE-2 and shows that emf measurements are useful in determining the concentration of lithium in Li-Bi solutions in contact with LiCl.

A larger metal transfer experiment (MTE-3) having salt and bismuth flow rates (LiCl, 1.25 liters/min; fuel carrier salt, 33 ml/min; and bismuth, 0.5 liter/min) that are about 1% of those required for removing rare earths from a 1000-MW(e) MSBR has been constructed and put into operation.[22,23] The materials used for the experiment (33.5 liters of 72-16-12 mole % LiF-BeF_2-ThF_4, 6.6 liters of 0.13 at. % Th-Bi solution, 7.3 liters of LiCl, and 4.0 liters of 5-95 at. % Li-Bi solution) were purified before being charged to the system. Mechanical agitators are used in the experiment to contact the salt and metal without dispersing either of the phases. The purpose of the experiment is to determine mass transfer coefficients for the transfer of rare earths in order to determine whether correlations from the literature[24] are applicable to this system. Thus far, two runs have been made to measure the rate of transfer of radium; the transfer rates for lanthanum, europium, and other rare earths will be measured in additional runs planned for the future.

A conceptual design has been prepared for a metal transfer experiment (MTE-4) in which the salt and bismuth flow rates are 10% of those required for processing a 1000-MW(e) MSBR. The materials of construction selected will be suitable for use in a processing plant.[25] A three-stage, mechanically agitated contactor will be used in this experiment. It will be constructed from a single block of graphite approximately 57 in. long, 37 in. wide, and 26 in. high, and will be enclosed in a stainless steel vessel approximately 4 ft in diameter and 8 ft long. The design of the contactor has been reviewed by a graphite manufacturer, who has determined that construction of a unit of this type is feasible.

1.8 CONTACTOR STUDIES OF A SIMULATED MOLTEN-SALT–LIQUID-BISMUTH SYSTEM

Mechanically agitated salt-metal contactors are being considered for application in the metal transfer process for rare-earth removal. The third metal transfer experiment (MTE-3) uses a contactor of this type, consisting of a 10-in.-diam vessel divided into two compartments by a central vertical partition that extends to within ½ in. of the bottom of the vessel. A pool of bismuth provides a seal between the two compartments. The liquid in each compartment is mechanically agitated by a paddle that operates in each phase at a speed that prevents dispersion of the phase.

The hydrodynamic characteristics of this type of contactor were investigated with the mercury-water system. The phenomenon that limited agitator speed was found to be entrainment of water in the mercury at agitator speeds in excess of a well-defined value. The major factors affecting the limiting agitator speed were found to be propeller diameter, propeller pitch, and the design of the baffles in the vessel. The limiting agitator speed was found to be inversely dependent on the diameter of the agitator. The mercury flow rate between the halves of the vessel was measured and

21. E. L. Youngblood and L. E. McNeese, *MSR Program Semiannu. Progr. Rep. Feb. 29, 1972*, ORNL-4782 (in press).

22. E. L. Nicholson et al., *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, pp. 209–12.

23. E. L. Youngblood et al., *MSR Program Semiannu. Progr. Rep. Feb. 29, 1972*, ORNL-4782 (in press).

24. J. B. Lewis, *Chem. Eng. Sci.* **3**, 260–78 (1954).

25. W. L. Carter et al., *MSR Program Semiannu. Progr. Rep. Feb. 29, 1972*, ORNL-4782 (in press).

found to be well in excess of the 0.5 liter/min required in experiment MTE-3.

Mass transfer coefficients in this type of contactor have been reported and correlated in various ways in the literature. Most of the experimental work has been done with partially miscible solvent-water systems that have been operated at Reynolds numbers almost an order of magnitude lower than those expected with salt-bismuth systems. A review of the suggested correlations indicated that the variables of greatest significance in correlating mass transfer between different fluids were probably the interfacial tension and kinematic viscosity. These properties of the mercury-water system are similar to those of molten-salt–bismuth systems; thus the water-mercury system was chosen for experimental determination of mass transfer coefficients.

The overall mass transfer coefficient was determined for the transfer of silver from a dilute aqueous $AgNO_3$ solution into mercury. The rate of change of concentration of $AgNO_3$ was determined and used for calculating the overall mass transfer coefficient. The individual mass transfer coefficients were then calculated from the value for the overall coefficient. The experimental results are shown in Fig. 1.2 in the manner suggested by Lewis, who reported the following relation[26] for predicting individual mass transfer coefficients in stirred-interface contactors:

$$\frac{60k_1}{\nu_1} - 1 = 6.76 \times 10^{-6} \left(\mathrm{Re}_1 + \mathrm{Re}_2\mu_2/\mu_1\right)^{1.65} ,$$

where

k_1 = individual mass transfer coefficient in phase 1,

$\mathrm{Re} = SD^2\rho/\mu$, Reynolds number for phase indicated,

S = stirrer speed, revolutions per sec,

ρ = density of phase indicated,

μ = viscosity of phase indicated,

D = diameter of paddle in phase indicated,

ν = kinematic viscosity (μ/ρ).

The general range of experimental values reported by several investigators using solvent-water systems is shown at the lower left; the experimental values obtained from the water-mercury system are shown at the upper right. The data indicate that extrapolation of the Lewis correlation is a valid procedure even over a

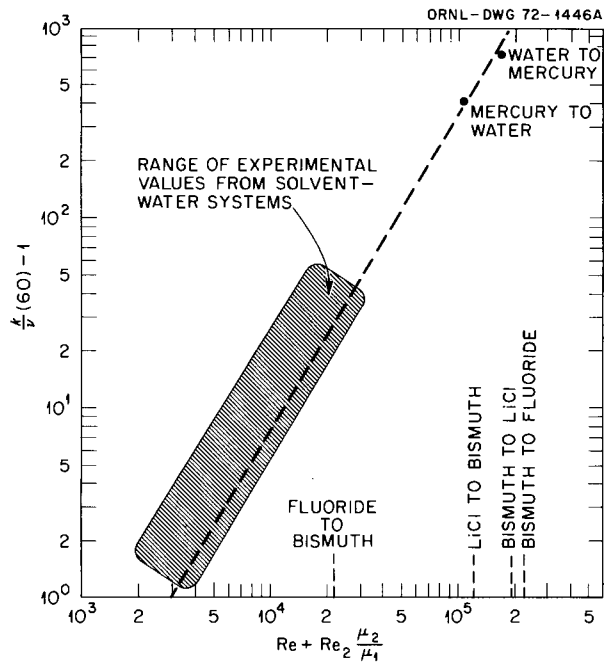

Fig. 1.2. Correlation of mass transfer data from solvent-water and mercury-water systems.

wide range of Reynolds numbers. Also shown in the figure are the expected Reynolds numbers for the various phases in experiment MTE-3. These Reynolds numbers are in the approximate range covered by the water-mercury system, which suggests that the mass transfer coefficient values observed in experiment MTE-3 will be reasonably close to values obtained by extrapolation of the Lewis correlation as was assumed in the design of experiment MTE-3.

1.9 AXIAL DISPERSION IN SIMULATED CONTINUOUS FLUORINATORS

Axial dispersion is important in the design of continuous fluorinators, which are envisioned as open columns through which fluorine will be bubbled countercurrent to a flow of molten salt. We have previously reported data[27–30] showing the variation of the dispersion coefficient and gas holdup with changes

26. J. B. Lewis, *Chem. Eng. Sci.* 3, 248–59 (1954).

27. *MSR Program Semiannu. Progr. Rep. Aug. 31, 1969,* ORNL-4449, p. 240.

28. *MSR Program Semiannu. Progr. Rep. Feb. 28, 1970,* ORNL-4548, p. 307.

29. *MSR Program Semiannu. Progr. Rep. Aug. 31, 1970,* ORNL-4622, p. 216.

30. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971,* ORNL-4682, pp. 31–32.

in gas and liquid flow rates, physical properties of the liquid, column diameter, and gas inlet design. Two experimental techniques were employed. Initially, a steady-state technique was used to demonstrate that the superficial velocity of the liquid was not important in the range of interest. A transient technique was then adopted in which a small quantity of KCl solution was introduced at the top of a column and the rate of buildup of KCl near the bottom of the column was observed.

Approximately 370 measurements of gas holdup and 430 measurements of axial dispersion were made in columns 1 to 6 in. in diameter. Table 1.1 shows the range of parameters used. The data on gas holdup were correlated by the relation

$$h = \frac{0.68 V_g}{V_g + 0.277\sqrt{g d_c}},$$

where

h = gas holdup, fraction of column volume,

V_g = superficial gas velocity, cm/sec,

g = gravity acceleration constant, cm/sec^2,

d_c = column diameter, cm.

Table 1.1. Values of parameters used during studies of gas holdup and axial dispersion in open bubble columns

Parameter	Values used
Column diameter, in.	1, 1.5, 2, 3, 6
Gas superficial velocity, cm/sec	0.013 to 49.7
Surface tension of liquid, dynes/cm	27, 37.6, 45, 53.2, 65.2, 68, 70, 72, 73
Viscosity of liquid, cP	0.9, 1.08, 1.8, 2.05, 10.7, 11.3, 12.1, 15
Density of liquid, g/cm^3	0.997, 1.05, 1.15
Number of orifices in gas inlet	1, 5, 19, 37
Gas inlet orifice diameter, mm	0.4, 1, 2, 4, 6.4

Two modes of gas flow through the column were noted. At low flow rates, the air bubbles ascended as discrete entities with essentially no coalescence; this mode was designated as bubble flow. At high flow rates, fairly extensive coalescence and bubbles having a diameter essentially equal to that of the column were observed; this mode was designated as slug flow. The data on axial dispersion were correlated by the following expressions:

for bubble flow,

$$N_{Pe} = 10.3\, N_{Re}^{0.82}\, N_{Ar}^{-0.44}\, n^{-0.10};$$

for slug flow,

$$N_{Pe} = 0.89\, N_{Re}^{0.77}\, N_{Su}^{-0.43}\, (1-h)^{3.0};$$

where

$$N_{Pe} = \frac{d_c V_g}{D} = \text{Peclet number},$$

$$N_{Re} = \frac{\rho_l d_c V_g}{\mu_l} = \text{Reynolds number},$$

$$N_{Ar} = \frac{d_c^3 \rho_l^2 g}{\mu_l^2} = \text{Archimedes number},$$

$$N_{Su} = \frac{d_c \rho_l \sigma}{\mu_l^2} = \text{Suratman number},$$

n = number of gas inlets in disperser,

d_c = column diameter,

V_g = superficial gas velocity,

D = axial dispersion coefficient,

ρ_l = density of the liquid,

μ_l = viscosity of the liquid,

σ = surface tension of the liquid,

g = acceleration of gravity.

1.10 DEVELOPMENT OF A FROZEN-WALL CONTINUOUS FLUORINATOR

The nonradioactive demonstration of the use of a frozen salt layer to protect against corrosion in a continuous fluorinator requires a heat source (in the molten salt) that is not subject to corrosion by the combined attack of fluorine and molten salt. We have considered high-frequency induction heating and 60-Hz autoresistance heating for this purpose. Results of experiments to evaluate these heating methods have indicated that autoresistance heating is preferable to induction heating because of the greater operating flexibility of low-frequency power supplies. The autoresistance heating experiments indicate that the temperature of the fluorinator wall may have to be below that of the salt solidus in order to obtain an electrically insulating frozen salt layer.

Study of high-frequency induction heating using aqueous electrolyte solutions in fluorinator simulations

indicated[31] that sufficient heat could probably be generated in molten salt if a suitable means could be found for introducing the induction coil into the vessel and supporting the coil during operation. Equipment was designed[32] and fabricated for the study of induction heating of molten salt. In initial tests with the equipment at room temperature, the dielectric strength of the cover gas (argon) was exceeded, and arcing between the coil and the vessel wall was observed. It is believed that operation with nitrogen or fluorine will prevent similar occurrences. Results of the tests indicate that induction heating is a practical method for generating heat in molten salt; however, the complexity of the required electrical equipment and the narrow range of acceptable operating conditions prompted our re-examination of autoresistance heating using 60-Hz power.

Experiments with autoresistance heating were carried out with two different types of test vessels using salt having the nominal composition 66-34 mole % $LiF-BeF_2$. The first vessel,[33] a small mockup of an actual fluorinator, was fabricated from 2.5-in.-diam nickel pipe. The vessel had a 3-ft-long vertical test section, a V-shaped side arm at the upper end of the test section for introduction of an electrode, an angled side arm at the lower end of the test section that was used as a gas inlet, and a 6-in.-diam gas-liquid disengagement region above the test section. During operation, flow of current between the electrode and the adjacent vessel wall was invariably observed. A second test vessel was then designed for determining the reason for the difficulty.

The second test vessel[33] was fabricated from 6-in.-diam nickel pipe and had a 4-ft-long vertical test section. An electrode was introduced into the top of the test section through a flange; the current path in the system was thus along the axis of the test section. Attempts to operate the second vessel have been partially successful, and autoresistance heating at the desired rates has been observed. The formation of an electrically insulating frozen salt layer has been more difficult than had been expected initially. The temperature of the wall may have to be below that of the salt solidus, rather than below that of the salt liquidus, in order to obtain the desired operating mode. It is believed that a method can be developed for reliabily forming a frozen layer that is electrically insulating.

1.11 DESIGN OF A PROCESSING MATERIALS TEST STAND AND THE FIRST MOLYBDENUM REDUCTIVE EXTRACTION EQUIPMENT

The cooperative project between the Chemical Technology Division and the Metals and Ceramics Division to design and construct an all-molybdenum packed column system to provide engineering data and information on the compatibility of molybdenum with molten salt and bismuth is continuing.

Final detailed design drawings for all major molybdenum components have been completed and approved for fabrication. Calculations were completed for the expansion loops to accommodate thermal expansion in the instrument purge, gas lift supply, and transfer lines. Stress calculations for the loops were based on the results of tensile strength tests made by the Metals and Ceramics Division on molybdenum tubes brazed in stainless steel sockets. A value of 6750 psi was used as the allowable design tensile stress (one-tenth the value observed for brittle failure).

A full-scale mockup of the molybdenum equipment and piping was constructed by the Metals and Ceramics Division from the preliminary piping drawings. The mockup has proved to be extremely useful in improving the piping arrangement and in ensuring that sufficient space is provided for the welding and brazing fixtures that are necessary for joining the piping from the various subassemblies of the system.

An improved system for field assembly of the molybdenum system was devised. This system should reduce the time required for the final assembly operation by a factor of 2 or more. Originally, the molybdenum vessels and piping subassemblies, which were fabricated in electron-beam vacuum chambers and inert-gas welding boxes in Building 4508, were to be moved to Building 4505 for field assembly. An existing multilevel platform was to be modified to allow vertical assembly of the system near the cell in which the test stand will be installed. This method of assembly would have been time-consuming, the working conditions would have been adverse, and protection of the completed work from inadvertent damage would have been difficult. In order to avoid such difficulties, a rigid, transportable field assembly jig was designed. This jig will permit horizontal assembly of the system at table-top level in Building 4508. An equipment alignment column (made from $2\frac{1}{2}$-in. sched 80 stainless steel pipe, attached to the underside of the containment

31. J. R. Hightower, Jr., *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, p. 214.
32. Ibid., p. 216.
33. J. R. Hightower, Jr., *MSR Program Semiannu. Progr. Rep. Feb. 29, 1972*, ORNL-4782 (in press).

vessel flange, and extending the full 17-ft length of the molybdenum equipment) will maintain proper alignment of system components during operation. The containment vessel flange and the alignment column will be securely fastened to the assembly jig by bolts and special clamps, and will provide the basic unit for assembly of the molybdenum equipment. During operation, the major components will be held in alignment by the pipe and will be supported vertically by molybdenum rods attached to the bottom of the flange. The use of molybdenum support rods will allow the equipment to expand without vertical restraint. The radial restraints, constructed of stainless steel, are free to move vertically on the alignment column by virtue of predetermined clearance with the support column. During assembly of the system, the radial restraints will be secured to the alignment column; these restraints, along with temporary clamps, will be used to support the molybdenum equipment.

All vessel forgings for the system have been completed and machined, except for the final fit of preselected molybdenum tubes with mating holes in the vessel bosses. All components and tubing have been inspected and shipped to the Thermo-Electron Company for final machining. The Metals and Ceramics Division has successfully demonstrated the welding, brazing, and roll bonding of test pieces typical of the various construction joints and is now prepared to begin assembling the system. Final piping drawings have been prepared and are being checked. A tentative starting date of April 22 has been set for assembly of the system. The assembly jig and flange subassembly are scheduled for completion by April 15. A practice of the transfer operations for the assembly frame with the flange subassembly in place will be made by moving the frame from Building 4508 to Building 4505, erecting the unit in a vertical position, and removing the flange and supporting pipe from the frame and lowering it into the cell. If feasible, the equipment mockup will also be used during this operation.

1.12 DEVELOPMENT OF A CORROSION-RESISTANT SALT-BISMUTH INTERFACE DETECTOR

An eddy-current type of detector that is resistant to corrosion by molten salt or bismuth is being developed to allow detection and control of the bismuth-salt interface in salt-metal extraction columns or mechanically agitated salt-metal contactors. The probe consists of a ceramic form on which bifilar primary and secondary coils are wound. Contact of the coils with molten salt or bismuth is prevented by enclosing the coils in a molybdenum tube. In operation, a current is induced in the secondary coil by passing a high-frequency alternating current through the primary coil. The induced current is dependent on the conductivities of the materials located adjacent to the primary and secondary coils; since the conductivities of salt and bismuth are quite different, the induced current reflects the presence or absence of bismuth. Two approaches for obtaining an output from the detector are being pursued. The first is based on measuring changes in the magnitude of the induced current; the second is based on measuring the phase shift that occurs between the voltage imposed on the primary coil and that which is induced in the secondary coil.

A series of calculations was made to determine the significant variables in the design and operation of the interface detector. The chosen probe design consists of an alumina core that is grooved to support two coils of 10-mil-diam platinum wire wound in a double-helix configuration. The wound core is sheathed in a molybdenum tube that has a 30-mil wall thickness, an outside diameter of 0.785 in., and a length of 14 in. The completed probe has been installed in a carbon-steel test vessel consisting of three chambers. The upper chamber is a reservoir for molten bismuth, the middle chamber contains the probe, and the lower chamber (which simulates the interior of the high-temperature containment vessel for the molybdenum reductive extraction equipment) contains 13 ft of high-temperature electrical cable in an inert atmosphere. Bismuth can be transferred between the upper and middle chambers to vary the level around the probe; this level can be measured with a bubbler system and compared with the level indicated by the probe.

A series of tests has been made at temperatures between 550 and 700°C with the phase-shift measurement technique. The readings that were obtained were linearly dependent on the bismuth level and were quite reproducible. The accuracy of the phase-shift readings was at least as good as that of the mercury manometer readings against which the probe was being calibrated. The temperature sensitivity was 0.008 in./°C at a bismuth level of 2 in., and 0.005 in./°C at a bismuth level of 12 in. This type of interface detector appears to be a very sensitive and practical device for measuring bismuth levels or determining the location of a salt-bismuth interface.

1.13 REMOVAL OF URANIUM FROM MOLTEN FLUORIDE SALTS BY OXIDE PRECIPITATION

Oxide precipitation processes are being considered as alternatives to fluorination for the removal of uranium

Table 1.2. Summary of data from oxide precipitation runs OP-1 through OP-8

Run No.	Temp. (°C)	Argon-H_2O comp. (% H_2O)	Water utilization (%)	HF evolved (moles)	Final uranium concentration (wt %)			Comp. of solid solution (% UO_2)
					Calculated[a]	Measured		
						Vessel	Feed tank	
OP-1	600	10-15				0.95	0.95	96
OP-2	600	10-15		0.60	0.44		0.53	91
OP-3	600	10		0.84	0.36		0.43	91
OP-4	600	25	14	0.85	0.33	0.38	0.44	89
OP-5	600	35	12	1.0	0.21	0.25	0.29	89
OP-6	540	10-15	10	0.76	0.41	0.41	0.46	92
OP-7	600	35	9	1.4	0.16	0.10	0.13	91
OP-8	630	35	11	1.7	0.16	0.033	0.065	89

[a]Assuming equilibrium between salt and oxide.

from protactinium-free MSBR fuel salt, and to reductive extraction for the removal of protactinium. The design and operation of equipment to perform engineering studies of the removal of uranium from MSBR fuel salt are described elsewhere.[34,35] Twelve experiments have been performed in the facility. The first eight were designed to investigate the effects of changes in the salt temperature and gas feed composition on the rate of precipitation and on water utilization, and to investigate the feasibility of separating the salt and oxide by decantation. The results of these experiments are summarized in Table 1.2.

The experiments were conducted at temperatures ranging from 540 to 630°C, and the composition of the argon-water mixture was varied from 10 to 35% water. Only a slight increase in reaction rate was observed with an increase in temperature, and the rate of precipitation appeared to vary directly with the rate at which water was supplied to the system. The values for the water utilization were uniformly low (about 10 to 15%) and did not vary with the composition of the gas stream. Higher utilization values should be obtained by improving the contact of the gas with the salt. The initial uranium concentration in the salt was about 1 wt % in the first seven experiments, and 50 to 90% of the uranium was precipitated as oxide in most of the experiments. The quantity of HF gas collected in each experiment (see Table 1.2) is directly related by the stoichiometry of the reaction to the quantity of oxide formed. The latter value was used in conjunction with the equilibrium data of Bamberger and Baes[17] to compute the composition of the oxide and the uranium concentration in the salt, assuming that the salt and oxide phases were in equilibrium. In several experiments, the measured uranium concentrations in the salt samples agree fairly closely with the calculated values. However, there is a trend in some of the early experiments for the uranium analyses to show slightly higher uranium concentrations than were calculated by assuming equilibrium; and, in the last two experiments, the measured uranium concentrations are below those calculated by assuming equilibrium.

The salt samples obtained from the feed tank showed uranium concentrations that are only slightly higher than those measured in the precipitator vessel. Sufficient data are not available at this time to determine whether the higher concentrations in the receiver tank resulted from entrainment of a small amount of oxide or from the salt heel in the receiver vessel (which contains some UF_4), but information will be obtained in the next few runs to resolve this uncertainty. Also shown in Table 1.2 are the compositions of the UO_2-ThO_2 solid solutions that were observed at the conclusion of each experiment. All of the samples contain about 90% UO_2 even though, at the lower uranium concentrations in the salt, the solid in equilibrium with the salt would contain 50% UO_2 or less.

Oxide samples from the system are composed of more than one face-centered cubic phase: a principal phase that is rich in UO_2, and one or more ThO_2-rich phases. In many cases, greater than 90% of the solid consists of a phase that is about 90% UO_2, and less than 10% of the solid consists of a thorium-rich phase. These results have led to a nonequilibrium precipitation model based

34. M. J. Bell and L. E. McNeese, *MSR Program Semiannu. Progr. Rep. Feb. 28, 1971*, ORNL-4676, p. 267.

35. M. J. Bell, D. D. Sood, and L. E. McNeese, *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, pp. 220–22.

on precipitation of UO_2-ThO_2 solid solutions which are in equilibrium with the salt at the moment of formation but which, once formed, do not rapidly re-equilibrate. Thus, solid solutions that are formed early in the precipitation process, and that contain 90 to 95% UO_2, are still present during the final stages of precipitation when the solid solutions being formed contain much less UO_2. Based on this model, 99% of the uranium could be precipitated from the salt in one stage as a solid containing 85% UO_2 (which is acceptable). The experimental data indicate that the oxides actually observed have a slightly lower UO_2 content than predicted by the model; this is believed to be the result of precipitation of a thorium-rich phase due to inadequate mixing of the salt phase. However, the compositions of solid solutions that have been observed are still well within the range of those required for operation of a flowsheet using a single-stage UO_2 precipitator.

Two experiments (OP-10 and OP-11) were performed in which a large fraction of the uranium in the system was precipitated and in which the precipitate was allowed to remain in contact with the salt for a period of about 1 week in order to observe the rate of equilibration of the two phases. Salt temperatures of 550 and 620°C were used in experiment OP-10 and experiment OP-11, respectively. In each experiment, gas was circulated through the draft tube in order to promote contact of the salt and oxide. Samples of salt and oxide were obtained at intervals during the experiments. No detectable increase was noted in the uranium concentration in the salt in either case, indicating that little or no equilibration of the two phases had occurred.

Samples of oxide obtained during experiment OP-11 have been washed free of salt and examined petrographically. Thus far, examination has revealed that particles with a high UO_2 content have an average diameter of 40 ± 10 μ, and that these particles are consistently larger than particles with a high ThO_2 content. More detailed information concerning the size distribution of the precipitate will be obtained from future samples. The slow rate of re-equilibration and the particle sizes observed in experiments OP-10 and OP-11 continue to make the oxide precipitation process appear attractive.

2. Development of Aqueous Processes for LMFBR Fuels

Beginning in the 1980s, reprocessing of large quantities of spent fuel from LMFBR reactors will be required. It appears feasible, with plant modifications, to process fuel from early LMFBR reactors, where preprocessing decay is acceptable, in existing fuel reprocessing facilities.

Processing of the LMFBR fuel after short decay periods will be advantageous, owing to the high fissile content (and high inventory costs) of the core material. The problem of fuel shipment, which is difficult even with LWR fuels, is aggravated in the case of LMFBR fuels by the high specific power of the fuel and the need to ship after only short decay times. We are working toward development of equipment and techniques for shipment that will ensure safety and containment under accident conditions.

The treatment of off-gas is a major consideration in the processing of all reactor fuels. Removal efficiencies for radioiodine of greater than 10^8 will be required for large-scale plants which process fuel that has been cooled for about 30 days. Development emphasis has been placed on plant design and operation and maintenance techniques that, along with the new iodine scrubbing processes, may make confinement factors of this magnitude attainable. Tritium can be released from the fuel by oxidative heat treatment before the dissolution step; and xenon, along with krypton, can be removed from the off-gas after dissolution by selective absorption with a fluorocarbon solvent.

Our work is directed toward the design of equipment and the development of process flowsheet conditions that are required to demonstrate safe and economic shipment and the "near zero release" processing of short-cooled LMFBR fuel. While this work presents challenging problems, we are reasonably confident that the objective is not beyond practical attainment.

2.1 SHIPPING

The shipment of spent fuel is a necessary adjunct to large-scale, economical fuel reprocessing. Efforts during this year were directed toward obtaining additional test data on cask integrity and heat transport, and toward performing design studies relative to economics and shipping cask design features.

With the exception of the fuel access port(s), the LMFBR shipping cask is envisioned as an all-welded, almost monolithic structure. The fuel access ports are sealed by all-metal gaskets. The resistance of a prototype $^1/_8$-scale access port seal to impact loads was demonstrated by tests in which model casks were dropped 30 ft onto an unyielding surface.[1,2] No leakage or perceptible damage occurred to the seal during impact of the cask in a vertical attitude even when a 10-in. column of mercury was located above the seal. Tests were also made to determine the life of the sealing surface and the anticipated leak rates. Results of incomplete tests indicate that seal leak rates $\leqslant 10^{-7}$ cm^3 of helium per second can be achieved in a practical system and that 100 or more makeups of a closure can be achieved before rework will be necessary.[3] Some problems with thermal cycling and seal lubricant have been encountered;[4] however, we believe that these can be resolved.

Additional heat transport tests with liquid sodium have shown that no significant convective transport of heat occurs to areas below the level of the lowest point of heat generation in a vessel in which open supports are used to suspend the fuel subassemblies. Experiments demonstrated that flow resistance through the fuel subassembly is too great to permit significant thermal convection through the flow duct.[5]

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1. *LMFBR Fuel Cycle Studies Progress Report for June 1971, No. 28,* ORNL-TM-3487, p. 2.
2. *LMFBR Fuel Cycle Studies Progress Report for November 1971, No. 33,* ORNL-TM-3663, p. 5.
3. *LMFBR Fuel Cycle Studies Progress Report for January 1972, No. 35,* ORNL-TM-3724, p. 2.
4. *LMFBR Fuel Cycle Studies Progress Report for April 1972, No. 38,* ORNL-TM-3823.
5. *LMFBR Fuel Cycle Studies Progress Report for August 1971, No. 30,* ORNL-TM-3571, p. 2.

Two studies pertaining to cask design and safety were completed.[6,7] Each was specifically concerned with an engineering evaluation of LMFBR spent fuel shipping and with a conceptual design and partial safety analysis of a prototype cask. In the second study, new concepts were presented for an access port seal assembly, neutron shielding, and accommodation of coolant expansion. The proposed access port seal assembly employs three seals in series, with pressurized inert-gas pockets located between pairs of sequential seals. With this system, zero leakage of coolant or fission products will occur even if the seals have a measurable leak rate and even if one of the three seals should fail. The proposed neutron shield, which is comprised of solid NaOH-LiOH eutectic housed in a metal enclosure, is expected to materially increase the tolerable fire duration. The system proposed for accommodating coolant expansion is a simple pressure vessel equipped with an entry (and exit) pipe having appropriate loop seals to prevent unwanted filling of the gas pocket with liquid.

Two cost studies were also completed. The first[8] dealt with the incremental cost of stationary facilities and operations associated with individual canistering of fuel subassemblies. This cost was estimated to be at least $24 per kilogram of fuel. The second study[9] was an economic comparison of various cask designs and modes of shipment. The optimum system for decay times ranging between 30 and 150 days was found to be the sodium-cooled, steel-shielded cask.

2.2 HEAD-END PROCESSING

Thermal Conductivity Measurements

Heat transfer calculations such as those involving the temperature profile across a basket of sheared fuel from decay heat emission require a knowledge of the effective thermal conductivity of the sheared fuel pieces. For this reason, experimental thermal conductivity measurements were made for simulated LMFBR core material,[10,11] including the gas plenum section, and the results were compared with those obtained for typical Light-Water Reactor (LWR) prototype sheared fuel[12] (see Fig. 2.1).

The conductivity of the sheared LWR fuel was significantly greater in all cases than that of the LMFBR fuel except in the 200 to 400°F range, where the values are approximately equal. The thermal conductivity of the sheared hulls, which simulate the sheared gas plenum sections from LMFBR fuel, and the thermal conductivity of the UO_2-filled sections, which simulate an LMFBR core, were essentially the same.

A final report,[13] *The Thermal Conductivity of Sheared Prototype LMFBR Fuels,* ORNL-TM-3772, is in preparation.

Disassembly

In preliminary disassembly studies, three plasma torches (PCM-4A, FSH-5, and PT-7) and a belt grinder were evaluated for slitting the hexagonal shroud or flow duct away from LMFBR prototype fuel. The torches were also tested to determine whether a subassembly could be crosscut at the gas plenum (217 empty shrouded tubes) and end caps (solid rods widely spaced).

The model PCM-4A plasma arc torch was demonstrated to be the best design for cutting the hexagonal corners because its smaller cone-shaped ceramic torch cup eliminated short-circuiting to the work piece, which was evident in the other torches evaluated. It was also successful in slitting 8-ft lengths of hexagonal shrouds without rupturing the fuel tubes (0.250-in.-OD tubes with 0.091-in.-OD wire wrap). None of the torches successfully crosscut a subassembly in a single pass. In trial cuts with each torch, two cutting passes were required; the second cut was made after the subassembly had been rotated 180°.

A scouting test to demonstrate high-speed belt grinding of the hexagonal corner of a prototype Atomics International core assembly was made using equipment located at the 3M Company. No damage to the fuel rods was noted; thus the performance was considered to be satisfactory.

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6. A. R. Irvine, *An Engineering Evaluation of LMFBR Fuel Shipment,* ORNL-TM-2723 (September 1971).
7. A. R. Irvine et al., *LMFBR Spent Fuel Transport: Conceptual Design and Partial Safety Analysis of a Sodium-Cooled Cask,* ORNL-TM-3689 (February 1972).
8. B. B. Klima, A. R. Irvine, and W. G. Stockdale, *LMFBR Spent Fuel Transport: Descriptions and Cost Estimates of Stationary Facilities and Their Operations,* ORNL-TM-2905 (November 1971).
9. J. P. Nichols and A. R. Irvine, *LMFBR Spent Fuel Transport: Parametric Studies,* ORNL-TM-3503 (February 1972).
10. *LMFBR Fuel Cycle Studies Progress Report for February 1972, No. 36,* ORNL-TM-3759.
11. *LMFBR Fuel Cycle Studies Progress Report for July 1971, No. 29,* ORNL-TM-3534.
12. *LMFBR Fuel Cycle Studies Progress Report for December 1971, No. 34,* ORNL-TM-3698.
13. S. D. Clinton and R. L. Cox, *The Thermal Conductivity of Sheared Prototype LMFBR Fuels,* ORNL-TM-3772 (in preparation).

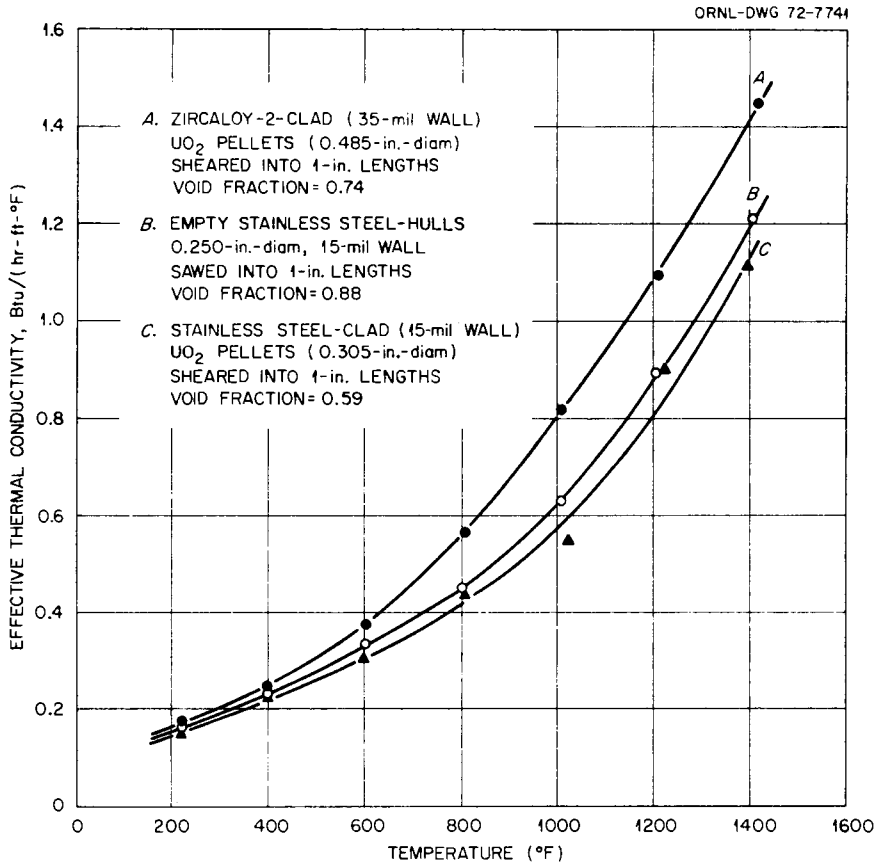

Fig. 2.1. Effective thermal conductivities of some prototype fuels. *A* = typical LWR fuel; *B* = simulated gas plenum sections from LMFBR fuel; *C* = simulated LMFBR core.

Shearing

Studies of the concept of bundle shearing (intact subassembly, including the shroud) were continued. Three different moving stepped-teeth shear blades with matching fixed blades were fabricated, and scouting tests were performed on the ORNL 250-ton shear with prototype fuel compacted by a gag at 50 tons of force. Two of the blades tested, a stepped shark's-tooth type and an elongated (center-tooth) stepped bottom and top blade, produced a more desirable product than an interrupted shark's-tooth stepped blade. However, neither blade consistently broke the shroud into sections as small as desired (i.e., ~1 to 1.5-in. lengths) while shearing at 1-in. lengths. Occasionally, a long shroud piece, 1 in. wide by 3 to 4 in. long, was produced. Such pieces would probably require special handling. Compacted fuel and the product from the elongated center-tooth blade are shown in Fig. 2.2. From these results, we conclude that compaction prior to shearing is a necessary requisite to the production of a desirable LMFBR sheared product when shearing whole bundles.

2.3 REMOVAL OF VOLATILE FISSION PRODUCTS

Studies were continued[14–16] on a new head-end processing step (voloxidation) that is designed to release tritium from spent LMFBR fuel and deactivate "tramp" sodium prior to aqueous processing. In the present process, sheared fuel is heated to about 575 to 650°C in flowing air or oxygen. Removal of tritium by voloxidation (in the absence of water) appears to be of particular advantage since it would avoid the dilution of ^3H_2O with large volumes of water in the subsequent fuel dissolution step. Some significant highlights of hot-cell, bench-scale, and engineering-scale results during the past year are as follows:

14. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1969,* ORNL-4422.
15. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1970,* ORNL-4572.
16. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971,* ORNL-4682.

Fig. 2.2. (*a*) Compacted fuel; (*b*) product from the elongated center-tooth blade.

1. During both voloxidation and dissolution of fuel in nitric acid,[17] in-line instrumentation indicated that the release of any ^{85}Kr occurred promptly (within 30 min).
2. In an experiment with irradiated fuel, only about 3% of the theoretical yield of tritium was found in the oxide fuel. The remaining tritium had apparently passed through the stainless steel cladding of the rods into an outer, water-cooled capsule containing NaK coolant.[11,18] Only small amounts of tritium were found in the stainless steel claddings of the fuel rods (0.07%) and the outer capsule (0.8%), in the puncture gases of the capsule (0.7%) and the gases of the individual fuel rods (0.6%), or in the clean NaK (0.23%). Although experimental difficulties prevented collection of all the tritium, a significant fraction of the missing tritium (~97%) was found in a scum on the metal surfaces of the rods and capsule exposed to the NaK.
3. In a simple calorimeter experiment using short-cooled fuel rods, close agreement was obtained between the measured decay heat and values calculated by the ORIGEN code.[18]
4. Voloxidation of sheared, short-cooled 25% PuO_2–75% UO_2 pellet fuel irradiated to 1.5 to 2.5% FIMA (Fig. 2.3) released about 75% of the total yield of krypton and xenon and 75% of the iodine.[11,19] The oxidized fuel contained only 0.2% of the theoretical yield of tritium.[11]
5. The quantity of ^{131}I in the plenums of fuel rods appears to increase as the linear heat rating of the rods increases during irradiation.[19]
6. Oxidation of restructured, irradiated fuel gave more effective removal of krypton and tritium than heating at the same temperature in vacuum or in an inert atmosphere.[20] Air oxidation at temperatures up to 750°C released as much as 45% of the ^{85}Kr and 99.9% of the ^{3}H, whereas only about 15% of the ^{85}Kr and less than 50% of the tritium were released in vacuum or in an inert atmosphere.
7. The amount of krypton released increases with increasing restructuring of the fuel.[20] For example,

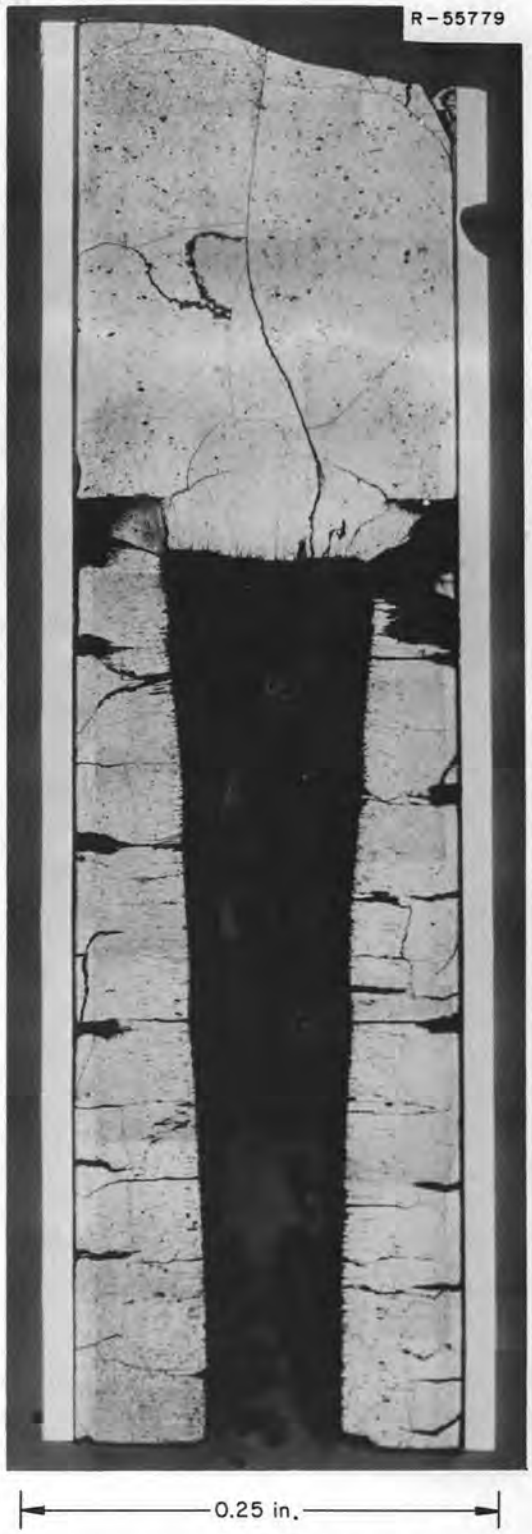

Fig. 2.3. Longitudinal section of rod 43-117-2, showing top UO_2 insulator pellet and top two 25% PuO_2–75% UO_2 "FTR Dissolution Reference" pellets. Irradiated in ETR to 2.3% FIMA at a linear heat rating of about 16 kW/ft.

17. *LMFBR Fuel Cycle Studies Progress Report for April 1971, No. 26,* ORNL-TM-3412.
18. *LMFBR Fuel Cycle Studies Progress Report for May 1971, No. 27,* ORNL-TM-3456.
19. *LMFBR Fuel Cycle Studies Progress Report for August 1971, No. 30,* ORNL-TM-3571.
20. *LMFBR Fuel Cycle Studies Progress Report for September 1971, No. 31,* ORNL-TM-3614.

segments of PNL 59-7, irradiated at 13.5 kW/ft to 66,000 MWd/ton, released 45% of the ^{85}Kr, whereas PNL X-3, irradiated to ~4,140 MWd/ton at 5.3 kW/ft, released only about 1% at 550 or 750°C. This difference in behavior is thought to be due to the release, on oxidation, of large bubbles of fission gases present at the grain boundaries of the restructured fuel. Unrestructured fuel contains small bubbles dispersed within the grains.

Results of bench-scale oxidation experiments[21,22] at 480°C with stainless-steel-clad unirradiated UO_2 pellets in a 3-in.-diam minivoloxidizer showed that (1) the effect of varying the rotational speed of the six-flight minivoloxidizer from 0 to 48 rpm was slight, with the time required for oxidation varying from 3.5 to 2.5 hr as the speed was increased; (2) the oxidation time was significantly decreased from 2.5 hr to 1.5 hr as the oxygen content was increased from 20% to 100% at 480°C and 12 rpm (however, with 80 to 100% oxygen, the pellets sintered in place rather than being pulverized and dislodged); and (3) the time required for urania oxidation was minimal at about 480°C and increased by a factor of 2 as the temperature was increased to 600°C.

In engineering-scale experiments with sheared (1-in.-long) unirradiated stainless-steel-clad urania in the 6-in.-diam Bartlett Snow calciner, 87 to 97% of the urania was dislodged in air at 475°C at rotational speeds and residence times of 2, 4, and 12 rpm and 150, 75, and 25 min, respectively. At 12 rpm and room temperature, 97% of the urania was dislodged, showing that tumbling of the sheared fractured material by the six flights of the unit, rather than the oxidation-pulverization reaction, was the cause of dislodgement of the fractured material.

A summary of all voloxidation experimental studies will be issued as a topical report.[23]

2.4 DISSOLUTION AND FEED PREPARATION

Various types of irradiated oxide fuel are being procured from as many sources as possible for use in tests to determine the effects of the fuel preparation and irradiation histories on its dissolution properties. Particular attention is also being given, both in laboratory and hot-cell studies, to the behavior of iodine in the dissolver-condenser system and to the use of fumeless dissolving techniques for minimizing the volume and fume content of the off-gas to facilitate containment and separation of iodine and ^{85}Kr.

Dissolution Studies

We have been studying the effects of irradiation on the dissolution characteristics of irradiated LMFBR fuels;[24,25] when available, unirradiated samples of the fuels are also tested. These experimental data are being accumulated for the preparation of statistical models that ultimately should be useful for optimization studies within the fuel cycle.

A batch of mechanically blended 25% PuO_2–75% UO_2 pellets, identified as "FTR Dissolution Reference Pellets," was prepared by WADCO for characterization and irradiation by ORNL. Dissolution of samples of the unirradiated fuel for up to 18 hr in boiling 8 *M* HNO_3 left a residue (~4 wt %) containing 14 to 16% of the original plutonium.[22,26] Metallography revealed that high plutonium concentration regions 10 to 20 μ in diameter were dispersed throughout the pellet. The residue, which contained 70 to 90% PuO_2, dissolved readily in boiling 8 *M* HNO_3–0.05 *M* HF solution. Since the heat treatment (4 hr at 1600°C) that had been given the fuel pellets was not very stringent, we performed additional heat treatments for 3 and 6 hr at 1700, 1750, and 1800°C. The latter treatments had a beneficial effect on the dissolution behavior, but, even under the best conditions (6 hr at 1800°C), 3 to 4% of the plutonium remained undissolved after 10 hr in boiling 8 *M* HNO_3 (Fig. 2.4).

Pellets from the same batch were also used to fabricate three irradiation capsules for hot-cell studies. Irradiation to about 20,000 MWd/ton, at a peak linear heat rating of about 16 kW/ft, made the PuO_2 more soluble; about 5% of the total plutonium was insoluble in 8 *M* HNO_3 but dissolved in 8 *M* HNO_3–0.05 *M* HF. The behavior of most of the fission products, except ruthenium, niobium, and the noble metals, was similar to that of plutonium[19] (Fig. 2.5).

21. *LMFBR Fuel Cycle Studies Progress Report for October 1971, No. 32,* ORNL-TM-3624.

22. *LMFBR Fuel Cycle Studies Progress Report for January 1972, No. 35,* ORNL-TM-3724.

23. J. H. Goode (ed.), *Volatile Fission Product Removal from LMFBR Fuels,* ORNL-TM-3723 (in preparation).

24. Staff of the Chemical Technology Division, *Aqueous Processing of LMFBR Fuels – Technical Assessment and Experimental Program Definition,* ORNL-4436 (June 1970).

25. V. C. A. Vaughen and J. H. Goode, *Proposed Program for Hot-Cell Tests of Head-End Processes for LMFBR Fuels,* ORNL-TM-3644 (December 1971).

26. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971,* ORNL-4682, p. 53.

Other irradiated, mechanically blended pellets were dissolved as a part of the voloxidation development program.[11,17,22] In some experiments, the voloxidation treatment slightly increased the amount of PuO_2 in the HNO_3-insoluble residue; however, the amount of plutonium dissolved from these pellets with 8 *M* HNO_3 was usually higher than 99.9%. Use of 8 *M* HNO_3–0.05 *M* HF solution in the initial dissolution reduced the time for achievement of 99.9% recovery to 1 hr, compared with 8 to 10 hr for 8 *M* HNO_3.

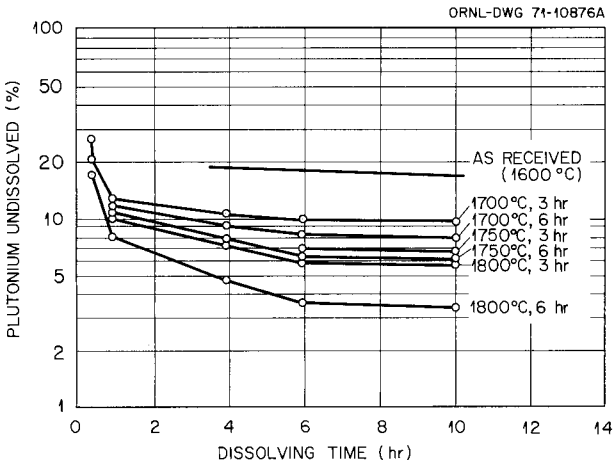

Fig. 2.4. Dissolution of heat-treated FTR pellets in boiling 8 *M* HNO_3.

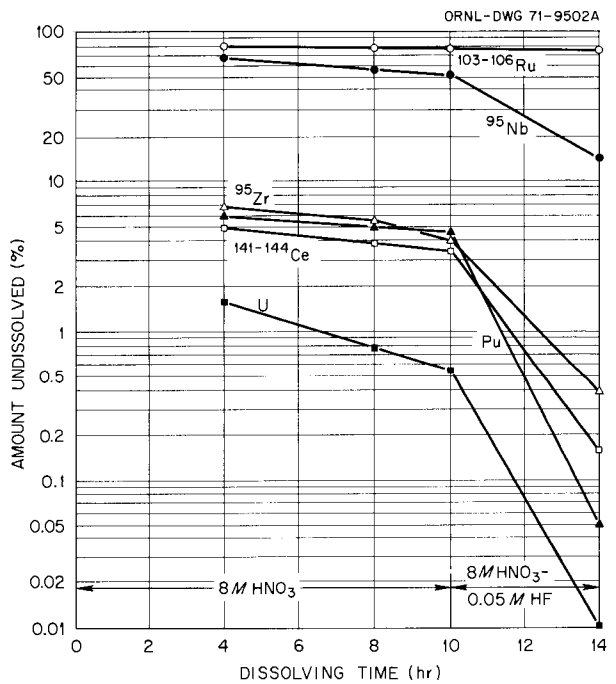

Fig. 2.5. Dissolution of mechanically blended 25% PuO_2–75% UO_2. The fuel, which was irradiated to ~2.5% FIMA and decayed 30 days, was subjected to two 4-hr and one 2-hr leaches in boiling 8 *M* HNO_3, followed by a 4-hr leach in boiling 8 *M* HNO_3–0.05 *M* HF.

Volatilization of Iodine from Feed Solutions

Removing essentially all of the iodine from the dissolver solution prior to solvent extraction is considered essential to the attainment of the very high processing plant retention factors for iodine that will be needed in processing short-cooled fuels. In tests with simple 4 *M* HNO_3–0.0004 *M* I_2 solution, removal of 95 to 98% of the iodine is usually obtained in the first 10% distillation fraction. Further removal of iodine, however, is extremely difficult, owing to the formation of a nonvolatile species that does not exchange isotopically with fresh carrier iodine.

Favorable results were obtained in dissolution experiments with short-cooled fuel that had been irradiated to about 20,000 MWd/ton. Less than 1% of the calculated yield of iodine was found in the dissolver solution at the completion of the dissolution step.[11] The dissolution system used in these experiments was designed to encourage removal of iodine from the system by minimizing reflux of solution to the dissolver.

2.5 OFF-GAS TREATMENT

The control and retention of the volatile fission products in off-gas systems is one of the major challenges in developing processing capability for LMFBR fuels. Our program is directed at understanding iodine behavior in the processing system and toward developing advanced systems for the removal of iodine from liquid and gaseous effluent streams. Systems for the evaluation and trapping of tritium are also under development, and a program aimed at selective adsorption of krypton from chemical plant off-gas is being expanded.

Tritium Removal

During this report period, we began studies[19,20,27] of methods for selectively removing tritiated water from the off-gases from head-end processing operations containing significant quantities of iodine.

Very selective removal of iodine from the moist air was obtained with the macroreticular resins Amberlite XAD-4 and XAD-12. Essentially all of the iodine and

27. *LMFBR Fuel Cycle Studies Progress Report for November 1971, No. 33,* ORNL-TM-3663.

very little of the water sorbed on the bed, yielding a decontamination factor (DF) for iodine, with respect to water, of $>1.7 \times 10^4$. The tritiated water can then be trapped on any common desiccant.

Selective sorption of tritiated water from the air stream was obtained with a molecular sieve (Linde 3A). The iodine DF achieved at 75°C was about 80. More efficient separation from iodine (a DF of 700) was obtained using Drierite (anhydrous calcium sulfate) as the sorbent at 25°C. In each case, the water was desorbed by passing air through the column at 120 to 130°C.

Scrubbing of Iodine from Off-Gas

Two efficient scrubbing systems for removing both massive quantities of elemental iodine and trace quantities of other iodine species are under development. One employs concentrated nitric acid in the range of 17 to 19 *M* at room temperature. All iodine species are oxidized by the nitric acid to iodate, which can be removed from the system as solid I_2O_5. Decontamination factors in the range of 10^4 for all iodine forms[28] appear feasible in either packed or bubble-cap scrubbers operating in the range of normal liquid and gaseous throughput rates. If the oxidizing potential of the scrubber is increased via the addition of ozone, a significant improvement in DF is obtained. Conversely, if the feed gas contains high concentrations of NO_2, some loss in DF results.

A second system,[12,22,27] which employs a mixture of nitric acid in the concentration range of 8 to 14 *M* and mercuric nitrate at concentrations of 0.2 to 0.4 *M*, provides essentially the same results as obtained in the concentrated acid system while avoiding the use of above-azeotropic acid. Use of a relatively high acid concentration overcomes the slow reaction kinetics encountered previously in tests at an acid concentration of 0.2 *M*. In the present version of the process, the scrub solution is circulated through the countercurrent scrub column in closed cycle. To remove accumulated iodine, a small fraction of the recycle stream is routed through an evaporator where the iodine is oxidized and concentrated. This results in the precipitation of mercuric iodate, which is withdrawn for storage. Measurements of the rate of reaction of methyl iodide with mercury in the aqueous phase showed that the reaction rate is directly proportional to the mercury concentration and increases by a factor of about 100 as the acid concentration is increased from 0.2 *M* to 13 *M*.

28. *LMFBR Fuel Cycle Studies Progress Report for March 1972, No. 37,* ORNL-TM-3807.

Tests to Determine the Life of Iodine Sorbents

Various iodine sorbents are being evaluated from the standpoint of performance after extended exposure to simulated process off-gas.[4,11,28,29] Air that contains ^{125}I-traced I_2 and small concentrations of dodecane and nitrogen oxide is passed continuously through the test beds. Periodically, the ability of the beds to trap methyl iodide is determined by injecting ^{130}I-traced methyl iodide into the system over a short period. Some of the test beds are preceded by a catalytic oxidation system[22,30,31] (containing Hopcalite catalyst at 350°C) to destroy organic vapors and prevent poisoning of the beds.

After 3 to 6 months of exposure, the silver zeolite (with either 25% or 99% silver-for-sodium exchange) and GX135 sorbents are still performing very efficiently (Table 2.1). The decontamination factors measured at the end of the designated period were $>10^4$ for methyl iodide and $>10^3$ for the continuously injected I_2. The performance of the beds that were protected by Hopcalite was only slightly better than that of the unprotected beds. The relatively poor performance of 88% silver zeolite is attributed to the large particle size of this material.

2.6 RADIATION, SHIELDING, AND CRITICALITY STUDIES

The studies of radiation properties and shielding requirements of LMFBR fuels involve correlation of basic nuclear data including decay schemes, neutron cross sections, energy spectra of radiation sources, and thermal power; development of computer programs for calculation of transient concentrations of radionuclides; calculation of shield attenuation kerma of shield materials of interest; and application of these data to LMFBR fuel cycle processes. The criticality studies include compilation and correlation of basic data, liaison with experimental groups, development and verification of computational techniques, and development of criticality parameters and control techniques for specific process applications. The objective of these

29. R. D. Ackley, "Life Cycle Tests of Silver Zeolites for Removal of Iodine Species from Off-Gases," to be presented at the 12th AEC Air Cleaning Conference, Oak Ridge, Tenn., Aug. 28–31, 1972; to be published in the *Proceedings.*

30. *LMFBR Fuel Cycle Studies Progress Report for March 1971, No. 25,* ORNL-TM-3375.

31. *LMFBR Fuel Cycle Studies Progress Report for June 1971, No. 28,* ORNL-TM-3487.

Table 2.1. Iodine decontamination efficiency of sorbents after exposure[a] to simulated process off-gas

Sorbent	Sorbent size	Temperature (°C)	Hopcalite[b] upstream?	Days of exposure	Decontamination factor for 2-in. depth	
					CH_3I[c]	I_2[d]
25% silver zeolite	1/16-in.-diam	200	No	196	$>10^4$	2×10^3
			Yes	196	$>10^4$	4×10^3
88% silver zeolite	1/8-in.-diam	200	No	196	2.2×10^2	2×10^2
			Yes	196	2.6×10^3	~90
99% silver zeolite	1/16-in.-diam	100	No	105	$>10^4$	3×10^3
			Yes	105	$>10^4$	4×10^3
GX135 (silver salt–alumina–silica)	−8 +16 mesh	100	No	119	$>10^4$	2×10^3
GX135	−8 +16 mesh	200	No	196	$\sim 2 \times 10^3$	2×10^3
			Yes	196	$>10^4$	4×10^3
Witco grade 42 iodized charcoal	−8 +16 mesh	66	Yes	196	$>10^4$	~2

[a]Exposure at the test temperature to flowing moist air that contained about 0.02 ppm of ^{125}I-traced I_2 and small concentrations of dodecane and nitrogen oxides; iodine loading of the beds at 196 days is estimated at about 5 mg per cm^3 of sorbent.

[b]Oxidizing catalyst bed operated at 350°C.

[c]^{130}I-traced methyl iodide injected over 10-min period; bed swept for 18 hr before counting the charcoal collection beds that followed the test beds.

[d]Decontamination factor over the total test period for the continuously injected ^{125}I-traced I_2.

studies is to provide basic nuclear data to support the design and development of the LMFBR fuel cycle.

During this report period, the ORIGEN code, which is widely used to compute the radiation properties of spent fuel, was evaluated and updated. The computed postirradiation properties of ^{235}U fuel irradiated in a thermal neutron spectrum were found to be in good agreement with the recommended values for these properties.[32] The computations were also found to be in excellent agreement with measured properties of ^{239}Pu that had been irradiated in the Dounreay Fast Reactor. Predictions were made of the postirradiation properties of plutonium fuels irradiated to high exposures in oxide-type LMFBRs.

A report that presents calculated criticality parameters of heterogeneous systems of mixed UO_2-PuO_2, water, and several neutron poisons was published.[33] These data, together with those for homogeneous systems that were published previously, are of value in the design of dissolvers, storage arrays, and shipping casks.

2.7 ENGINEERING STUDIES

Studies were continued to evaluate technological, safety, and economic aspects of the reprocessing of spent LMFBR fuels in an existing plant.[34] The difficulties associated with modifying such a plant to provide for short-cooled processing of LMFBR fuel, including the greatly enhanced effluent control which is required, lead to the conclusion that construction of new plants to satisfy these objectives would be more economical.

A method for calculating the time-dependent behavior of countercurrent solvent extraction processes has been applied to a dilute-Purex flowsheet proposed for use in the recovery of spent LMFBR fuels.[35] This effort led to the development of a computer program, SEPHIS, which employs a combination of approximate mathematical equilibrium expressions and the transient, stagewise process calculational method to allow the prediction of stage and product stream concentrations

32. M. J. Bell, *Radiation Properties of Spent Plutonium Fuels,* ORNL-TM-3641 (January 1972).

33. W. R. Cobb, *Calculated Criticality Data for LMFBR (U + Pu)O_2-Water Systems,* ORNL-4711 (January 1972).

34. C. D. Watson et al., *A Study of the Reprocessing of Spent Fast Test Reactor Fuel (and Other LMFBR Fuels) in the Nuclear Fuel Services Plant,* ORNL-TM-2906 (August 1971).

35. W. S. Groenier, *Calculation of the Transient Behavior of a Dilute-Purex Solvent Extraction Process Having Application to the Reprocessing of LMFBR Fuels,* ORNL-4746 (April 1972).

with accuracy and reliability. The applications of SEPHIS to process analysis and control, criticality analysis, and inventory control for nuclear safeguards purposes are particularly intriguing.

Processes for removing noble-gas fission products from nuclear reactors and fuel reprocessing plants, as well as possibilities for handling and disposal of the recovered gases, were reviewed and analyzed.[36] The two most promising separations processes are based on cryogenic distillation and absorption in fluorocarbons. Initially, the recovered noble gases will probably be collected in gas cylinders, shipped to a remote site, and stored under controlled conditions.

2.8 EFFLUENT CONTROL IN FUEL REPROCESSING PLANTS

The importance of protecting the environment from insult is becoming increasingly important in all areas of endeavor. This trend is necessitating a reevaluation of systems and philosophies of effluent control at reactor fuel reprocessing plants. In the near term, it will be desirable to have effluent control systems that will minimize the impact of all noxious effluents on the environment. In the future, the higher burnup and higher specific power of LMFBR fuels, coupled with a trend toward reduced decay times, will place stringent demands on effluent control systems. In order to meet the increasing demands imposed by higher input levels of radioactivity to future LMFBR plants, several advanced systems for the control and removal of activity in fuel reprocessing plant effluent streams are in various stages of development. A study was conducted to incorporate these specific removal systems into containment and operating philosophies directed at reducing the release of activity from the plant to "near zero." The objectives of the study are summarized as follows:

1. To define the major sources and distribution of fission products throughout the many process steps that make up a reprocessing plant.
2. To identify the optimum locations and required retention factors for various fission product removal systems, and to study the effects of such variables as off-gas flow rate, use of recycle cell air, and the efficiency of fission product control and removal systems on the retention factors.
3. To indicate areas where insufficient information is available to accurately predict the behavior of important fission products.

To achieve these objectives, a mathematical model of a reprocessing plant incorporating all the fission product control systems under consideration has been developed. The plant model includes subsystem models for 23 process steps and 8 cell enclosures. Twenty-two chemical and fission product constituents are followed throughout the plant. By varying inputs, a wide variety of conditions and assumptions can be studied.

A simplified flowsheet of the system retaining only the detail that is necessary to illustrate important effluent control steps is presented in Fig. 2.6. Tritium, krypton, and iodine are evolved in head-end operations and routed to their respective primary removal systems. The total cell off-gas and equipment off-gas beyond dissolution and feed adjustment is treated in a secondary off-gas treatment system, which includes filters for particulates and scrubbers for nitrous oxides, iodine, and ruthenium. Part of the output from this system is recycled, while the excess receives additional treatment

36. J. P. Nichols and F. T. Binford, *Status of Noble-Gas Removal and Disposal,* ORNL-TM-3515 (August 1971).

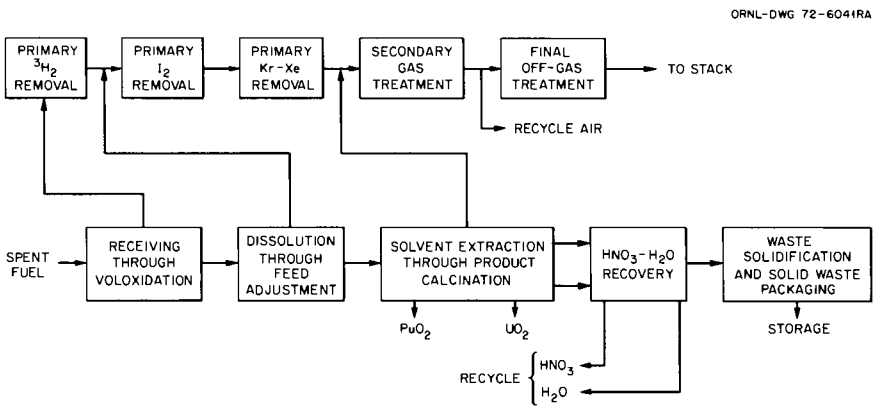

Fig. 2.6. Schematic diagram showing the steps required for the "zero release" reprocessing concept.

for removal of particulates, iodine, tritium, and krypton before being released to the atmosphere.

Results of the study indicate that very high fission product decontamination factors can be obtained in future plants, providing the advanced removal systems currently under development have the expected operating characteristics and providing the systems can be incorporated into operating and containment designs which limit total plant gaseous and liquid effluents to very low volumes.

3. Development of Methods for Reprocessing HTGR Fuels

The reprocessing of HTGR fuels requires the burning of graphite blocks containing coated fuel particles in the form of fuel sticks. Our studies have primarily consisted of hot-cell tests with irradiated HTGR fuel specimens, development of burner technology using unirradiated fuel, and development of methods for decontaminating the burner off-gas. We have also provided assistance relative to the planning of HTGR fuel reprocessing at the Idaho Chemical Processing Plant in the areas of overall equipment flowsheets, layouts, and cost information.

3.1 HEAD-END REPROCESSING STUDIES WITH UNIRRADIATED FUEL

Preparation of feed for the burner. Several techniques were investigated as alternatives (to crushing and sieving) for separation of either fuel sticks from fuel blocks or fuel particles from fuel sticks. Intercalation with fuming HNO_3 was tested, since earlier work had shown that pyrolytic carbon particle coatings were immune to its attack.[1] Fort St. Vrain fuel block graphite[2] was readily disintegrated by the reagent at room temperature, while Fort St. Vrain fuel sticks were unaffected. (However, other fuel sticks with different bondings did disintegrate.) Although a process could be developed for separating Fort St. Vrain fuel sticks from the block graphite, the economics of disposing of the waste graphite and acid, together with the probable inability of such a process to handle other types of fuel sticks and block graphite, discouraged further development efforts involving this approach. Removal of the fuel stick by means of fluted and spade drills was also investigated. The drilling rate was satisfactory (~2 ft/min with Fort St. Vrain fuel rods); however, particle coating breakage was high, ranging from 10 to 20% for either fertile or fissile particles. Also, the mechanical complexities of gang drilling the 210 fuel holes in a Fort St. Vrain fuel block appear formidable. In other tests, high-pressure steam oxidation and pressurized aqueous combustion techniques were evaluated, but neither gave satisfactory separations. In summary, no significant advantages over crushing the entire block to prepare burner feed were noted.

Burner technology. The HTGR head-end reprocessing flowsheet could be greatly simplified by burning intact or whole fuel blocks. A burner capable of holding one-sixth of a Fort St. Vrain fuel block was designed, built, installed, and tested. Studies are being made to determine burning rates, oxygen utilization, block temperature, heat removal, off-gas composition, particle breakage, and burner ash removal. The data obtained will permit evaluation and comparison of the whole-block burner concept with the current crush-burn flowsheet.

Waste handling. Studies to define the problems involved in handling and disposing of the waste streams generated during the proposed radioactive demonstration of the HTGR fuel reprocessing and refabrication facility to be carried out at the Oak Ridge National Laboratory under the National HTGR Recycle Development Program were completed. The waste streams generated by the Head-End, Acid Thorex, and Refabrication Pilot Plants were identified; the processes and facilities necessary to prepare this waste for disposal were determined; and an order-of-magnitude estimate of the cost of building these facilities was made.[3] (It should be noted that the decision has now been made to carry out the fuel reprocessing demonstration at Idaho Chemical Processing Plant.)

1. L. M. Ferris, A. H. Kibbey, and M. J. Bradley, *Processes for the Recovery of Uranium and Thorium from Graphite Based Fuel Elements, Part II,* ORNL-3186 (Nov. 16, 1971).

2. Type H-327 graphite, manufactured by Great Lakes Carbon Corp.

3. R. S. Lowrie, *Study of the Waste Handling Requirements for the HTGR Fuel Recycle Development Program,* ORNL-TM-3597 (March 1972).

3.2 HEAD-END REPROCESSING STUDIES WITH IRRADIATED FUEL

The hot-cell studies with irradiated fuel samples are an important part of the HTGR head-end development work. These studies allow us to compare the results for irradiated material with those obtained in "cold" engineering studies, and to determine the distribution of the fission products in the various streams generated by each step in the reprocessing flowsheet. We are particularly interested in the fission products that find their way into the off-gas stream since decontaminating this stream involves developing processes which are unique to the HTGR fuel reprocessing plant.

Irradiated compacts from the Dragon project. A second set of irradiated fuel compacts and unirradiated controls was obtained through the courtesy of the Dragon project. We have completed experimental work on the unirradiated controls and on three types of irradiated compacts: 2M4, which contains BISO-coated mixed oxide fuel; 19M, which contains a combination of large TRISO-coated thorium carbide particles and smaller TRISO-coated uranium carbide particles; and 413-7-22, which contains BISO-coated sol-gel oxide particles prepared at ORNL. (TRISO coatings consist of a porous carbon buffer layer on the fuel kernel, a thin sealer layer, and two isotropic pyrocarbon layers separated by a silicon carbide layer; BISO coatings consist of a porous carbon buffer layer on the fuel kernel, a thin sealer layer, and an outer isotropic pyrocarbon layer.) Preliminary results from the data analysis (which is still in progress) have been published;[4] a summary of the fission product distribution results obtained to date is given below.

Similar experiments were made with the 2M4 compacts and with 413-7-22. In each case, the compact was crushed and then separated into two samples which were burned in replicate experiments, and the burner residues were leached. Only the krypton and tritium release data from the compact with sol-gel-derived oxide (413-7-22) are available. The bulk of the ^{85}Kr (97 to 98%) and the tritium (98 to 99%) was released during the burning step; the remainder reported to the leach solutions.

A different experimental procedure was used for the 19M compact. First, the compact was crushed; then it was divided into two samples, which were burned in replicate experiments. The burner residue from each experiment was divided into a +20-mesh (>841-μ) fertile fraction, a +42-mesh (>400-μ) fissile fraction, and a −42-mesh fines fraction. Each fraction was ground, burned, and the residue leached. Material balances for the experiments averaged 96.2%. Only data from the R-2 test are available. In this test, about 7% of the ^{85}Kr was released during the initial burning. Leaching the −42-mesh fines fraction released about 0.6%. Most of the ^{85}Kr associated with the +20-mesh fertile fraction (i.e., ~7.5%), was released during the grind, roast, and burn steps for the fertile fraction. Essentially all the remaining ^{85}Kr (84.6%), which was associated with the +42-mesh fissile fraction, was released during the grind, roast, and burn steps for the fissile fraction. In each test, less than 0.1% was left in the ash.

Experiments with irradiated recycle test elements. As part of a cooperative program between ORNL and Gulf General Atomics, several recycle test elements (RTEs) are being irradiated in the Peach Bottom reactor. Most of the various types of fuel particle combinations proposed for HTGR fuel are included in this series.[5,6] During the year, RTE-7 became available for experiments. It had been irradiated for 252 effective full-power days and allowed to cool for 210 days when we started the experiments. Although RTE-7 contained several types of fuel, we chose to study type *i*, which contained large TRISO-coated ThC_2 particles and smaller TRISO-coated UC_2 particles. The fuel stick weighed 10.8 g and contained approximately 2.2 g of thorium and 0.6 g of enriched ^{235}U.[7] The experimental procedure used was to burn the entire stick using a low oxygen flow rate (quiescent burn). The burner residue was separated into a +42-mesh (>400-μ) fertile fraction, a +80-mesh (>177-μ) fraction, and a −80-mesh (<177-μ) fraction consisting mostly of the Al_2O_3 bed on which the fuel stick was placed. The fissile and fertile fractions were ground and burned, and the residue was leached twice with Acid Thorex reagent. The +80-mesh fraction was roasted at 750°C for 12 hr after the initial active burn period to determine if additional fission products would be evolved. The off-gases passed, first, through two sintered nickel (porosity, 20 μ) primary filters and, then, through a series of fiber filters with decreasing porosities. The filtered off-gas was scrubbed successively with boiling 6 *M* HCl and cold 4 *M* NaOH; subsequently it was dried, analyzed (for ^{85}Kr, CO, and

4. *GCR-TU Programs Annu. Progr. Rep. Sept. 30, 1971*, ORNL-4760 (in preparation).

5. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, pp. 92–94.

6. R. P. Marissitte and K. P. Steward, *Recycle Test Element Program Design, Fabrication and Assembly*, GGA-10109 (September 1971).

7. R. P. Marissitte and K. P. Steward, *Recycle Test Element Program Design, Fabrication and Assembly*, GGA-10109 (September 1971), p. 68.

CO_2), and collected. This rather elaborate off-gas train was devised to study the carryover of particulates in the off-gas during the burning step. Figure 3.1 shows the flowsheet used and the material balance results obtained with the RTE-7 (3,8,4) experiment. Analysis of the results is in progress; only the tritium and ^{85}Kr release data are available at this time (Table 3.1).

About 20% of the tritium and 0.2% of the krypton were released during the initial burn period. Most of the tritium and ^{85}Kr associated with the fertile (+42-mesh) fraction (i.e., ~99.98% of the tritium and ~95.8% of the ^{85}Kr in that fraction) were released during the grind and burn operations; about 97.4% of the total ^{85}Kr was associated with the fissile (+80-mesh) fraction, and 98.3% of that was released during the burn and grind operations. A different and surprising release pattern was observed for tritium from the fissile (+80-mesh) fraction. About 85.5% of the tritium in the

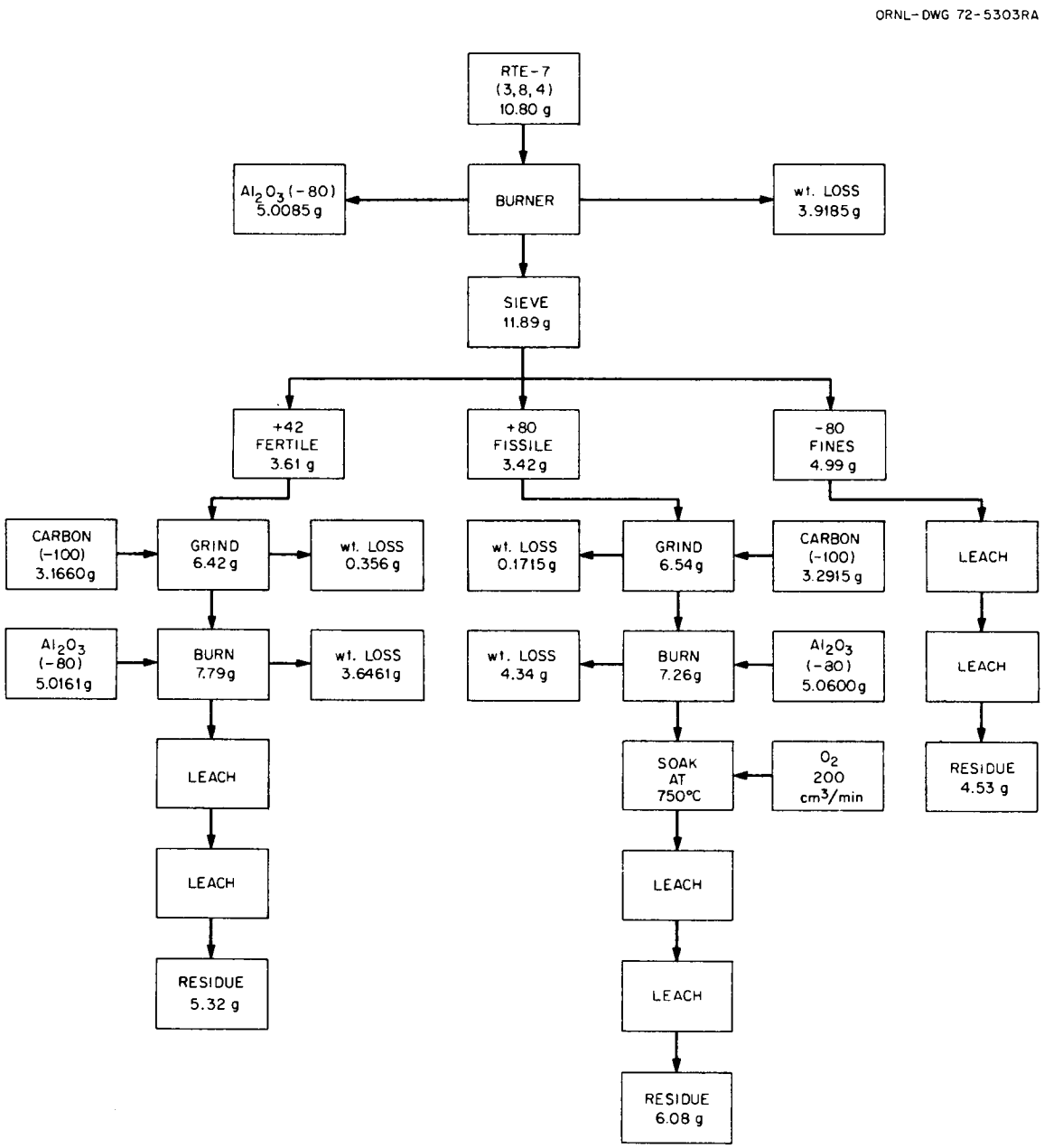

Fig. 3.1. Flowsheet used for fuel stick RTE-7 (3,8,4).

Table 3.1. Fission gas release for RTE-7 (3,8,4) hot-cell test

Operation	Percent of total ^{3}H released	Percent of total ^{85}Kr released
Initial burn	20.562	0.135
Fertile (+42-mesh) fraction		
Grind	33.771	1.263
Burn	2.685	0.989
Leach	0.008	0.106
Total	36.464	2.358
Fissile (+80-mesh) fraction		
Grind	1.431	70.072
Burn[a]	4.594	25.696
Soak[b]	35.803	1.565
Leach	0.042	0.091
Total	41.870	97.424
Fines (−80-mesh) fraction		
Leach	1.104	0.083

[a]Three-hour active burning period.
[b]Held for 12 hr at 750°C after completion of burning.

fissile fraction was released sometime during the 12-hr-long 750° soak period following the grind and burn operations. Since the tritium release during grinding is measured separately and the entire off-gas train downstream of the primary filters was replaced between the burn and soak steps, the release pattern seems to be real. We intend to recheck these values as soon as the hot cells have been renovated and experimental work can be resumed.

3.3 ENGINEERING STUDIES OF BURNER OFF-GAS DECONTAMINATION

The burner off-gas produced during the reprocessing of spent HTGR fuel blocks is, on the average, predominantly composed of CO_2 (>90%), with varying amounts of light gases such as O_2, N_2, and CO. The contaminants are principally (~100 ppm) krypton and xenon but also include particulates containing $^{89,90}Sr$, alpha emitters, iodine, and tritium. It is important to note, however, that during the various parts of the burner cycle (e.g., startup and burning after particle grinding) the off-gas composition and impurity levels will differ greatly from the average values.

Separation of the krypton from both the lighter gases and the CO_2 poses a unique decontamination problem. Several processes commonly employed or suggested for noble gas retrieval have been reviewed[8] for possible application in the burner gas cleanup, but certain similarities in behavior of krypton and CO_2 preclude their use. Specifically, membrane permeation, sorption on charcoal and molecular sieves, and selective physical absorption by a third component have proved to be unsuitable. Considerations of quantity and composition of the gas to be treated also rule out such processes as thermal diffusion, hot-metal trapping, and certain kinds of chemical reactions.

Of the processing schemes considered, four appear to have potential usefulness for effecting the desired separation. Three of these use the CO_2 produced in the burning operation as the separation medium. The remaining one uses a carbonate salt (K_2CO_3). In order of our preference, the four processes are: (1) *K*r *A*bsorption in *L*iquid *C*O_2 (KALC), (2) controlled solidification of CO_2, (3) aqueous hot potassium carbonate sorption of CO_2, and (4) simple distillation of liquid CO_2. Only the KALC process accomplishes the separation of krypton from both the less-volatile CO_2 and the more-volatile O_2 and N_2.

The KALC system requires three separations: the absorption of krypton from the burner off-gas by liquid CO_2, the fractionation of gases coabsorbed with the krypton, and finally, the stripping of the absorbed krypton from the liquid CO_2 to give a concentrated krypton product. The flow of liquid CO_2 should be sufficiently large to absorb more than 99.9% of the krypton entering the process but not large enough to coabsorb an excessive quantity of the lighter gases. During fractionation, the gas flow must be sufficiently large to provide adequate removal of the lighter gases but small enough to minimize the recycle of krypton. In the stripping operation, the krypton and any remaining light gases are discharged as a concentrated gas stream, and part of the purified liquid CO_2 is recycled as fresh solvent to the absorber system. Decontaminated liquid CO_2 in excess of that required as solvent is discharged.

Idealized calculations show that, to achieve a decontamination factor of 1000, the towers for each of the three separations will require from 10 to 15 theoretical stages when the KALC system is operated at a pressure of 20 atm. Corresponding system temperatures range from −45 to −20°C. Experimental vapor-liquid data for the components of interest are rather limited; however, efforts to combine and extend these data into a form suitable for use in equipment design are progressing.

8. R. W. Glass, P. A. Haas, R. S. Lowrie, and M. E. Whatley, *HTGR Head-End Processing: A Preliminary Evaluation of Processes for Decontaminating Burner Off-Gas,* ORNL-TM-3527 (in press).

The Rare Gas Removal Pilot Plant[9] at the Oak Ridge Gaseous Diffusion Plant (ORGDP) was used to explore the operability of a KALC system. The initial campaign was designed to provide experience necessary for subsequent KALC system development. Although not designed for KALC-type operations, the ORGDP system provided a means of qualitatively evaluating the major operations of the KALC process such as CO_2 liquefaction, fluid-vapor behavior, and partial condensation. Areas that will require careful study for KALC system development were noted.

In addition to demonstrating the feasibility of the KALC process, the initial pilot campaign suggested that the KALC process will serve as an attractive means of removing krypton from the burner-type off-gases. Moreover, literature data[10,11] on the solubilities of water (tritium) and iodine in liquid CO_2 indicate that these contaminants also may be removed from the off-gas using distillation.

3.4 LABORATORY STUDIES OF BURNER OFF-GAS DECONTAMINATION

The major effort in the laboratory studies of burner off-gas decontamination has been to obtain gas-liquid (G/L) separation factors for krypton in liquid CO_2. This information is needed for engineering design and evaluation of the KALC process (see Sect. 3.3). Other work has involved literature searches with regard to the related problems of radiolysis of CO_2, the solubilities of iodine and water in liquid CO_2, and the solubility of krypton in water.

An apparatus for obtaining data on the distribution of krypton between gaseous and liquid CO_2 based on in situ counting of ^{85}Kr was built (Fig. 3.2). The results of our in situ determinations are summarized in Fig. 3.3. Thirty-one values were measured, spanning the entire liquid range of CO_2. Counting of ^{85}Kr was done at two energy levels: >40 and >400 keV. These two sets of results agreed very well after corrections were made for varying internal attenuation due to the different CO_2 densities. On selected samples, it was shown that equilibrium was attained within the 90 min allowed to elapse before readings were taken; this was done by approaching a particular temperature from temperatures both above and below, and by taking readings over an extended period of time. The calculated curves are also shown in Fig. 3.3. Those based on assumed ideality (i.e., Raoult's and Dalton's laws) reflect the use of different extrapolation functions to estimate the vapor pressure of krypton above its critical pressure. Subsequently, more refined calculations were carried out, allowing for nonideality in both phases.[12] Some data obtained at KFA Jülich were also made available to us.[13] The Jülich data fall close to the

9. M. J. Stephenson et al., *Experimental Investigation of the Removal of Krypton and Xenon from Contaminated Gas Streams by Selective Absorption in Fluorocarbon Solvents: Phase I Completion Report,* K-1780, Oak Ridge Gaseous Diffusion Plant (Aug. 17, 1970).

10. H. W. Stone, *Ind. Eng. Chem.* 35(12), 1284 (1943).

11. E. L. Quinn, *J. Amer. Chem. Soc.* **50,** 672 (1928).

12. W. Davis, Jr., *Calculated Liquid-Vapor Equilibria in the Systems CO_2-Xe and CO_2-Kr at −55 to +5°C,* ORNL-TM-3622 (December 1971).

13. KFA Jülich, *Reprocessing of Thorium-Containing Nuclear Fuels, Progress Report for Second Half 1970* (February 1971), pp. 67–71.

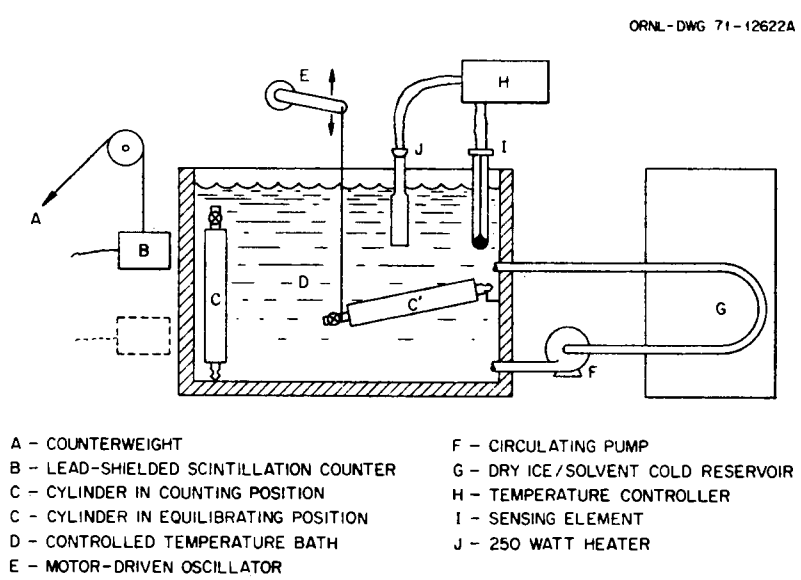

Fig. 3.2. Apparatus for in situ measurement of ^{85}Kr in CO_2 liquid and gas.

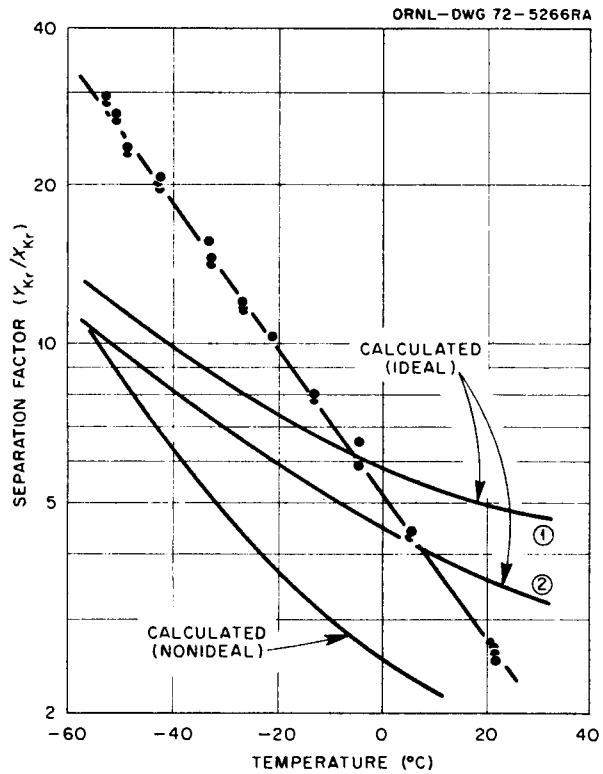

Fig. 3.3. Solubility of krypton in liquid CO_2. Curves 1 and 2 differ in the choice of extrapolation for krypton vapor pressure above its critical pressure.

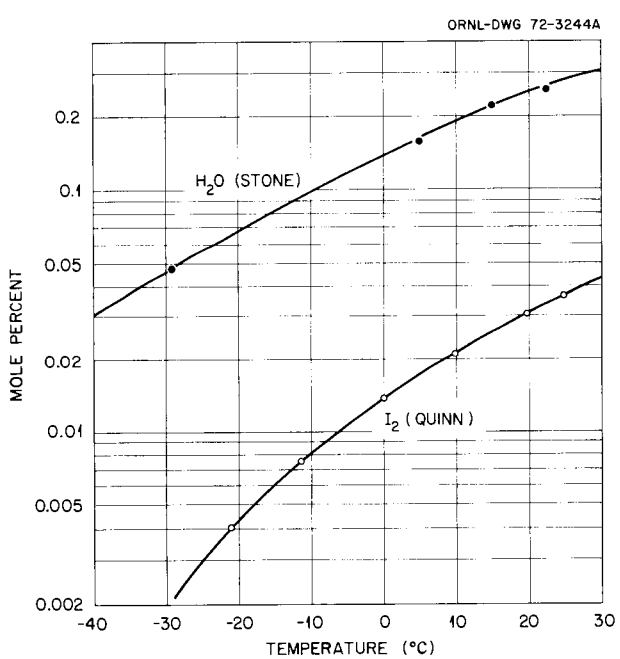

Fig. 3.4. Solubilities of H_2O and I_2 in liquid CO_2.

calculated nonideal curve but rise above it below 0°C. The experimental work will be discussed in papers to be presented at the 1972 national meeting of the American Nuclear Society[14] in Las Vegas, Nevada, and at the 12th AEC Air Cleaning Conference[15] at ORNL in August 1972.

An alternative method being considered for ^{85}Kr separation is the aqueous hot carbonate process, in which CO_2 is removed from the off-gases by catalyzed chemical sorption under pressure in K_2CO_3 solution at about 120°C. The fraction of krypton dissolved during this step will determine the number of sorption-desorption cycles required to achieve the desired decontamination. A compilation of literature data and references on krypton solubility in aqueous systems is given in ref. 16. In summary, it can be stated that all factors – the temperature dependence, the effect of alkaline solutes, and the diluting effect of the light gases (O_2, N_2, and CO) which are also present – tend to work in a favorable direction (i.e., toward a low krypton solubility). Experimental measurements are planned, using the equipment described above for the Kr-CO_2 system.

The KALC process for separating krypton from CO_2 may also provide a means of separating tritium (as ^3H_2O) and radioiodine. G/L separation factors were calculated by using literature values for the solubilities of H_2O and I_2 in liquid carbon dioxide[10,11] (Fig. 3.4) and assuming ideality in the gas phase and saturation in the liquid phase. These results are favorable for removal of both iodine and ^3H_2O, particularly at lower temperatures. At 0 and −40°C, the factors for water are 7 and 24 respectively; the corresponding factors for iodine are 110 and 330.

The KALC process removes oxygen from CO_2 at an early stage, thereby preventing the radiolytic formation of ozone. (Any buildup of ozone is potentially hazardous, due to the large release of energy that occurs when ozone reverts to molecular oxygen.) However, radiolysis

14. R. W. Glass, A. B. Meservey, P. A. Haas, J. W. Snider, K. J. Notz, M. E. Whatley, and R. S. Lowrie, "Removal of Krypton from the HTGR Fuel Reprocessing Burner Off-Gases," to be presented at the Annual Meeting of the American Nuclear Society, Las Vegas, Nev., June 1972; abstract to be published in the *Proceedings*.

15. M. E. Whatley, R. W. Glass, P. A. Haas, A. B. Meservey, and K. J. Notz, "Decontamination of Reprocessing Off-Gases. Part I – Engineering Aspects of Liquid CO_2 Scrubbing. Part II – Solubility of Krypton in Liquid CO_2," to be presented at the 12th AEC Air Cleaning Conference, Oak Ridge, Tenn., August 1972; to be published in the *Proceedings*.

16. *GCR-TU Programs Annu. Progr. Rep. Sept. 30, 1971*, ORNL-4760 (in press), Sect. 1.8.

in ^{85}Kr-CO_2 mixtures might still constitute an ozone hazard. Using the best available data[17] and reasonable estimates of concentrations and exposure times, it was calculated that a buildup of ozone would be of no consequence in KALC-type equipment but would pose a potential problem in long-term ^{85}Kr storage cylinders. This problem could be circumvented in three ways: (1) by complete removal of CO_2, (2) by addition of an ozone decomposition catalyst, or (3) by storage above 300°C, the upper limit of the thermal stability of ozone.

17. D. L. Baulch, F. S. Dainton, and R. L. S. Willix, *Trans. Faraday Soc.* **61**, 1146 (1965).

4. Waste Treatment and Disposal

4.1 RADIOACTIVE WASTE REPOSITORY

We continued our participation in the various phases of the Salt Mine Repository Project, particularly those concerned with the conceptual design, safety analysis, and experimental studies of alpha waste characteristics and isotope migration in crushed salt. Drafts of a conceptual design report (CDR) and a preliminary safety analysis report (PSAR) were prepared for review; however, questions concerning the suitability of the Lyons-Carey site have resulted in a redefinition of this Project's near-term objectives. A decision has recently been made to construct a pilot-plant repository for only high-level wastes at a new site yet to be selected. Two reports (a CDR and a PSAR) and an environmental impact statement for this pilot plant will be prepared during the forthcoming year.

Thermal Stability of Alpha Wastes

A series of heating tests was carried out to study the oxidation and pyrolysis of typical combustible solid wastes in combustible and noncombustible containers at temperatures up to 215°C.[1] A mixture of 75 wt % cellulosic materials and 25 wt % thermoplastic material was selected to simulate alpha-contaminated combustible wastes. In some tests, CaO was added to the waste to serve as a getter for the water, CO_2, and other acidic gases evolved during limited oxidation and pyrolysis. The measured weight losses ranged from about 2% at 145°C to about 4% at 160°C, and to about 12% at 200°C. The pressures attained in the sealed noncombustible containers (steel drums) were about 7 to 36 psi greater than expected from expansion of the original air in the drum. The pressures that developed after addition of CaO were less than those predicted from expansion of air in the drum. The combustible containers did not ensure against the entrance of air to the waste or prevent the release of smoke and fumes.

The general conclusions drawn from these tests were: (1) combustible wastes in combustible containers should not be accepted at a repository; (2) combustible wastes sealed in noncombustible containers, such as DOT 17C and 17H specification metal drums or the equivalent, should be acceptable at a final repository; and (3) the quantity of gases evolved during heating of these wastes can be reduced substantially by adding a getter such as CaO.

Isotope Migration in Crushed Salt

We are currently performing a series of experiments designed for studying the conditions to which solid wastes containing fission products or actinides would be subjected during exposure to crushed salt backfill. In the studies of wastes containing fission products, two 4-in.-ID by 40-in.-high Inconel columns, each positioned within a furnace, are used to hold the crushed salt and simulated waste tagged with appropriate radioactive tracers. In the initial experiments, calcined waste containing ^{137}Cs in one setup and ^{106}Ru in the other was placed at about the midplane of a column of crushed salt, and the column was then positioned within its furnace. Each column contains about 12 kg of crushed salt and about 68 g of calcined waste tagged with 1 mCi of ^{137}Cs or ^{106}Ru tracer. About 50 ml/min of air is passed through the columns, which are held at about 300°C. In the studies of wastes containing actinide elements, the experimental apparatus is identical in concept but consists of four 2-in.-ID by 11-in.-high plastic columns, each loaded with about 700 g of crushed salt and 6 g of plutonium. Initial tests with these columns are being carried out at ambient temperatures.

The transport of isotopes up or down a given column is monitored by scanning the column for cesium and ruthenium using a detector (crystal) encased in a lead

1. H. W. Godbee, *Spontaneous Combustion, Oxidation, and Pyrolysis of Combustible Solid Wastes Containing Transuranium Elements in Combustible and Noncombustible Containers*, ORNL-4768 (May 1972).

collimator and shield; plutonium is followed by using a Geiger-Müller survey meter. The results show that, after about 4 months of exposure for cesium and ruthenium and about 3 months for plutonium, no transport of activity through the crushed salt has occurred.

4.2 ENGINEERING, ECONOMIC, AND SAFETY EVALUATIONS

During the past year, studies were completed on a parametric analysis of high-level waste shipping casks, the management of spent fuel cladding, and the long-term hazard of wastes from the thorium, uranium, and plutonium fuel cycles.

In view of the present requirement that the high-level liquid wastes generated by the reprocessing of spent fuels be solidified for eventual shipment to a federal repository, a study was made of the design features of casks for shipping solid wastes that are encapsulated in cans 6 to 24 in. in diameter by 10 ft long.[2] Lead, iron, and depleted uranium were investigated as shielding materials, and casks were designed to dissipate the decay heat via conduction and radiation by using internal metal inserts and external circumferential fins. Data were presented from which economically optimal designs could be specified, based on the number and diameter of waste cans per shipment and on the age and concentration of the radioisotopes within the waste solids.

The plutonium (several hundredths of a percent) that is associated with the metal cladding of spent reactor fuels will probably necessitate the future storage of such cladding in a federal repository. Results of a study of the design parameters for packaging, interim storage, shipment, and disposal of this waste material in the proposed salt mine repository indicated that economic considerations favor compacting the hulls as densely as possible, packaging them in 9-in.-diam cylindrical containers, and shipping them to the repository without interim storage at the reprocessing plant.[3] The minimum total costs for their management in this fashion (excluding the cost of compaction) were estimated to be 0.004 mill/kWhr(e) for LWR cladding and 0.009 mill/kWhr(e) for LMFBR cladding. Estimates show that, by the end of this century, 69,000 ft^3 of compacted cladding containing 3200 kg of plutonium will have accumulated and a total of 112 acres of salt-mine area will be required for its burial.

The hazards of high-level and alpha wastes produced by reprocessing typical LWR, LMFBR, and molten-salt breeder reactor fuels were computed for times as long as 30 million years after reactor discharge.[4] It was found that the volumes of water required for dilution to levels specified in the radiation concentration guides (RCG) for ingestion were similar for high-level wastes generated by the reprocessing of enriched uranium, Pu-^{238}U, and ^{233}U-Th fuels when evaluated at the same age and exposure. The volume of water necessary to dilute any of these wastes aged 1000 years (and the associated salt in the proposed federal repository) to RCG levels is less than that required to dilute an equivalent amount of uranium ore tailings to the RCG. The high-level wastes deposited in the repository will result in an alpha activity of less than 10 μCi/kg at 10,000 years after burial, when averaged over the total mass of the repository.

4.3 COMBUSTION OF PLUTONIUM-BEARING SOLID WASTES

The problem of reducing the volume of combustible radioactive wastes has assumed added importance as plans for long-term storage are reviewed. Although compaction and conventional incineration have been and are being used, each of these approaches exhibits significant disadvantages when compared with a process called wet-air oxidation, or pressurized aqueous combustion (PAC).

The broad programmatic objectives of the Plutonium Burning Program include a complete study of chemical and engineering problems and an evaluation of economic parameters associated with the PAC process. Specific objectives are: (1) to develop a suitable PAC unit, (2) to develop an efficient off-gas purification scheme, and (3) to determine appropriate methods for containment, operation, and remote maintenance of the resulting system. The chemical feasibility of the process has already been established.[5,6]

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2. J. J. Perona and J. O. Blomeke, *A Parametric Study of Shipping Casks for Solid Radioactive Wastes*, ORNL-TM-3651 (February 1972).

3. J. O. Blomeke and J. J. Perona, *Storage, Shipment, and Disposal of Spent Fuel Cladding*, ORNL-TM-3650 (January 1972).

4. M. J. Bell and R. S. Dillon, *The Long-Term Hazard of Radioactive Wastes Produced by the Enriched Uranium, Pu-^{238}U, and ^{233}U-Th Fuel Cycles*, ORNL-TM-3548 (November 1971).

5. Walter E. Clark, *The Status of Pressurized Aqueous Combustion for Burning Solid Wastes Contaminated by Radionuclides*, ORNL-TM-3170 (October 1970).

6. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, pp. 105–9.

The PAC process was used to gather combustion data for a simulated waste consisting of a mixture of blotter paper, cheesecloth, polyethylene, and rubber over a temperature range of 225 to 285°C (437 to 545°F), with system pressures between 800 and 1525 psig and air flow rates of 2.0 to 10.1 std liters/min.[7] Combustion rates of 0.67 to 2.26%/min, based on the potassium dichromate method of analysis for determining the chemical oxygen demand (COD) of the effluent, were obtained. Volume reduction factors were conservatively estimated to be >120. Oxidation in the range of about 85 to 95% was usually sufficient to burn or solubilize practically all of the combustible material.

Before work on the Plutonium Buring Program was suspended, 15 experiments were performed in which fairly consistent results were obtained. Seven of these experiments were conducted after the equipment had been modified by addition of a reflux condenser to the off-gas line. In each case, the same diffuser–draft tube combination was used for contacting and mixing purposes.

Results indicate that the reaction as carried out in the experimental equipment is mass transfer controlled. The addition of a reflux condenser permitted operation at pressures nearer the vapor pressure of water at the temperatures of interest, and also improved the quality of the effluent. More data to determine the effects of refluxing and of the addition of chemicals for pH control on combustion rates are needed.

The PAC process produces acid effluents unless an alkali or a suitable buffer is added to maintain a slightly basic pH.[5,6] Considering the selection of the proper materials of construction, such an adjustment will be especially important when the waste includes appreciable quantities of materials such as PVC, Tygon, and Neoprene. Evaluation of materials of construction for service in the hot, aqueous, chloride-containing environment likely to exist in the PAC reactor is, therefore, of critical concern.

The potential of the PAC process lies in its unique attractiveness as a solution to two of the most important problems associated with the long-term storage of radioactive wastes – safety and economics. PAC not only provides a solution to the problem of safely storing combustible wastes but also produces cost savings as a result of the large volume reduction factors attainable with this process.

A simplified economic analysis[7] revealed that the effective life of the Alpha Waste Storage Facility of the proposed National Radioactive Waste Repository could be extended by as much as 30 years by using the PAC process to burn the combustible portion of the waste received there. It was estimated that a PAC system for this purpose would produce an actual present-worth net saving of about $9.7 million, based on a unit waste storage charge of $5/ft^3; a present-worth cost of about $1.4 million was projected, based on an incremental operating cost for the facility of $2.64 per cubic foot of waste storage volume. The "break-even" point for the necessary PAC system occurs at a cost of about $3 per cubic foot of waste storage space.

Exploiting the potential of the PAC process makes possible additional savings not included in the above analysis. Smaller PAC units, located at or near sources of waste generation such as fuel reprocessing plants or nuclear "power parks," would reduce shipping costs significantly. In addition, the PAC process offers the possibility of recovering and recycling plutonium that might otherwise be buried. The compact physical form of the waste residue resulting from combustion in a PAC system would also facilitate retrieval of the waste from its storage place, thereby reducing the cost of this operation, if it should become necessary.

At the time work on the Program was suspended, planning was in progress for the assembly of a low-cost, short-term engineering experiment to study feed-slurry pumping characteristics and the operation of a small (about 20-gal) continuous reactor. This experimental arrangement was to become the core of a unit-operations-scale demonstration plant capable of handling 0.1 ton of combustible waste per day, if operated on a continuous basis. The goal of this plant is the attainment of the programmatic objectives listed above.

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7. W. C. Ulrich, *Plutonium Burning Program Status Report*, ORNL-TM-3799 (July 1972).

5. Transuranium-Element Processing

The Transuranium Processing Plant (TRU) and High-Flux Isotope Reactor (HFIR) are operated at ORNL as the primary production facilities for the USAEC Heavy Element Program. During this period, the sixth year of operation of these facilities, efforts at TRU included the recovery of 300 mg of ^{252}Cf for the commercial sales program sponsored by the Production Division in addition to the recovery of transuranium elements for the research program.

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 the Transuranium Processing Plant (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 purpose of this section is 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 approximately 75 mg of ^{252}Cf was recovered. The californium and the associated transuranium elements (americium through fermium) were distributed to researchers. Last year, the scope of processing operations was expanded considerably. The TRU operations group was increased by about one-third in order to process 164 curium slugs that had been irradiated as part of the Californium-I program at the Savannah River Plant (SRP), a Production Division program to evaluate the commercial market for ^{252}Cf. This year, operations continued at the expanded level; and, as before, the increased operating costs were borne by the AEC's Production Division.

TRU's primary role as supplier of research materials has continued throughout this report period. Shipments to researchers throughout the country continue to average about 100 annually.

Production and Processing

Five processing campaigns (3 tubes per campaign) were made to recover californium from 15 irradiated, plutonium-aluminum SRP reactor tubes, and two processing campaigns were made to recover transuranium elements from 19 irradiated HFIR targets.

About 300 mg of ^{252}Cf was recovered from the reactor tubes for the Production Division program. The by-product materials, 39 mg of ^{249}Bk, 6 μg of ^{254}Es (a rare isotope even by transuranium-element standards), and 30 g of plutonium (especially valuable because it contains 25% ^{244}Pu), were made available for research use.

The processing of the materials made available by the Californium-I program was interrupted twice so that HFIR targets could be processed in order to produce materials required for research. Nine HFIR targets were processed in one campaign, and ten in a second campaign. The total amounts of transuranium elements

1. 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).

2. W. D. Burch, J. E. Bigelow, and L. J. King, *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending December 31, 1971*, ORNL-4767 (June 1972).

recovered were: 17 mg of ^{249}Bk, 170 mg of ^{252}Cf, 800 μg of ^{253}Es in a mixture of einsteinium isotopes, 170 μg of isotopically pure ^{253}Es, and 1.7×10^9 atoms of ^{257}Fm.

About 200 g of the curium that was recovered from SRP slugs last year was converted to oxide this year and returned to the Savannah River Plant. This demonstrated that the processes and techniques used result in oxide which meets SRP specifications for high purity and low emission of penetrating radiation. The SRP requirements are much more restrictive than TRU requirements because of differences in target designs, fabrication techniques, and shielding of the fabrication facilities.

Processes and Equipment

The processes and equipment that were used in the operations involving the reactor tubes were generally the same as those used with HFIR targets and SRP slugs. However, a few changes were required because of the size and composition of the tubes.

The tubes, which are annular, are 4 in. in diameter. They were originally 15 ft long but were cropped to 5 ft 4 in. (slightly longer than the active length) for shipment to TRU for processing. A 23-ton carrier was fabricated to allow three irradiated target tubes to be shipped simultaneously after being allowed to cool for three months. The dissolver vessel that had been used for HFIR targets and SRP reactor slugs was replaced with a new 11-ft-high vessel to permit dissolution of the 5-ft-4-in.-long sections of SRP tubes. The new vessel has a small-diameter bottom section to make it useful for dissolving HFIR targets.

The procedure used for dissolving aluminum from the tubes was different from that used for dissolving aluminum from HFIR targets and SRP slugs. The capacity of the dissolver off-gas system is insufficient to handle hydrogen at the rate that it would be evolved if we contacted a tube (about 4 kg of aluminum) with sufficient caustic-nitrate solution to dissolve the aluminum. Therefore, we placed a tube, along with $NaNO_3$ solution (heated to 92°C), in the dissolver and added NaOH solution at a controlled rate to maintain the dissolver off-gas vacuum and keep the hydrogen concentration in the dissolver vapor space below 4%.

Fabrication of Targets

Twenty-three targets were fabricated in order to recycle curium to the HFIR. Eight of them were fabricated from curium recovered during the processing of research materials, and 15 were fabricated from curium recovered from Californium-I targets. All of the curium for the targets was prepared by sorbing curium on ion exchange resin, which was subsequently calcined to destroy the resin and convert the curium to oxide (see Sect. 5.4).

5.2 ISOLATION AND PURIFICATION OF TRU PRODUCTS

The final purification of transplutonium elements, the isolation of second-growth isotopes, and the fabrication of actinide shipping packages and neutron sources are accomplished in equipment installed in cell 5 in TRU, the californium facility at TURF, and in supporting shielded-cave facilities. When products reach certain levels of purity, they are moved into these cleaner facilities, which are used only for handling products.

Final Purification of Transplutonium Elements and Isolation of Second-Growth Isotopes

The purified products are obtained from the transcurium fraction (from the LiCl anion exchange process) that is produced routinely in the plant equipment. The purification process, which has been previously described,[3,4] consists of the separation of fermium, einsteinium, californium, and berkelium from each other and from residual actinides by selective elution from cation exchange resin with ammonium α-hydroxyisobutyrate; berkelium is further decontaminated from residual actinides by oxidation to Bk^{4+} by $NaBrO_3$ and subsequent extraction from 8 M HNO_3 into di(2-ethylhexyl)phosphoric acid (HDEHP). The products obtained from this processing during the past year are reported in Sect. 5.1.

Various special separations were made during this report period. These included the isolation of 4.1 mg of ^{249}Cf (a daughter of ^{249}Bk) and 4.6 mg of ^{248}Cm, which had grown into highly purified californium during storage. An additional 93 mg of ^{252}Cf was purified and loaded into platinum capsules for storage. This material will be processed at six-month intervals to isolate ^{248}Cm. About 20 mg of ^{248}Cm will be obtained from this source during the forthcoming year.

Isotopically pure ^{248}Cm is obtained by the alpha decay of ^{252}Cf which has been isolated from large amounts of ^{244}Cm. In order to minimize the ^{244}Cm content in ^{248}Cm products, the ^{252}Cf must be highly

3. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1967*, ORNL-4145, pp. 136–51.

4. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1968*, ORNL-4272, pp. 100–101.

purified. In the californium TURF facility we have been able to routinely obtain ^{248}Cm containing less than 0.001 at. % ^{244}Cm.

5.3 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 Californium

Much of the californium recovered at TRU is incorporated into neutron sources, which are subsequently loaned to researchers. Twenty-nine sources containing from 4 μg to 11 mg of ^{252}Cf were fabricated this year. Most of them were doubly encapsulated in type 304L stainless steel in a standard configuration.[5] One was in the standard singly encapsulated form. Seven were doubly encapsulated in Zircaloy-2 to reduce the neutron capture in the source container. One, which was doubly encapsulated, was specially fabricated to the same external dimensions as a lower-intensity source that it replaced. This source was used in criticality experiments with the ZRP-1 at the National Reactor Testing Station. One source was made with a special design for the National Bureau of Standards. They were trying to approach the "dimensionless point" concept. The final version of the source was a cylinder 0.3 in. in diameter by 0.3 in. high, topped with a $^1/_8$-in.-long stub, which was threaded for attaching a handling fixture. One source, containing about 4 mg of ^{252}Cf, was prepared in the configuration of the standard Savannah River SR-Cf-100 series sources.

Calibration of ^{252}Cf Source with a Fast-Neutron Detector

Equipment for assaying californium sources and shipping packages by means of fast-neutron counting has been installed in the source and target decontamination facility and in the TURF californium facility. For our use, fast-neutron counting is preferable to thermal-neutron counting or the manganese sulfate method because of the smaller shielded space required.

In the source and decontamination facility, two parallel detectors, which are located in a box in the water shield just outside the cubicle, measure fission events in ^{238}U caused by absorption of fast neutrons emitted from a californium source located on a measuring bar inside the cubicle. Capture of thermal neutrons is discriminated against by minimizing the ^{235}U content of the uranium and by wrapping each detector in a cadmium sheath.

We found that the system is excellent for comparing sources and shipping packages with a standard source assayed during the same test period. The reproducibility is almost always within 1% and usually better than 0.5%. Scattering from the walls and water shield, from miscellaneous items in the facility (such as the manipulator hand), from moisture in the source container, and from the source container itself were found to have little effect on the reproducibility. Background corrections, which are readily determined, are usually 1% or less. One difficulty that arose was the uncertainty as to the location of the source within the capsule. This problem was significantly reduced by rotating the capsule to four different positions during the counting period. The loss of counts at the higher count rates is the major effect requiring correction. The worst loss observed was 17% at a count rate of 15,000 counts/sec. An empirical relationship between the fraction of the counts lost (FL) and the observed count rate (CR),

$$\ln(FL) = 0.679 \times \ln(CR) - 8.309 ,$$

was derived by counting a series of sources at different geometries. Corrections for sources up to 10 mg can be calculated with enough accuracy to introduce negligible error into the calibration.

Preparation of Gamma-Ray Sources for Mössbauer Studies

Three Mössbauer sources, GS-3, GS-5, and GS-6, were made for experimenters working at the Transuranium Research Laboratory. In these sources, plutonium oxide was deposited in a very thin layer (only a few mils thick) over a disk which is about 1 in. in diameter. The disk was doubly encapsulated in aluminum, making the overall container dimensions $1^3/_8$ in. in diameter by 1 in. high. Source GS-3 was loaded with 1.0 g of ^{242}Pu as the oxide, GS-5 was loaded with 0.50 g of ^{240}Pu as the

5. 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.

oxide, and GS-6 was loaded with 0.50 g of ^{238}Pu as the oxide.

We also prepared three $1\frac{3}{8}$-in.-diam by $\frac{1}{16}$-in.-thick absorbers, fabricated from ^{238}U, ^{236}U, and ^{234}U for use with the GS-3, GS-5, and GS-6 sources, respectively. Fabrication involved mixing the uranium oxide with epoxy resin and allowing the resulting product to harden.

Other Special Projects

A rabbit containing 250 μg of ^{240}Pu was prepared, irradiated, and shipped to the customer. Irradiation of a rabbit containing ^{252}Cf was continued intermittently, with checks being made of the ^{252}Cf content by fast-neutron counting. No problem with gamma sensitivity was noted. A special target containing test pellets to study production of ^{244}Pu, ^{250}Cm, transcalifornium isotopes, and ^{32}Si was prepared and irradiated.

5.4 DEVELOPMENT OF CHEMICAL PROCESSES

Laboratory support was provided to assist the mainline processing in TRU. Progress was made in developing a resin-loading–calcination process to produce curium oxide in the desired size range for HFIR targets, and the laboratory development of actinide separation processes was continued.

In further studies to develop methods for preparing curium oxide particles, two procedures were demonstrated at full-scale activity levels (5 to 15 g of curium) to produce more than 200 g of curium oxide which was successfully used to prepare HFIR targets.

The two resins that have produced satisfactory products are Dowex 50W, which contains sulfonic acid exchange groups, and Amberlite IRC-50, which contains carboxylic acid exchange groups. Studies were made with both systems because each has certain advantages and disadvantages. With Dowex 50W, feed preparation is not critical, although high calcination temperatures (1350 to 1450°C) are required to obtain high densities and to adequately remove sulfur. Feed adjustment is more critical with Amberlite IRC-50 in that the metal-salt solution must be adjusted to a pH of about 5.5 and a complexing agent, such as ammonium acetate, must be used to prevent precipitation; however, calcination temperatures of 600 to 1000°C are adequate to provide satisfactory densities.

During this report period, we developed techniques that circumvent the major disadvantage of each resin. In the Dowex 50W system, the high calcination temperature was avoided by heating the dried resin in a reducing atmosphere (4% H_2-Ar) prior to calcination in air. With this procedure, a temperature of 1000 to 1100°C is adequate to obtain satisfactory density. With Amberlite IRC-50 resin, the feed adjustment was greatly simplified by loading the curium feed onto Dowex 50 resin and eluting with a 1.0 to 1.5 *M* $NH_4C_2H_3O_2$ solution adjusted to a pH of 5.5. The actinide fraction of the eluate can be readily isolated in a small volume, which is then diluted to 0.1 *M* acetate and loaded onto an IRC-50 resin column. With either process, we can now consistently prepare spherical particles of adequate density (40 to 60% of the theoretical crystal density) and mechanical strength.

In the laboratory development of actinide separation processes, studies were continued to separate actinide elements by chromatographic elution from ion exchange resins with 1,2-propanediaminotetraacetic acid (PDTA). This aminopolyacetic acid gives unusually high separation factors between californium and curium (Cf/Cm ~50). Previous problems with double elution peaks for the individual elements have been alleviated. Spectrophotometric studies with americium and PDTA show that a 1:1 complex is formed in the pH range 1.2 to 2.2, and that a 1:2 complex is formed slowly in the pH range 6.0 to 8.5. Chromatographic elutions at high-alpha activity levels are in progress to fully evaluate the use of this complexing agent.

5.5 TRANSPLUTONIUM-ELEMENT RESEARCH

A systematic study of actinide-element chemistry and of comparative lanthanide chemistry is being made as significant quantities of new isotopes become available. Such a study materially increases our basic understanding of actinide systems. This part of the USAEC Heavy Element Program includes work on problems involving solution chemistry, with particular emphasis on the formation of complexes and on the preparation of solid actinide compounds that are characterized by x-ray and electron diffraction, electron microscopy, thermogravimetry, differential thermal analysis, and metallographic examination.

Sulfate Complexes of Trivalent Actinides

The investigation of lanthanide and actinide sulfate complexes by amine extraction was completed with final refining of the calculation of the formation constants, and a summary of the work has been accepted for publication.[6] In connection with the final

6. W. J. McDowell and C. F. Coleman, "The Sulfate Complexes of Some Trivalent Transplutonium Actinides and Europium," *J. Inorg. Nucl. Chem.* (in press).

ORNL-DWG 71-9050

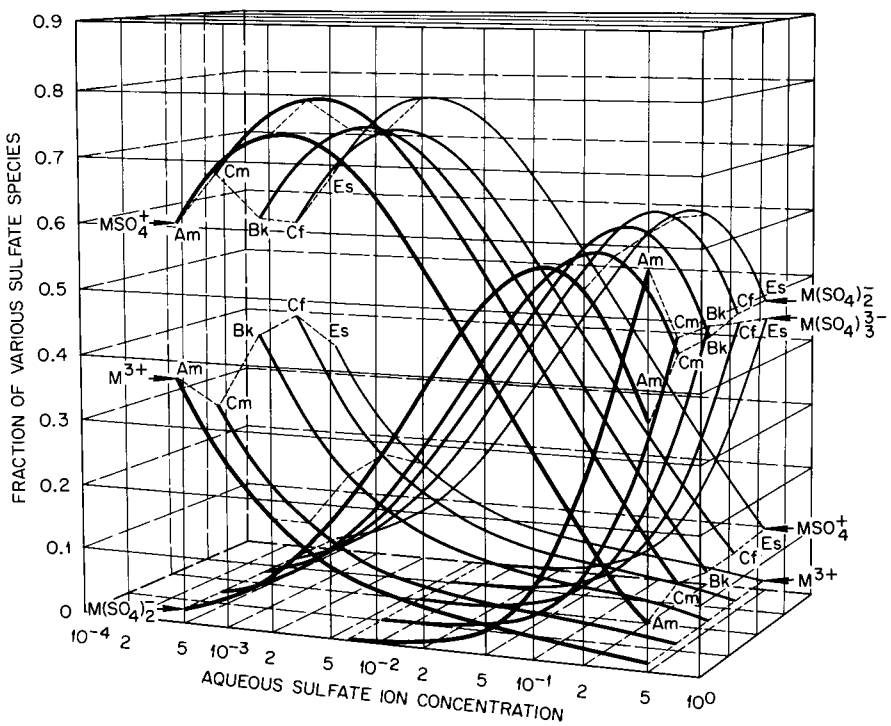

Fig. 5.1. Fractional distribution of complex species as a function of sulfate concentration and atomic number in the aqueous actinide(III) sulfate system.

calculations, a FORTRAN IV computer code using programs LOGAMS, LOWSO4, HIGAMS, SULFATE,[7] and program SULCOM[8] was written to calculate the fractional distribution in sulfate media of the trivalent actinide species M^{3+}, MSO_4^+, $M(SO_4)_2^-$, and $M(SO_4)_3^{3-}$. A set of the desired total sulfate concentrations and the desired sulfuric acid activity must be specified. Solution composition (total sulfate and sulfuric acid molarity), sulfate ion concentration, and ionic strength are tabulated. Actinide species distribution is tabulated and may be plotted as a function of total sulfate or sulfate ion concentration. Figure 5.1 shows the resulting plots vs sulfate ion concentration for Am to Es, displayed in a three-dimensional, true-perspective array with atomic number as the Z axis. It also shows the variation of the fraction of each species with changing atomic number at a fixed sulfate ion concentration, and illustrates the tetrad periodicity pattern that has been observed for both lanthanide and actinide complexes by other workers.[9,10]

Thiocyanate Complexes of Trivalent Actinides

The study of the aqueous thiocyanate complexes of the trivalent transplutonium actinides, by absorption spectroscopy and solvent extraction, has been completed.

Results of the spectrophotometric study of the formation of Am(III) thiocyanate complexes[11] at an ionic strength of 1.0 *M* enabled calculation of $\beta_1 = 5.79$ ($\sigma = 0.33$) and $\beta_2 = 6.77$ ($\sigma = 1.05$) for $Am(SCN)^{2+}$ and $Am(SCN)_2^+$, respectively. Additional studies of Am(III)

7. W. J. McDowell, *Computer Methods of Calculating Sulfuric Acid Activity, Sulfate Ion Concentration, and Ionic Strength of Sodium Sulfate-Sulfuric Acid Solutions,* ORNL-4407 (August 1969).

8. W. J. McDowell, *A Computer Program for Calculating the Fractional Distribution of Trivalent Actinide Species in Sodium Sulfate-Sulfuric Acid Solutions,* ORNL-4648 (April 1971).

9. H. D. Harmon, *The Thiocyanate and Chloride Complexes of Some Trivalent Actinides* (Thesis), ORNL-TM-3486 (July 1971).

10. D. F. Peppard, C. A. A. Bloomquist, E. P. Horwitz, S. Lewa, and G. N. Mason, *J. Inorg. Nucl. Chem.* **32,** 339 (1970).

11. H. D. Harmon, J. R. Peterson, J. T. Bell, and W. J. McDowell, "A Spectrophotometric Study of the Formation of Americium Thiocyanate Complexes," *J. Inorg. Nucl. Chem.* (in press).

in KSCN solutions of variable ionic strength suggested that Am(III) is strongly complexed and provided qualitative evidence for the existence of anionic complexes in 5 to 10 *M* KSCN. The "effective stability constant" approach was applied to the data at low KSCN concentrations to calculate $\beta_1{}^* = 7.6$ ($\sigma = 2.5$) for $Am(SCN)^{2+}$.

A solvent extraction technique, with bis(2-ethylhexyl)phosphoric acid as the extractant, was used to examine the formation of Am(III), Cm(III), Bk(III), Cf(III), and Es(III) thiocyanate complexes[12] in an $NaSCN$-$NaClO_4$ medium at ionic strength $I = 1.0\,M$ and pH = 2.00. Mathematical analysis of the data led to the conclusion that the mono-, di-, and trithiocyanate species exist in the thiocyanate concentration range studied in this work. Values of the overall stability constants β_1, β_2, and β_3 were calculated. As the atomic number of the actinides increased, the β_1 values exhibited a gradual increase in stability, which is consistent with the expected effect on complex stability due to the actinide contraction. The β_2 values decreased rapidly across the series from americium to einsteinium, with a concomitant increase in β_3. In addition, the β_3 values showed evidence of the tetrad effect, leading to the tentative conclusion that the $Act(SCN)_3$ complexes (where Act = Am, Cm, Bk, Cf, and Es) are of the inner-sphere type. The thermodynamic parameters of the Am(III) thiocyanate complexes were calculated from temperature-dependence measurements. Enthalpy and entropy changes were used to aid in the distinction between outer- and inner-sphere complex formation.

Preparation of High-Purity Curium Metal

In collaboration with the Isotopes Division, 2.6 g of high-purity ^{244}Cm metal was prepared by reduction of CmO_2 with thorium metal.[13] The curium metal was volatilized at 1650°C for 30 min, giving a 17% yield of deposited material. When the temperature was increased to 2000°C for 1 hr, an additional 60% yield was achieved. On examination by x-ray diffraction analysis, the vapor-deposited metal was found to be a face-centered cubic (fcc) structure with $a_0 = 5.039 \pm 0.002$ Å. This gives a metallic radius of 1.781 Å and a metallic valence of +3.0. The fcc structure transformed to the double-hexagonal closest-packed (dhcp) structure on cooling in liquid nitrogen for five days. The lattice parameters for the dhcp structure are $a_0 = 3.492 \pm 0.002$ and $c = 11.338 \pm 0.06$ Å. Since the fcc phase converts to the dhcp phase on cooling, it is the high-temperature form of curium metal. The curium metal prepared in this experiment will be used as starting material for preparing other compounds.

Actinide and Lanthanide Hydrides and Metallides

Studies involving the preparation and characterization of actinide hydrides and other binary compounds were continued, in part to obtain experimental evidence pertinent to the electronic structures and in part to search for semiconductor or other properties of specific interest.

Metal hydrides are being prepared by a slightly modified Sieverts reaction system.[14] The following equilibrium dissociation temperature relationship was obtained for the two-phase region of americium solid solution plus dihydride:

$$\log_{10} P = \frac{-9920 \pm 42}{T} + 11.02 \pm 0.05 ,$$

where P is equilibrium hydrogen pressure, in torrs, and T is absolute temperature, in degrees Kelvin. The enthalpy and the entropy of the reaction were evaluated as $\Delta H = -45.4 \pm 0.2$ kcal per mole of H_2 and $\Delta S = -37.2 \pm 0.2$ cal per degree · mole of H_2, compared with the single literature values of $\Delta H = -40.3$ and $\Delta S = -33.0$. X-ray diffraction analysis near the dihydride composition showed the structure to be fcc (CaF_2) with $a_0 = 5.344$ Å, in good agreement with the literature value of 5.348 Å.[15]

The alloying behavior and crystal structure were examined by making binary preparations of americium with arsenic and bismuth at nearly equiatomic proportions. AmAs was found to be an NaCl-type compound with $a_0 = 5.890$ Å. The bismuth compound was tentatively indexed as a hexagonal structure of the Mn_5Si type with $a = 9.69$ Å and $c = 6.36$ Å.

12. H. D. Harmon, J. R. Peterson, W. J. McDowell, and C. F. Coleman, "The Tetrad Effect: The Thiocyanate Complex Stability Constants of Some Trivalent Actinides," *J. Inorg. Nucl. Chem.* **34**, 1381 (1972).

13. R. D. Baybarz and H. L. Adair, "Preparation of the High Temperature Form of Curium Metal," accepted for publication in *J. Inorg. Nucl. Chem.*

14. A. Sieverts and G. Müller-Goldegg, *Z. Anorg. Allgem. Chem.* **131**, 65 (1923); *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1970*, ORNL-4572, p. 127.

15. W. M. Olson and R. N. R. Mulford, *J. Phys. Chem.* **70**, 2934 (1966).

Preparation of Divalent Americium Halides

There is substantial indirect evidence for a divalent oxidation state of americium; however, no Am(II) compounds have been reported in the literature. We have been successful in preparing the first divalent americium compounds – $AmCl_2$, $AmBr_2$,[16] and AmI_2[17] – by the reaction of high-purity ^{243}Am metal with a stoichiometric quantity of mercuric halide at 300°C. The metallic mercury was subsequently distilled away from the americium dihalide compound.

The americium dihalide compounds are black, salt-like compounds, and their only observable absorption spectra, before the $f \rightarrow d$ absorption edge, consist of a weak, broad band at 837 nm. The lattice parameters for the orthorhombic $AmCl_2$ are $a_0 = 8.963 \pm 0.008$, $b = 7.573 \pm 0.008$, and $c = 4.532 \pm 0.006$ Å; and the lattice parameters for the tetragonal $AmBr_2$ are $a_0 = 11.592 \pm 0.004$ and $c = 7.121 \pm 0.003$ Å. The AmI_2 has a monoclinic structure with lattice parameters of $a_0 = 7.677 \pm 0.003$, $b = 8.311 \pm 0.004$, $c = 7.925 \pm 0.003$ Å, and $\beta = 98.46 \pm 0.03°$. The magnetic susceptibility of the AmI_2 sample was measured at Los Alamos Scientific Laboratory, and μ_{eff} was determined to be 6.7 ± 0.7 BM, which verifies the $5f^7$ configuration of Am(II).

Phase Diagram of the Transplutonium-Element Sesquioxides

The phase diagram for the transplutonium-element sesquioxides, Am through Cf, has been evaluated from room temperature to the melting point.[18] It was found that the melting point increased slightly from Pu to Cm and then decreased for Bk and Cf. The sesquioxide crystal structure phase transformations, as a function of temperature, are cubic → monoclinic → hexagonal. Newly identified structures, which previously had not been known, are the quenched hexagonal phase of $^{248}Cm_2O_3$, monoclinic and hexagonal forms of $^{249}Bk_2O_3$, and the hexagonal form of $^{249}Cf_2O_3$.

Preparation of Actinide Metals by Vapor Deposition, and Analysis by Electron Diffraction Techniques

A program to prepare and identify the actinide metals, Am through Es, by vapor deposition onto electron microscope grids and subsequent identification of the crystal structure by electron diffraction techniques has been initiated. For the very volatile metals such as californium and einsteinium, this method appears to be particularly attractive. Excellent electron diffraction patterns for Am, Cm, Cf, and Es have been obtained and are presently being evaluated. The excellent quality of the einsteinium metal diffraction patterns has been very encouraging since the high specific activity of ^{253}Es (5.61×10^{10} α dis min^{-1} μg^{-1}) tends to destroy the crystal structure via extensive radiation and x-ray diffraction techniques have not been very successful in obtaining crystal structure data. Because electron diffraction analysis inherently requires extremely small particles, most of the alpha particles escape from the crystallites and thus do not destroy the structure.

Analysis of Actinide Oxides by Electron Diffraction

Electron diffraction studies of the actinide oxides were continued. Investigation of the Cf_2O_3-CfO_2 system by x-ray and electron diffraction has been reported.[19] Additional work on einsteinium oxide has given a refined bcc lattice parameter of 10.766 ± 0.006 for Es_2O_3.[20] The ionic radius of Es^{3+} calculated from this parameter is 0.928 Å, which is midway between the values calculated for Gd^{3+} and Tb^{3+} from their sesquioxides.

Investigation of the Actinide Hydroxides by Electron Microscopy

Electron microscopy, electron diffraction, and x-ray diffraction techniques[21-23] were used in a continuing

16. R. D. Baybarz, "The Preparation and Crystal Structures of Americium Dichloride and Dibromide," submitted for publication to *J. Inorg. Nucl. Chem.*

17. R. D. Baybarz, L. B. Asprey, C. E. Strouse, and E. Fukushima, "Divalent Americium: The Crystal Structure and Magnetic Susceptibility of AmI_2," *J. Inorg. Nucl. Chem.* (in press).

18. R. D. Baybarz, "The Actinide Sesquioxide Phase Diagram and the Lattice Parameters of Hexagonal Cm_2O_3, Bk_2O_3, Cf_2O_3, and Monoclinic Bk_2O_3," to be submitted for publication in *J. Inorg. Nucl. Chem.*

19. R. D. Baybarz, R. G. Haire, and J. A. Fahey, *J. Inorg. Nucl. Chem.* **34**, 557 (1972).

20. R. G. Haire and R. D. Baybarz, "Identification and Analysis of Einsteinium Sesquioxide," submitted for publication in *J. Inorg. Nucl. Chem.*

21. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1970,* ORNL-4572, pp. 129–33: *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971,* ORNL-4682, pp. 128–31.

22. R. G. Haire, M. H. Lloyd, T. E. Willmarth, and W. O. Milligan, *Proceedings of Symposium on Sol-Gel Processes and Reactor Fuel Cycles, Gatlinburg, Tennessee, May 4–7, 1970,* pp. 464–75.

23. R. G. Haire, M. H. Lloyd, M. L. Beasley, and W. O. Milligan, *J. Electron Microsc.*, **20**(1), 8–16 (1971).

study of the actinide hydroxides and hydrous oxides. Preparation and analysis of the hexagonal trihydroxides of Am, Cm, and Bk have been completed, and the lattice parameters have been determined. The ^{249}Cf preparations made to date have not produced diffraction patterns of sufficient quality to permit determination of the lattice parameters. Information on crystalline $Es(OH)_3$ cannot be obtained, since the rate of destruction from self-radiation is greater than the rate of conversion to the crystalline form.

When tetravalent Am and Bk are precipitated with hydroxide, the resulting crystalline material gives electron diffraction patterns identical to those obtained for the dioxides. A study of Ce, Am, and Bk hydroxide preparations has shown that, when a mixture of the trivalent and tetravalent oxidation states is precipitated, the crystalline products consist of mixtures of rodlike trihydroxide particles and symmetrical particles of the hydrous dioxide.

The radiation-induced decomposition of ^{241}Am trihydroxide was studied as a function of time. It was found that, after several months of aging in water, the $Am(OH)_3$ rod structures disintegrate to give small amorphous particles. In the solid state, $Am(OH)_3$ converts to crystalline AmO_2, and the rate of conversion to the dioxide is dependent on storage conditions.

5.6 COLLABORATIVE RESEARCH WITH THE TRANSURANIUM RESEARCH LABORATORY

Several research projects are being carried out in collaboration with personnel at the Transuranium Research Laboratory (TRL). This work is summarized briefly here. More detailed information can be obtained in annual reports published by the Chemistry Division and in papers published in the open literature.

An investigation is being carried out to determine the coordination numbers of the lanthanide and actinide elements. Solid compounds of elements from the two groups are being prepared, and the coordination number is being determined by single-crystal x-ray diffraction. Crystals of $Am_2(SO_4)_3 \cdot 8H_2O$ were analyzed by x-ray diffraction and by thermal analysis, and the americium compound was found to be isostructural with the corresponding praseodymium and samarium salts. Each americium atom is coordinated by four oxygen atoms of a sulfate group and by four water molecules. Cross-linking of americium atoms occurs through sharing of sulfate ions, and extensive hydrogen bonding involving the water molecules is indicated. The monoclinic unit cell has dimensions of $a_0 = 13.916 \pm 0.007$, $b = 6.837 \pm 0.002$, $c = 18.405 \pm 0.004$ Å, and $\beta = 102° 40' \pm 5'$. Each unit cell contains four formula units.[24]

The development of a method for determining the (II-III) and (III-IV) oxidation potentials of the actinide and lanthanide elements by correlation of electron transfer and $f \rightarrow d$ absorption bands to known redox potentials has been completed, and a summary of the work has been submitted for publication.[25,26] As a result of this work, a series of experiments has been initiated to check the accuracy of the redox potentials predicted by the absorption spectroscopic measurements.

Polarographic studies in nonaqueous media of the transplutonium elements in correlation with some of the lanthanide elements have been undertaken to determine which of these elements may have a divalent state that is obtainable in the solvents studied. Some of the solvents that have been investigated are acetonitrile, dimethylsulfoxide, propylene carbonate, and dimethylformamide. In acetonitrile, it was found that the Cf(III-II) reduction potential was essentially the same as for Sm(III-II).[27] The potentials in this medium vs the standard calomel electrode are Sm(III-II) = −0.97 V and Cf(III-II) = −1.00 V. Difficulties with radiation damage to the solvent were encountered when ^{253}Es and ^{244}Cm were used. This study is being continued with other solvents and different salts of the metals.

The divalent state of californium has also been verified by the successful preparation of californium dibromide.[28] It was found that hydrogen would reduce the $CfBr_3$ to $CfBr_2$ at a temperature near the melting point of $CfBr_3$. It was also noted that the $CfBr_3$ could be partially reduced simply by heating to near the melting point. The lattice parameters of the tetragonal

24. J. H. Burns and R. D. Baybarz, "The Crystal Structure of Americium Sulfate Octahydrate," submitted for publication in *Inorganic Chemistry*.

25. L. J. Nugent, R. D. Baybarz, J. L. Burnett, and J. L. Ryon, *J. Inorg. Nucl. Chem.* **33**, 2503 (1971).

26. L. J. Nugent, R. D. Baybarz, J. L. Burnett, and J. L. Ryon, "Electron Transfer and $f \rightarrow d$ Absorption Bands of Some Lanthanide and Actinide Complexes and the Standard (II-III) Oxidation Potentials for Each Member of the Lanthanide and Actinide Series," submitted for publication in *J. Phys. Chem.*

27. H. A. Friedman, J. R. Stokely, and R. D. Baybarz, "Polarographic Evidence for the Divalent Oxidation State of Californium," accepted for publication in *Inorg. Nucl. Chem. Lett.*

28. J. R. Peterson and R. D. Baybarz, "The Stabilization of Divalent Californium in the Solid State: Californium Dibromide," *Inorg. Nucl. Chem. Lett.* **8**, 423 (1972).

$CfBr_2$ are a_0 = 11.500 ± 0.007 and c = 7.109 ± 0.006 Å. The ionic radius of the Cf(II) is smaller than that of Eu(II) by about 0.01 Å.

The absorption spectra of solid crystals of the di- and tribromides of Sm, Yb, Tm, Am, and Cf are being measured, and an attempt at correlating the $f \rightarrow d$ absorption edge with known potentials will be made. This method may be the only way to measure the (II-III) potential for Es.

The chemistry and the spectral properties of Am(III) indicated that this actinide may have laser potentiality. A laser can be made from a solution of neodymium in $POCl_3$-$ZrCl_4$; however, attempts to produce a laser from a similar solution of americium were unsuccessful.[29] Similarly, Am(III) doped into a $CaWO_4$ host matrix showed no laser activity. Failure of these efforts is attributed to the short lifetime for the excited state of Am(III).

29. H. A. Friedman and J. T. Bell, *A. Search for Laser Phenomena in the Actinides: Studies of Investigations of* Am^{3+} *in Liquid* $POCl_3$, ORNL-TM-3728 (Feb. 25, 1972).

6. Development of the Thorium Fuel Cycle

Our work associated with development of the thorium fuel cycle (thorium and ^{233}U) is primarily concerned with the preparation of small spheres of oxide fuels to be coated with pyrolytic carbon for use in high-temperature gas-cooled reactor (HTGR) fuel blocks. Sol-gel processes are used to prepare high-density oxide spheres. Low-density spheres prepared from ion exchange resins offer an alternative type of "fissile" particle with internal void volume to accommodate fuel swelling and gas release.

6.1 SOL-GEL PROCESS DEVELOPMENT FOR THE PREPARATION OF MICROSPHERES

These studies were primarily aimed at finding methods for controlling the composition of the 2-ethyl-l-hexanol (2EH) used to extract water from sol drops to form gel spheres. Satisfactory operation of a periscope was demonstrated for remote observation of a sol disperser and of the shape and size of gel spheres in 2EH.

Recycle of the 2EH for more than 250 hr of UO_2 sphere preparation from CUSP sols was demonstrated in a nonfluidized column system (see Sect. 6.2). An ion exchange step to remove formic acid from the 2EH used with UO_2 sols prepared by the CUSP process is essential because the accumulation of formic acid results in excessive doublets, clustering, sticking, or coalescence. The ion exchange step also removes nitric acid and prevents degradation of surfactants by nitric acid in the still. Pure 2EH or 2EH containing 0.1 to 0.5 vol % Ethomeen S/15 or Pluronic L-92 is sometimes satisfactory for forming gel spheres from CUSP-prepared UO_2 sols in a nonfluidized column, but may give an undesirable number of doublets or partially coalesced drops. The best composition for long-term operation of a nonfluidized column with UO_2 sols has been found to be 2EH containing 0.1 to 0.3 vol % Span 80 that has undergone several cycles through the ion exchange step. The ion exchange step has been previously shown to hydrolyze or otherwise change the Span 80[1] to a form that is effective for preventing the formation of doublets in the nonfluidized column without causing the surface roughness or dimples characteristic of operation with virgin Span 80.

The only effective procedure we have found for maintaining a satisfactory 2EH composition for fluidized-bed formation of UO_2 spheres from CUSP sols consists of removing waste 2EH and replacing it with repurified or fresh 2EH containing the appropriate amounts of surfactants and nitric acid. The critical factor is prevention of the accumulation of Span 80 degradation products, which contribute to excessive cracking of large UO_2 spheres and clustering of small UO_2 spheres. The concentrations of the other components can be controlled as previously reported.[1]

6.2 ENGINEERING DEMONSTRATION OF THE PREPARATION OF UO_2 MICROSPHERES

Continuous operation for the formation of UO_2 microspheres was demonstrated for two 110-hr periods using CUSP-prepared UO_2 sols in a nonfluidized sphere-forming column. The selected 125- to 210-μ range, or a mean size of about 160 μ, was consistent with the proposed sizes of fissile UO_2 particles for HTGR fuels. The nonfluidized column was selected to simplify the alcohol recycle requirements as summarized in Sect. 6.1. A capacity of 3 kg of UO_2 per day or 7.8 cc of sol per minute was previously demonstrated as practical for making 550-μ sol drops using the two-fluid nozzle dispersers.

The CUSP-prepared UO_2 sols were produced in 15-liter batches (4 kg of UO_2 per batch) using the spray column contactor and procedures reported previously.[2] The eight batches of sol appeared to be identical and

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, pp. 154–58.

2. J. P. McBride et al., "The CUSP Process for Preparing Concentrated, Crystalline Urania Sols by Solvent Extraction," *Nucl. Technol.* 13 (2), 148–58 (1972).

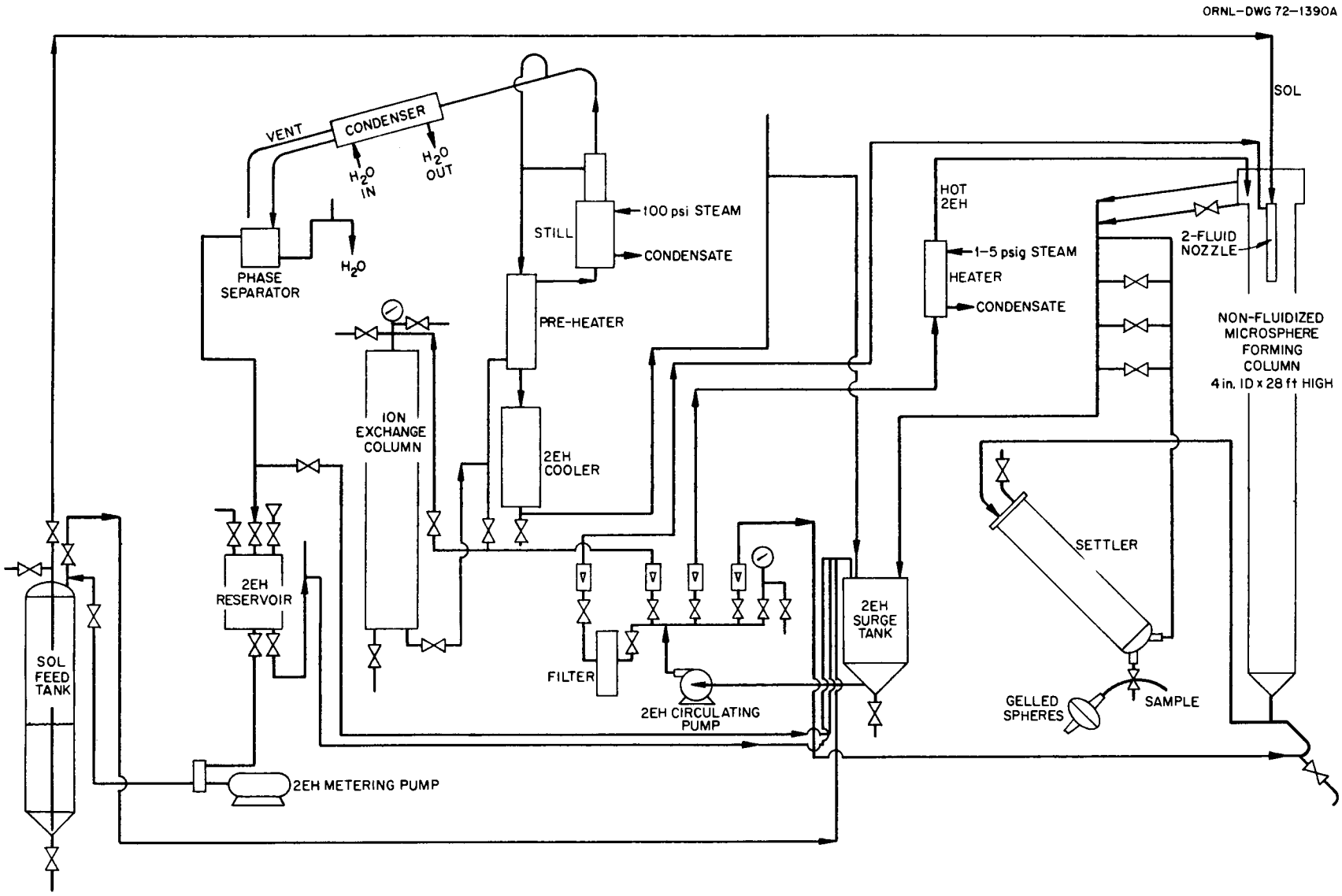

Fig. 6.1. Equipment flowsheet for the nonfluidized microsphere-forming column, including the 2EH distillation system, ion exchange column, and sol feed system.

Table 6.1. Summary of physical and chemical properties of calcined UO_2 microspheres produced during nonfluidized column demonstration runs 1 and 2

	Run 1		Run 2	
	Batch 1-2	Batch 2-3	Batch 3	Batch 7
Weight of calcined product, g	924.8	628.5	1132.5	727.2
125- to 210-μ-diam fraction, g	662.7	475.4	965.0	649.9
125- to 210-μ-diam fraction, wt %	71.6	75.6	85.2	89.4
Mean size, μ	174.0	155.0	158.0	167.0
Standard deviation, μ	32.0	19.0	15.0	16.0
Roundness ratio, D_{max}/D_{min}	1.03	1.03	1.02	1.02
Density, % of theoretical	98.0	97.0	98.6	100.0
BET surface area, m^2/g	0.04	0.015	0.009	0.008
O/U atom ratio	2.0028	2.005	2.0051	2.005
Carbon content, ppm	30	40	60	24
Iron content, ppm	31	46	33	12
Gas release to 1200°C, cc/g	0.0046	0.004	0.004	0.004
Average crushing strength, g	1623	1286	1435	1444

maintained good properties throughout a period of three weeks; we consider this a reasonable shelf-life specification.

The formation of gel spheres was carried out with cocurrent downflow of sol drops and 2EH in a 4-in.-ID by 28-ft-high column (Fig. 6.1). The 2EH was heated to a temperature of about 80°C at the top of the column and 50°C at the bottom; these temperatures are required in order to achieve complete gelation of the 210-μ spheres formed from 1 *M* UO_2 sol.[3] The complete system (Fig. 6.1) includes an ion exchange step (using Amberlyst A-21 resin) to remove formic and nitric acids from the 2EH and distillation to remove water. The operation of the nonfluidized column with the CUSP-prepared UO_2 sol was improved after several cycles of the 2EH (containing 0.1 to 0.3 vol % Span 80 surfactant) through the ion exchange column. Use of 2EH containing no Span 80 allowed some doublet particles to be formed as the result of partial coalescence, while fresh Span 80 tended to produce a slight surface roughness or dimples. The same charge of 2EH was used for more than 250 hr of UO_2 sphere preparation and appears to be suitable for additional runs.

In the second 110-hr run, the UO_2 sphere sizes after firing were distributed as follows: 125 to 210 μ, 87 wt %; <125 μ, 13 wt %; and >210 μ, less than 1%. The sol drops were formed by a single two-fluid nozzle operated at 7.8 cc/min. The other properties of the product were satisfactory as shown by typical results (Table 6.1) and photomicrographs (Fig. 6.2). The principal waste for recycle would contain about 4% of the uranium from sol preparation; the waste material from the sphere formation consisted principally of samples dried in air for size and shape examinations.

6.3 PROCESS DEVELOPMENT FOR THE PREPARATION OF MICROSPHERES BY USING ION EXCHANGE RESINS

Uranium-loaded resin beads, which are subsequently carbonized and coated, are being developed for possible use as fissile particles in HTGRs. Irradiation tests of this type of particle have shown good results, with promise of superior performance relative to conventional kernels.[4] A major advantage of this fabrication method is that the spherical resin particles may be inspected, and off-specification material rejected, before ^{235}U or ^{233}U is present. Another important advantage is the simplicity of the method. Both of these advantages lead to simplified, more foolproof operations and attendant decreased costs. Uranium can be loaded onto cation exchange resins from uranyl nitrate solution. If a strong-acid (sulfonate) resin is used, the final product will contain some sulfur; a weak-acid (carboxylate)

3. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, pp. 137–40.

4. C. B. Pollock, J. L. Scott, and J. M. Leitnaker, "Recent Developments in Pyrolytic-Carbon-Coated Fuels," *Trans. Am. Nucl. Soc.* **14**(1), 139–40 (1971).

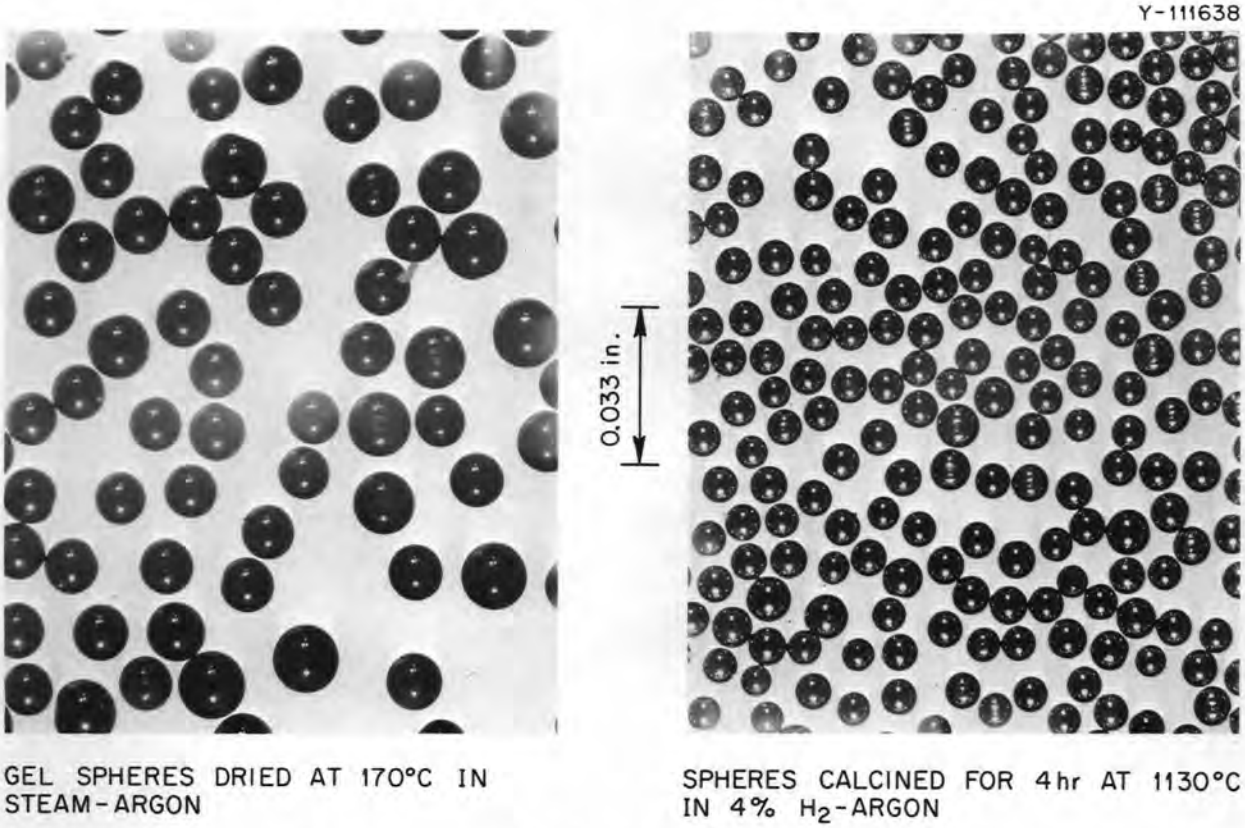

Fig. 6.2. Photomicrographs of dried and calcined UO_2 microspheres.

resin yields a sulfur-free product. The loading characteristics of the two resin types are quite different. Previous work, primarily with sulfonate resins, utilized concentrated UNH solutions for loading and required a large excess of uranium and a contact time of at least 2 hr at ambient temperature.[5] Loading of carboxylate resins is made difficult because the exchange equilibrium between the weakly acidic resin and the uranyl ion is unfavorable. We are developing chemical flowsheets that will optimize the loading processes and will also be suitable for engineering scaleup.

We have greatly improved the efficiency of uranium utilization in loading sulfonate resins from UNH solution, primarily by using a dilute feed, as suggested by the exchange equilibrium

$$2\text{resin}\cdot\text{H} + UO_2(NO_3)_2 \rightleftharpoons \text{resin}_2\cdot UO_2 + 2HNO_3 \ .$$

The beneficial effect of dilution is illustrated in Fig. 6.3, which is taken from ref. 6. A UNH concentration of about 0.1 *M* is optimum since greater dilutions require excessively large liquid volumes. The optimum flow rate is about 10 bed volumes per hour or 5 cm/min. A minimum contact time of 70 min (at room temperature) is required to permit diffusion to the centers of 20- to 50-mesh resin. Under these conditions, a 50% uranium surplus will fully load a 1-ft-long column. Since the uranium excess from one column will load onto a fresh column, by connecting three columns in sequence and adding a fresh one at the tail end each time a loaded one is removed from the head end, no uranium is lost.

A more sophisticated means of achieving the above result on an automatic, semicontinuous basis is to use a modification of the Higgins-type intermittently pulsed contactor.[7] A column of this type, constructed of 1-in.-diam glass pipe, is shown in Fig. 6.4. This column is 7 ft tall overall and can load 2600 ml of resin per 8-hr day, which is equivalent to 3.4 kg of uranium per 24-hr

5. *GCR-TU Programs Semiannu. Progr. Rep. Sept. 30, 1970,* ORNL-4637 (July 1971), pp. 3–7.

6. *GCR-TU Programs Annu. Progr. Rep. Sept. 30, 1971,* ORNL-4760 (in press), Sect. 2.3.

7. I. R. Higgins, *Mechanical Features of the Higgins Continuous Ion Exchange Column,* ORNL-1907 (October 1955).

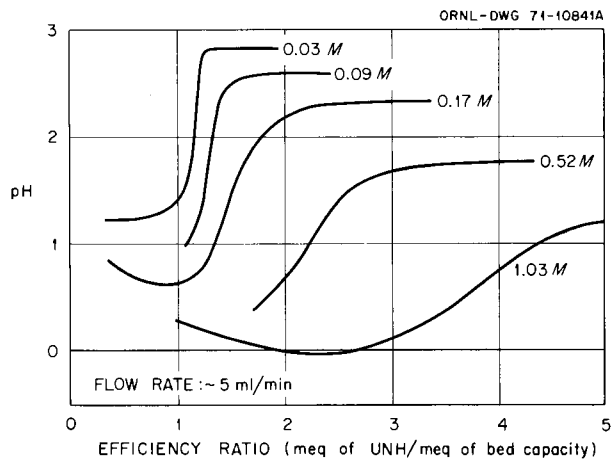

Fig. 6.3. Effect of UNH concentration on the efficiency of uranium utilization for resin loading.

day. This column could be scaled up by a factor of 50 (by doubling the length and increasing the cross-sectional area by a factor of 25), with a corresponding increase in capacity, and still be within criticality limitations. Appropriately placed conductivity probes, indicated by the white rectangles in Fig. 6.4, provide all the sensory input needed for fully automatic control. With strong-acid resin, the composition of the spent liquor is merely that of dilute nitric acid.

Very favorable results have been obtained in investigations of the direct use of UO_3 to load resins.[8] However, some UNH (or HNO_3) must also be present to provide an ionic medium. The overall reaction,

$$2\text{resin}\cdot H + UO_3 \rightarrow \text{resin}_2\cdot UO_2 + H_2O\ ,$$

is actually the sum of these two steps:

$$2\text{resin}\cdot H + UO_2(NO_3)_2 \rightarrow \text{resin}_2\cdot UO_2 + 2HNO_3\ ,$$

$$2HNO_3 + UO_3 \rightarrow UO_2(NO_3)_2 + H_2O\ .$$

The obvious advantages of loading via UO_3 are the direct use of a solid feed and the elimination of waste solution (since the acidity is neutralized). However, the most important advantage is that reaction of the UO_3 with the UNH solution produces an "acid-deficient" UNH, which has a higher pH than does stoichiometric UNH and, therefore, loads effectively onto weak-acid resins. Another potential advantage is the possibility of increased loading as the result of the formation of polymeric species in acid-deficient solutions:

$$UO_2^{2+} \xrightarrow{UO_3} U_2O_5^{2+} \xrightarrow{UO_3} U_3O_8^{2+}\ .$$

The UO_3 method has been demonstrated with sulfonate resin (Dowex 50W-X8) as well as various carboxylate resins (mainly Amberlite IRC-72, which gives the best combination of physical and chemical properties), and has been used to prepare kilogram quantities of loaded resin. Three different types of batch contactors have been used: (1) agitated, baffled vessels; (2) screen-bottom baskets and resin-in-pulp type contacting; and (3) a fluidized resin bed with a separate mixer for adding UO_3.

The UO_3 loading technique has also been demonstrated with a static column, and work in progress is intended to demonstrate it with the continuous column method. Other work deals with loading from uranyl fluoride solution, loading to a controlled level other than stoichiometric exchange, and devising and testing methods for quality assurance testing of the resin beads prior to loading.

6.4 PREPARATION OF TEST MATERIALS

As in previous years, sol-gel oxide spheres were prepared for a number of HTGR programs and for various specific applications. Some needs were met by sphere samples that had been prepared in development studies (see Sect. 6.2); however, in most cases, special preparations were necessary. A new type of test material, ion exchange resin loaded with uranium, was prepared for use in making resin-based spheres.

Special preparations during this report period have included:

1. Seventeen hydrothermal denitrations to convert thorium nitrate into about 250 kg of dispersible ThO_2.
2. More than 100 kg of ThO_2 spheres, 350 to 550 μ in mean diameter, for use in coating development studies and in test elements for reprocessing and irradiation studies.
3. About 3 kg of ThO_2-UO_2 and UO_2 spheres of several ^{235}U contents for irradiation tests.
4. About 20 liters, or 10 kg, of Dowex 50W-X8 ion exchange resins (strong-acid type) loaded with ^{238}U.
5. About 10 liters, or 8 kg, of Amberlite IRC-72 ion exchange resin (weak-acid type) loaded with ^{238}U.

8. P. A. Haas, *HTGR Fuel Development: Use of UO_3 to Load Cation Exchange Resin for Microsphere Preparation*, ORNL-TM-3817 (in preparation).

ORNL PHOTO 0785-72A

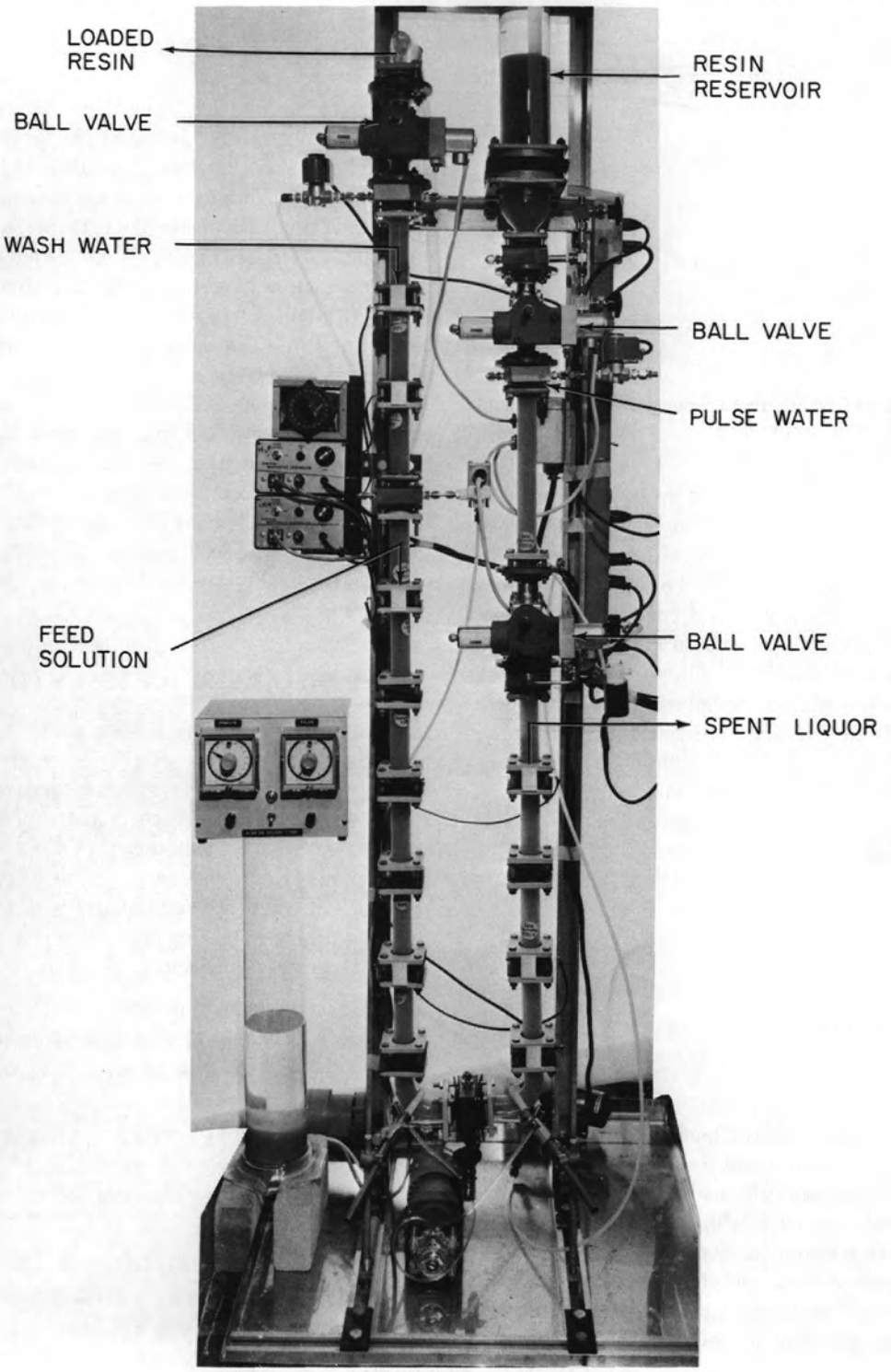

Fig. 6.4. Photograph of semicontinuous resin loading column.

6. About 5 liters, or 4 kg, of Amberlite IRC-72 ion exchange resin loaded with uranium having a ^{235}U content of 7.2%.
7. About 100 g of uranium (with a ^{235}U content of 93%) loaded on Amberlite IRC-72 ion exchange resin.
8. About 400 g of uranium (with ^{235}U contents of 7.25, 20, and 30%) loaded on Dowex 50W-X8 ion exchange resin.
9. About 5500 g of 350-μ spheres of ThO_2–20% UO_2 (93% ^{235}U) for Gulf General Atomic test element irradiations.
10. About 2000 g of UO_2 (93% ^{235}U) spheres for Gulf General Atomic test element irradiations.
11. Sixteen high-quality, stable UO_2 sols, each containing about 275 g of uranium, prepared from $UO_2(NO_3)_2$ (^{235}U content, 93%) according to the standard precipitation-peptization flowsheet. Thirteen of these sols were used in preparing $^{235}UO_2$ and ThO_2-$^{235}UO_2$ fuel for HTGR irradiation test specimens as listed above. The remaining sols were used in the preparation of PuO_2-$^{235}UO_2$ pellet fuel for GCFBR irradiations.
12. About 40 kg of ThO_2-UO_2 spheres formed using ^{238}U. The feed sols had been prepared according to the standard solvent extraction flowsheet and had a Th/U atom ratio of 3.

6.5 ^{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 solutions 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 above capacities include the new facilities, nine dry wells containing 186.2 kg of ^{233}U as UO_3 and six storage tanks containing 568.4 kg of ^{233}U as $UO_2(NO_3)_2$ solution, needed for the storage of feed material for the Light-Water Breeder Reactor (LWBR) support program; later, the solids storage facility will be required for storing 200 kg of ^{233}U from the Elk River reactor. (However, the material must first be recovered and converted to oxide at the Italian CNEN Plant.)

Table 6.2. ^{233}U inventory as of March 31, 1972

Form	Isotopic purity (wt %)	^{232}U content (ppm)	Quantity (kg)
Nitrate	92	22	58.5
	98	7	184.3
	98	8–9	568.4
Oxide	98	6–7	186.2
	96	50	11.0
	91	250	61.7
	98	6	2.3
	97	35	0.6
Fluoride	91	250	2.9
Metal	97	42	5.1
Nitrate[a]	9.7	126	101.6
Total			1182.6

[a]Contains 800.2 kg of ^{235}U. Stored in the TRUST facility.

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. At present, all the ^{233}U that is processed in the facility is shipped as nitrate solution. The system is presently being modified to increase its reliability and flexibility, and an ion exchange and nitrate-to-oxide conversion line with a capacity of 22 kg of ^{233}U per week has been installed for the LWBR support program (see Sect. 7).

Table 6.2 shows the inventory of ^{233}U in the facility as of March 31, 1972; the form, isotopic purity, and ^{232}U content are given.

The solution stored in the TRUST (Thorium Reactor Uranium Storage Tank) facility[9] has been analyzed at six-month intervals, and the uranium and soluble poison (Cd and Gd) concentrations have been found to remain constant.

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

7. Preparation of $^{233}UO_2$ for Light-Water Breeder Reactors

ORNL participation in the Light-Water Breeder Reactor (LWBR) Program, under contract with Bettis Atomic Power Laboratory (BAPL), involves (1) the purification of several hundred kilograms of ^{233}U (presently stored in the facility) at the rate of approximately 20 kg of ^{233}U per week, (2) the conversion of the purified UNH to ceramic-grade UO_2 powder at the rate of about 20 kg of ^{233}U per week, (3) the packaging and shipping of the UO_2 to BAPL for blending with thoria and pressing into pellets, and (4) the recovery of ^{233}U from the $^{233}UO_2$ scrap generated at ORNL and the $^{233}UO_2$-ThO_2 scrap generated at BAPL.

During the past year, modifications to the solvent extraction system were completed; and the UO_2-ThO_2 dissolver, the ion exchange system, and the conversion equipment were installed. The solvent extraction and ion exchange systems were tested with ^{233}U; the conversion system is now ready for testing.

7.1 PROCESS DEVELOPMENT AND FLOWSHEETS

The dissolution procedure for converting $^{233}UO_2$-ThO_2 sintered recycle pellets to a nitrate solution suitable as feed for the solvent extraction purification system was modified slightly from that reported last year.[1] The revised procedure, as developed in laboratory-scale equipment, calls for 8 to 12 *M* HNO_3 that is 0.04 *M* in F^- and 0.1 *M* in $Al(NO_3)_3$ and an increase in the heel to 400% (e.g., if 250 kg of UO_2-ThO_2 is charged, only 50 kg is dissolved). These conditions will prevent the deposition of crystalline $Th(NO_3)_4 \cdot 4H_2O$ on cooling and permit simple dilution with water to meet feed specifications. Dissolution studies in the plant dissolver, utilizing sintered ThO_2 pellets provided by BAPL, are scheduled throughout the next three months.

During the past year, the solvent extraction purification system was operated to purify five batches of ^{233}U. The sizes of the batches varied from 12.5 to 18.5 kg of ^{233}U. Data from these runs showed that a satisfactory thorium separation factor (2.5×10^4), which is equivalent to a thorium concentration in the uranium product of less than 1000 parts per million parts of uranium, can be obtained only by utilizing a scrubbing length of 23 ft out of the total 42 ft available for extraction and scrubbing. Operation with this scrubbing length resulted in a loss of 7% of the uranium in the feed to the aqueous raffinate. The loss was reduced to only 0.5% by using a combination of 30 ft of extraction and 12 ft of scrubbing; however, the thorium separation factor was decreased by a factor of 10. Although several more runs will be made to verify the data, it is anticipated that an additional 10 ft of height must be provided in order to achieve sufficiently small losses (0.2% of the uranium in the feed) to the raffinate as well as a satisfactory thorium separation factor (2×10^4).

Five test runs, in which the batch sizes varied from 15 to 20 kg of ^{233}U, were made with the ion exchange system.[2] The thorium content of the original material ranged from 1000 to 6500 parts per million parts of uranium. In each case, the product contained less than 10 parts of thorium per million parts of uranium, and the residual gamma radiation decayed at the rate predicted for complete removal of ^{228}Th. These results indicate that the two columns are capable of removing 100 g of thorium without breakthrough occurring. Following elution of the uranium with HNO_3, the thorium was removed from the resin beds with an ammonium acetate–acetic acid solution, which could be discarded to waste since it contained only 0.05% of the uranium in the feed.

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 163.

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

The process development work for conversion of the nitrate solution to ceramic-grade oxide was performed by the Metals and Ceramics Division. The results of this work, along with the recommended process parameters, are reported elsewhere.[3]

7.2 DESIGN AND INSTALLATION OF EQUIPMENT FOR THE UO_2 CONVERSION LINE

Nine stainless steel alpha enclosures and all the associated processing equipment were installed and tested. Except for a malfunctioning power transformer on the microwave-oven generating unit, the equipment performed satisfactorily in tests with simulated material. The defective unit was returned to the factory for replacement.

The reduction furnace was tested, and the heat profile was adjusted to meet process requirements.

The alpha ventilation system, which handles the exhaust from all the alpha enclosures, was installed, tested, and placed in service. The system contains three fans that operate sequentially to provide the necessary negative pressure, and the exhaust is directed through two sets of absolute filters. Emergency power is provided by a diesel-powered generator which operates automatically in the event of power failure.

We expect to begin testing the conversion system with ^{233}U in May 1972.

7.3 PLANT SAFETY

Two reports, one dealing with nuclear safety considerations,[4] and the other pertaining to conventional safety,[5] were issued during this report period. Safety reviews by the AEC Pre-operational Review Committee, the ORNL Criticality Review Committee, and the ORNL Radioactive Operations Review Committee were completed, and approvals were obtained to place the plant in operation with ^{233}U.

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3. J. M. Leitnaker, M. L. Smith, and C. M. Fitzpatrick, *Conversion of Uranium Nitrate to Ceramic-Grade Oxide for the Light Water Breeder Reactor: Process Development,* ORNL-4755 (April 1972).

4. R. W. Horton, *Criticality Analysis: LWBR Assistance Program in Bldg. 3019,* ORNL-TM-3469 (March 1972).

5. R. W. Horton, *Safety Analysis: LWBR Support Program in Building 3019 Pilot Plant,* ORNL-TM-3567 (March 1972).

8. Separations Chemistry Research

New separations methods are being developed, principally for uses in radiochemical processing but also for other purposes extending from extractive metallurgy to biochemical separations. The program in separations chemistry divides into three parallel, interdependent, and frequently overlapping types of research activity: (1) descriptive chemical studies (Sects. 8.1, 8.5, and 8.6) of the reactions of substances to be separated and of separations reagents, of the controlling variables in particular separations, and of potential new reagents and methods; (2) development (Sects. 8.2 to 8.5) of selected separations and methods into specific complete processes, both where no workable process exists and where existing processes can be improved, carried where warranted to the point that large-scale performance can be predicted; and (3) fundamental chemical studies (Sects. 8.6 to 8.9) of the species, equilibria, and reaction mechanisms involved in separations systems, both to increase knowledge and to help define potential applications.

8.1 NEW SEPARATIONS AGENTS

We are continuing to investigate, for potential utility in solvent extraction or other separations methods, compounds that are (1) newly available commercially, (2) submitted by manufacturers for testing, or (3) specially procured for testing of class or structure.

A limited survey has been started of the possibilities of coating porous supports with ion exchange materials in order to obtain better combinations of chemical and physical properties. Without barring organic exchangers, the interest is primarily on inorganic exchangers with potential radiation resistance but limited ability for self-support, and initial emphasis has been on efficient cesium sorbers. Titanium phosphate or ammonium molybdophosphate coated on nonpolar macroreticular resins such as Amberlite XAD-4, on unfired Vycor, or on silica gel by a special vacuum technique appears promising for cesium scavenging.

In the anion exchange purification of plutonium, equilibrium is slow because of the low rate of diffusion of the large plutonium anion through the gel surface of the exchange resin. An investigation was undertaken to determine if the rate of exchange would be faster with resins prepared by the macroreticular polymerization process. Thorium was used as a stand-in for plutonium since the anion exchange properties of the two elements are quite similar.[1] Results of batch shakeouts and column experiments indicated that equilibrium was established more rapidly with Amberlite IRA-900 than with the control gel-type resin, Dowex 1-X8, and that it may be useful for the purification of plutonium.

The batch contacts compared Amberlyst A21, A26, and A28 and Amberlite IRA-68, -91, -93, -900, -904, and -910 with Dowex 1-X8. The nitrate-form, 20- to 30-mesh resin was contacted for 10 to 1000 min with 7 *M* HNO_3 having a thorium concentration of 2 mg/ml. The two most promising resins were Amberlite IRA-900, a strongly basic anion exchanger with quaternary ammonium functionality, and Amberlite IRA-93, a weakly basic anion exchanger with polystyrene polyamine functionality. Runs comparing these resins with Dowex 1-X8 were made with columns 1 cm in diameter and about 28 cm long. At flow rates of 0.4 ml/min and a feed of 7 *M* HNO_3 having a thorium concentration of 4.8 mg/ml, 0.2% thorium breakthrough occurred after 7, 9, and 15 bed volumes had passed through the IRA-93, Dowex 1-X8, and IRA-900, respectively.

Trifluoromethane sulfonic acid (F_3CSO_3H), HTMS, was first prepared in 1954 and shown to be stronger (in acetic acid medium) than sulfuric and hydrochloric acids by Haszeldin and Kidd,[2] and shown to be stronger than perchloric acid (in acetic acid) by Grimstad.[3] Lane found it comparable to perchloric acid for titrations in acetic acid medium, and less likely to form precipitates, but not enough better to compensate for its cost as a

1. J. L. Carroll, *Absorption of Thorium on an Anion Exchange Resin*, HW-70536 (September 1961).
2. R. N. Haszeldin and J. M. Kidd, *J. Chem. Soc. (London)* **1954**, 4228.
3. T. Grimstad, *Tidsskr. Kjemi, Bergr., Metallurgi* 19, 30 (1959).

specialty reagent.[4] We recently obtained some commercial HTMS[5] to examine its characteristics in aqueous media, primarily to learn whether or not it complexes metal ions significantly, and if not, whether it could be substituted for perchloric acid as a "noncomplexing" supporting electrolyte. For a preliminary test, the extraction of iron(III) by di(2-ethylhexyl)phosphoric acid (HDEHP) was compared from 1 *M* HTMS-NaTMS vs 1 *M* $HClO_4$-$NaClO_4$ at pH values near 1 (0.99 to 1.04). Since HDEHP extracts iron by cation exchange, the extraction should be impaired by any aqueous-phase complex formation. With TMS^- replacing ClO_4^- in increments of 10 mole % through a series of extractions, the uncorrected extraction coefficients decreased gradually from ~17 to ~15. When normalized to pH 1.00 according to the relation $\log E_{1.00} = \log E_{pH} - 3\,(pH - 1.00)$, they decreased slightly more, from ~18 to ~12. These results, while suggesting that there is more association of iron with TMS^- than with ClO_4^-, warrant further study of HTMS as a potential supporting electrolyte.

8.2 PLUTONIUM PURIFICATION WITH AMINES

Numerous investigators have studied the use of amines for extracting and purifying plutonium in the reprocessing of reactor fuels. Most of our tests[6–8] have been made with secondary amines, rather than the usual trilaurylamine, because they are easily stripped with dilute nitric acid.

We are currently comparing the extraction and other process characteristics of two secondary amines, di(tridecyl)amine and Amberlite LA-1, with those of trilaurylamine and TBP. Since plutonium extraction has been fairly well characterized, emphasis is being placed upon the behavior of the major fission products; ruthenium is receiving the initial attention.

The coefficients for extraction of ruthenium with 0.3 *M* solutions of di(tridecyl)amine or Amberlite LA-1 in diethylbenzene decreased from 0.06-0.08 to 0.02-0.04 as the HNO_3 concentration was increased from 2 to 8 *M*. (Slightly higher values were obtained in extractions with trilaurylamine.) In these studies, ruthenium was primarily in the form of the nitrosyl-nitrato complex, the most extractable form, and the contact time was 10 min. The extraction coefficient increased slowly as the contact time was extended to 4 hr and then became essentially constant. Ruthenium extraction coefficients with 0.6 *M* TBP were approximately equivalent to those for the secondary amines at low acid concentrations (2 to 4 *M*) but were about an order of magnitude lower than those for the amines at acid concentrations of 6 to 8 *M*.

8.3 RECOVERY OF URANIUM FROM COMMERCIAL PHOSPHORIC ACID

Laboratory testing of a promising two-cycle solvent extraction process for recovering uranium from wet-process phosphoric acid with the synergistic extractant combination of di(2-ethylhexyl)phosphoric acid (D2EHPA) plus trioctylphosphine oxide (TOPO) was completed.[9,10] A pilot plant is being built at a phosphoric acid plant in Florida to test the process. Commercial phosphoric acid produced from Florida phosphate rock contains 0.1 to 0.2 g of uranium per liter and represents a potential source of about 2000 tons of U_3O_8 per year.

Alternative Process

A new process, which uses a mixture of mono- and dioctylphenyl phosphoric acid (OPPA), rather than D2EHPA-TOPO, has been developed for the first extraction cycle. This process appeared highly promising and superior to the D2EHPA-TOPO process in initial batch tests. However, some serious problems were encountered in continuous tests, and these must be solved before the process can be considered competitive with the D2EHPA-TOPO process.

The octylphenyl phosphoric acid reagents have been studied previously by Peppard[11,12] for extracting thorium, rare earths, and other elements. More recently

4. E. S. Lane, *Talanta* 8, 849 (1961).
5. "Trimsylate Acid FC-24," Minnesota Mining and Manufacturing Co. Technical Information (October 1970).
6. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1967,* ORNL-4145, p. 55.
7. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1968,* ORNL-4272, p. 54.
8. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1969,* ORNL-4422, p. 82.
9. F. J. Hurst, D. J. Crouse, and K. B. Brown, "Recovery of Uranium from Wet-Process Phosphoric Acid," *Ind. Eng. Chem., Process Design Develop.* **11**(1), 122–28 (1972).
10. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 21, 1971,* ORNL-4682, pp. 170–73.
11. D. F. Peppard, G. W. Mason, W. J. Driscoll, and R. J. Sironen, "Acidic Esters of Orthophosphoric Acid as Selective Extractants for Metallic Cations – Tracer Studies," *J. Inorg. Nucl. Chem.* 7, 276–85 (1958).
12. D. F. Peppard, G. W. Mason, and S. McCarty, "Extraction of Thorium(IV) by Diesters of Orthophosphoric Acid," *J. Inorg. Nucl. Chem.* **13**, 138–50 (1960).

they were examined by Murthy[13] for recovering uranium from phosphoric acid. Uranium(IV) is extracted more strongly than uranium(VI) with these reagents. If the concentration of ferrous iron in the acid is about 0.5 g/liter or higher, which is usually the case for fresh acid, the uranium is present in the tetravalent state and no valence adjustment is necessary. Much higher uranium extraction coefficients are obtained with a mixture of the mono- and di- acids than with either alone. We are using an approximately equimolar mixture that is commercially available at low cost. With an extractant concentration of 0.35 *M*, the coefficient for extraction of U(IV) from wet-process acid at 40°C is about 16.

In the proposed process, uranium is extracted at 40 to 50°C and stripped by contacting the extract with 10 *M* H_3PO_4 containing sodium chlorate; the chlorate oxidizes the uranium to the less-extractable hexavalent state. A convenient source of strip solution is the 45 to 55% P_2O_5 product acid from the evaporators. The strip solution can be loaded with uranium to about 15 g/liter; this solution, after dilution to 6 *M* H_3PO_4, would be fed directly to a second extraction cycle, which would use D2EHPA-TOPO solvent, to produce a relatively pure U_3O_8 product.

13. T. K. S. Murthy, V. N. Pai, and R. A. Nagle, "Study of Some Phenyl Phosphoric Acids for Extraction of Uranium from Phosphoric Acid," pp. 341–50 in *Proceedings of a Symposium on the Recovery of Uranium from Its Ores and Other Sources,* organized by the International Atomic Energy Agency and held in São Paulo, Brazil, August 17–21, 1970.

Process Demonstration

A continuous demonstration of the process flowsheet was made in a small mixer-settler test array, using 0.35 *M* OPPA in Amsco 450 to recover uranium from a sample of wet-process acid produced from Florida rock. Since all of the uranium was tetravalent, no pretreatment of the acid was necessary. Figure 8.1 shows the test conditions and the distribution of uranium and other components in the system after ten complete cycles of solvent through the system. At this point, the uranium recovery was only 70%, compared with 90% earlier in the run. This was due primarily to a factor of 2 decrease in the extraction power of the solvent with cycling. Titration of the reagent indicated that no loss of extractant had occurred but that appreciable organic material (humus) had accumulated in the solvent and may have interfered with uranium extraction. This and other possible reasons for the loss of extraction power are being investigated.

About 90% of the uranium was stripped to give a first-cycle product solution with 15.5 g of uranium per liter. Sodium chlorate consumption was found to be excessive in this test (about 3 lb of $NaClO_3$ per pound of uranium). Later batch tests indicated that this problem can be solved by operating at 25 to 30°C rather than 50°C, but confirmation in continuous tests is required.

Physical operation of the extraction system was satisfactory, provided the extraction contactors were operated with the aqueous phase continuous; operation in the organic continuous mode resulted in slow-break-

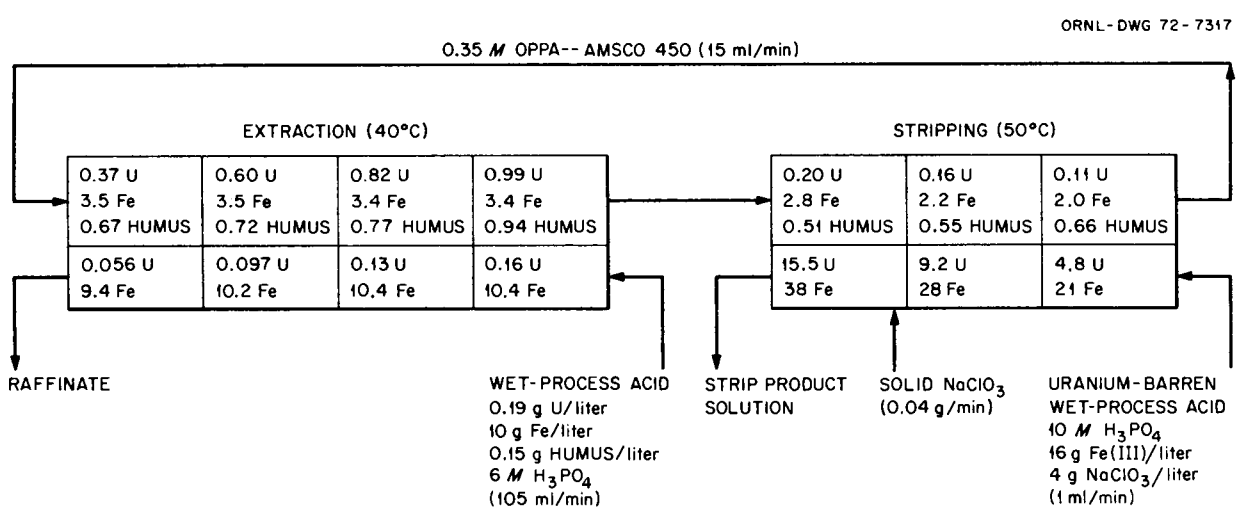

Fig. 8.1. Solvent extraction recovery of uranium from phosphoric acid with OPPA. Numbers in blocks show concentrations in grams per liter after ten cycles of operation.

ing emulsions that severely limited throughput capacity. The accumulation of solids at the aqueous-organic interfaces in this system was more troublesome than in the D2EHPA-TOPO system.

Some of the more troublesome problems encountered in applying the OPPA process arise from the presence of organic material in the acid feed. In two plants that process Florida phosphate rock, the rock is calcined to destroy organic material. The resulting "green" acid appears, on the basis of preliminary tests, to be much more amenable to treatment by the OPPA process than acid produced from uncalcined rock.

8.4 EXTRACTION OF LITHIUM FROM SALT SOLUTIONS

The extraction of lithium from salt solutions with the synergistic extractant combination of a β-diketone and trioctylphosphine oxide has been reported previously.[14,15] However, practicable extraction levels were not obtained at pH values below 11. We have reported that effective lithium extraction can be obtained from near-neutral salt solutions using fluorinated β-diketones.[16]

We recently demonstrated lithium recovery from a concentrate of Searles Lake (California) salt brine (0.08 g of Li, 145 g of Na, and 29 g of K per liter, pH 9.5) in a batch countercurrent system. Three stages of extraction with 0.3 *M* heptafluorodimethyloctanedione–0.1 *M* trioctylphosphine oxide in dodecane and two stages of scrubbing with 0.2 *N* HCl were used. Recovery of lithium was 94% complete with a concentration factor of 5 and decontamination factors of 1200 from sodium and 76,000 from potassium. Loss of extractant by distribution to the raffinate was less than 5 ppm. The lithium is readily stripped with dilute acid, and large concentration factors across the stripping system are obtainable.

8.5 HIGH-RESOLUTION RARE-EARTH SEPARATIONS

The pressurized ion exchange separation of all the rare earths was applied at the Lawrence Radiation Laboratory, Livermore, and a joint paper has been submitted for publication.[17] The principal conclusions were: "Using the techniques of high-pressure liquid chromatography, it has been possible to separate mass quantities of all 14 rare earths in less than 5 hr. The importance of solvent gradient, particle size and resin cross-linkage were examined. . . . Using XI2 resin, bead diameters of 25 ± 7 μ, and a flow rate of 10.3-13.5 ml/cm^2/min, the mean resolution for the complete separation was 1.28. Baseline resolution was obtained for all components except the Lu-Yb pair. For this pair, R = 0.96, indicating a small cross contamination. It is possible to obtain a baseline Lu-Yb separation if the α-but [α-hydroxyisobutyrate] concentration is maintained at 0.05 *M* until after the lutetium has eluted. . . . There have been essentially no "scale-up" difficulties. . . .Once the resin was obtained, it was only necessary to optimize the solvent gradient for the resin cross-linkage and particle size, and acceptable separations were obtained."

The emphasis in other continuing studies of pressurized ion exchange has been on further reduction of the time required for given separations. Although several elements can be easily separated in 1 hr, the purification of the ever-increasing amounts of californium that are being produced at TRU (Sect. 5.1) would benefit from more rapid processing. In general, the optimum procedure is that which provides the required separation in the minimum time. Both theoretical considerations and experimental studies with rare earths indicate that, compared with present methods, the separation time can be reduced substantially without loss of resolution by using smaller resin particles, shorter but larger-diameter columns, and higher flow rates, with about the same pressure drop. It has not been practical to demonstrate such extremely rapid production-scale separations because of limitations in available equipment and methods.

8.6 DISTRIBUTION EQUILIBRIA AND MECHANISMS

Previous investigation of uranium extraction by a primary amine from sulfuric acid solutions showed low extraction of uranium(VI) and very high extraction of uranium(IV), both decreasing with increasing acid concentration up to 3 *M*. The extraction isotherms were approximated by the empirical equations E(U-VI) ≈

14. T. V. Healy, *Chem. Div. Progr. Rep. Nov. 1964–April 1965,* AERE PR/Chemistry 8, Harwell, Berks. (1965).

15. D. A. Lee et al., *J. Inorg. Nucl. Chem.* **30**, 2807–21 (1968).

16. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971,* ORNL-4682, pp. 168, 170.

17. D. H. Sisson, V. Alan Mode, and D. O. Campbell, "High-Speed Separation of the Rare Earths by Ion Exchange – Part II," *J. Chromatog.* **66**, 129 (1972).

4([Amine] − 6[U-VI]) and E(U-IV) ≈ 10^7 ([Amine] − 8[U-IV])^3, for Primene JM in Amsco 125-82–10% tridecanol and 3 M H_2SO_4 + 0.5 M Na_2SO_4.[18] Current work extending the extraction range shows that the mechanisms of extraction of both valence states change at higher sulfuric acid concentrations. With Amberlite XLA-3 (similar to Primene JM) in n-dodecane–10% tridecanol, the extraction of uranyl sulfate reached a minimum near 6 M H_2SO_4 and then increased with increasing acid concentration up to at least 10 M (Fig. 8.2). In contrast, the extraction of uranous sulfate decreased very sharply with increasing acid concentration up to at least 8 M. At 5 M acid the extraction coefficient varied with nearly the third power of the free amine concentration, consistent with the empirical equation cited above for extraction from 3 M acid. However, at 6 and 8 M acid the power dependences (represented by the log E vs log [Amine] slopes, Fig. 8.3) decreased, especially at the higher amine concentrations, approaching approximately first power.

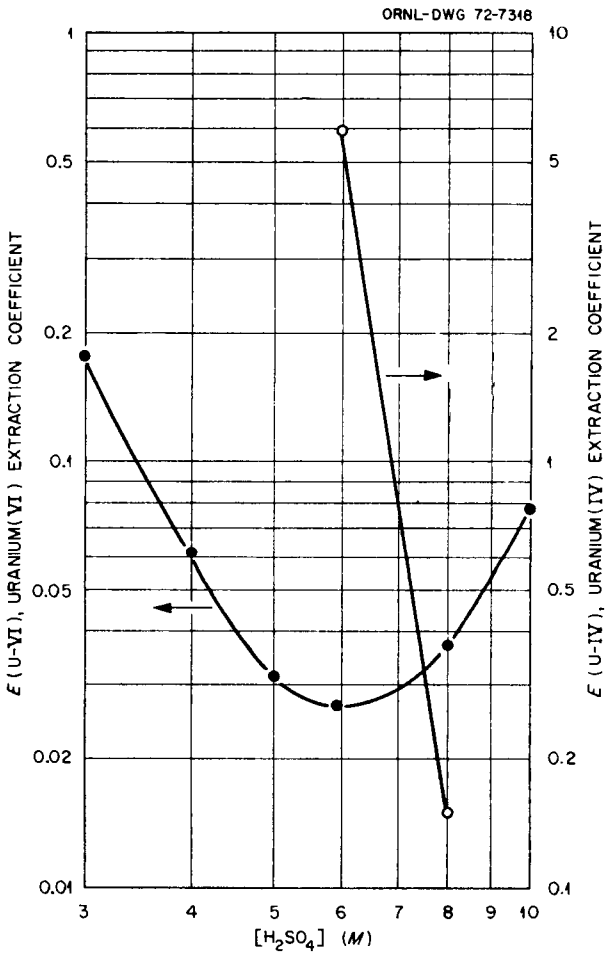

Fig. 8.2. Effect of sulfuric acid concentration on extraction of U(VI) and U(IV) by primary amine Amberlite XLA-3 in n-dodecane–10% tridecanol. □ U(IV); [free amine] = [Σ amine] − 8[U(IV)]$_0$ ≈ 0.04 M. ○ U(VI); [Σ . mine] = 0.1 M, with E normalized to 0.1 M free amine according to the relation $E \propto$([Σ amine] − 6[U(VI)]$_0$). [U] ≤ 0.05 [Σ amine].

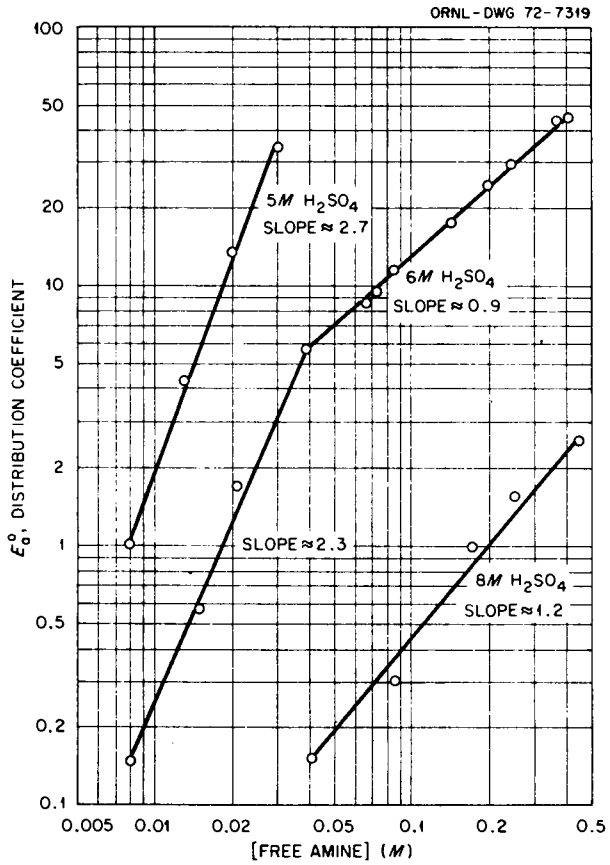

Fig. 8.3. Effect of amine concentration on extraction of U(IV) from sulfuric acid solutions. Primary amine Amberlite XLA-3 in n-dodecane–10% tridecanol; [free amine] = [Σ amine] − 8[U(IV)]$_0$. [U] ≤ 0.05 [Σ amine].

The solubility of uranous sulfate in sulfuric acid solution decreased rapidly as the acid concentration increased, but crystallization from supersaturated solutions was slow. We do not yet have quantitative data at the higher acid concentrations; hence, the coefficients at 8 M in Figs. 8.2 and 8.3 might apply to metastable aqueous solutions.

Study and use of the "tagged-ligand transfer" technique[19] continued in the measurement of chloride/iron

18. D. E. Horner and C. F. Coleman, *Recovery of Uranium and Plutonium from Sulfuric Acid Decladding Solutions*, ORNL-2830 (November 1959).

19. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 176.

ratios by extraction with an amine from concentrated lithium chloride solutions and in the measurement of water/sulfate ratios in extraction of sulfuric acid with an amine. In tagged-ligand transfer, the ligand in one phase of a distribution system is tagged radioactively. The ligand/solute transfer ratio is determined, corrected for transport of ligand via other paths, and extrapolated back to zero time to show the average ligand/solute association number in the species that cross the interface before any disruption of the initial conditions has been caused by the progress of the extraction.

The chloride system is of particular interest, both because chloride forms weak complexes typical of those for which improved methods of investigation are being sought and because high-ionic-strength chloride systems are of process interest in separating the lanthanides and higher actinides. The lithium chloride system constitutes a severe test for the tagged-ligand method in that large amounts of chloride transfer to the organic phase even without complexed-metal transfer. The desired answer must thus result from small differences between large numbers, so that analyses must be exceedingly accurate. Current efforts in the system iron(III)–chloride–H_2O–Adogen 464 (R_4NCl)–xylene are directed at refining equilibration techniques and analytical methods and purifying reagents. The results found for the average Cl/Fe association numbers in transfer are 3.1 at 4 *M* Cl^-, 4.7 at 7 *M* Cl^-, and 3.2 at 9 *M* Cl^-. The corresponding average association numbers for the iron chloride complexes in aqueous solution are 3, 3.25, and 4, respectively.[20]

The ratio of water to sulfate transferred at the start of sulfuric acid extraction by an amine is being measured for comparison with previous measurement of the ratio at equilibrium,[21] in each case as a function of varying water activity. This is part of a long-standing and so far unsuccessful attempt to account for large apparent anomalies in amine extraction systems.[22] The results obtained in the system H_2SO_4–H_2O–tri-*n*-octylamine (TOA)–toluene, with tritium-traced water and ^{35}S-traced sulfate, are compared in Fig. 8.4 with equilibrium curves for a similar system in the previous study.[21] While the transfer ratio results show expectably large scatter, and indicate slightly higher initial than equilibrium ratios at the same amine concentration, they follow a very similar pattern as a function of water activity.

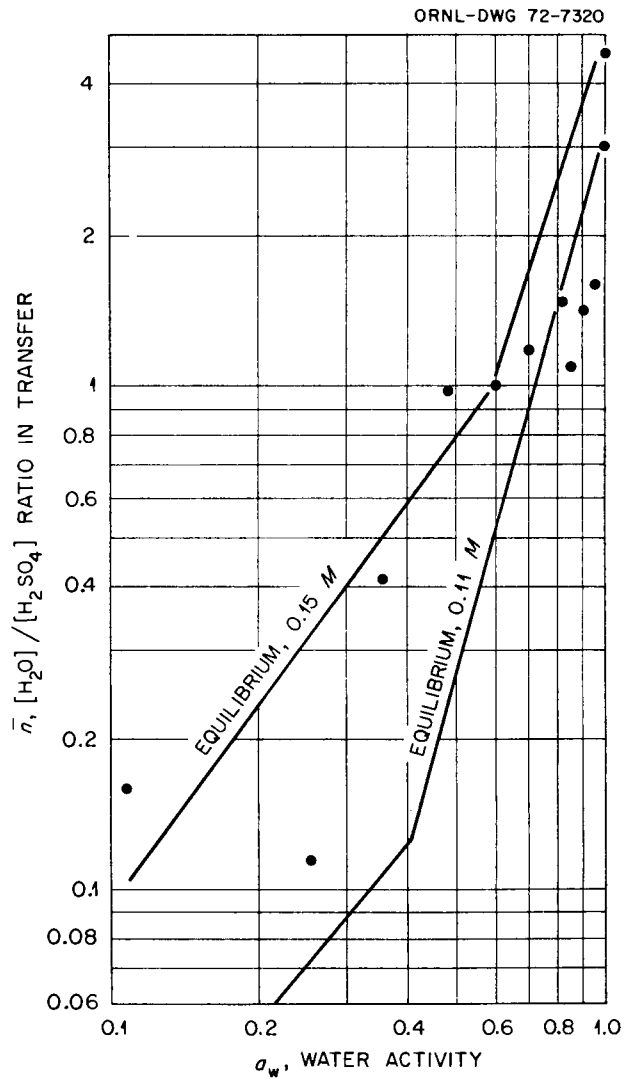

Fig. 8.4. Ratio of water extracted to sulfuric acid extracted by tri-*n*-octylamine. Points: ratio at the start of extraction (0.1 *M* TOA in toluene). Lines: representing ratios at equilibrium, from ref. 21 (0.11 and 0.15 *M* TOA in benzene).

A study was completed of chloride complexing of trivalent berkelium and einsteinium in solutions of up to 1 *M* NaCl.[23] Ionic strength was held constant at 1 *M*

20. G. A. Gamelin and D. O. Jordan, *J. Chem. Soc. (London)* **1953**, 1435.

21. J. W. Roddy and C. F. Coleman, "The Extraction of Water by Tri-*n*-octylamine and Several of Its Salts in Benzene and Phenylcyclohexane," *J. Inorg. Nucl. Chem.* 31, 3599 (1969).

22. C. F. Coleman and J. W. Roddy, "Mass Action and Non-Ideality in Extraction by Amine Sulfate," in *Solvent Extraction Chemistry*, ed. by D. Dyrssen et al., North Holland Publishing Company, Amsterdam, 1967, p. 362.

23. H. D. Harmon, J. R. Peterson, and W. J. McDowell, "The Stability Constants of the Monochloro Complexes of Bk(III) and Es(III)," *Inorg. Nucl. Chem. Lett.* 8, 57 (1972).

with $NaClO_4$, pH 2. The extent of complexing was measured by its competition with cation exchange extraction by di(2-ethylhexyl)phosphoric acid (HDEHP), expressed as the ratio of the extraction coefficients without and with the ligand:

$$(E^{\circ}/E) = 1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2 + \ldots$$

Both linearity of plots and computer fitting suggested that only the $\beta_1 = [MCl^{2+}]/[M^{3+}][Cl^-]$ terms, for $M^{3+} + Cl^- \rightleftharpoons MCl^{2+}$, are significant for both Bk and Es in this chloride concentration range. For both, $\beta_1 = 0.96 \pm 0.01$. From this, the calculated fraction of Bk or Es complexed rises to almost 0.5 at 1 *M* Cl^- (Fig. 8.5).

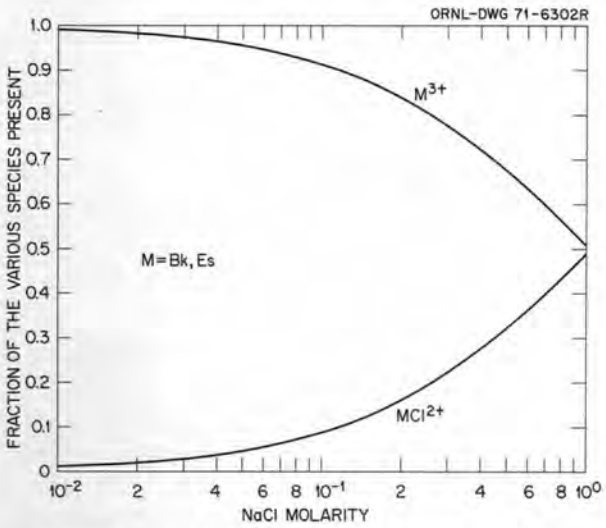

Fig. 8.5. Fraction of aqueous Bk(III) or Es(III) complexed as a function of NaCl molarity. $NaCl$-$NaClO_4$ at ionic strength = 1 *M*, pH 2, 25°C.

In continued development and use of liquid scintillation alpha counting, significant improvements were made in the composition of the scintillator, and in the light-gathering effectiveness and the electronics of the detector. Together, these have improved the energy resolution for alphas to about 0.2 MeV and about 0.3 MeV (peak width at half maximum) at alpha energies of 4 MeV and 7 MeV respectively (see Fig. 8.6). A brief study to determine the usefulness of the combined solvent extraction–liquid scintillation technique for detecting and identifying alpha emitters in very-low-count-rate samples was reported in ORNL-TM-3676. The abstract follows:

An Evaluation of the Possibility of Detecting and Identifying Alpha Emitters in Low-Count-Rate Samples Using Some New Liquid Scintillation Counting Techniques, by W. J. McDowell and L. C. Henley. *Abstract:* Several tests in which a high-resolution liquid scintillation method was applied to samples having a low count rate (i.e., urine samples and waste water) are described. With the present shielding and resolution, the identification of an alpha energy to ±0.1 MeV at a count rate as low as 1 count/min appears to be feasible. Since many waste or environmental samples are above this count rate, application of this method to such samples appears attractive. Methods of improving energy resolution and reducing background are noted.

It is often desirable to present information as a function of two variables by means of a two-dimensional representation of a three-dimensional plot. While the conventional draftsman's isometric and oblique "perspectives" are satisfactory for simple plots, true-perspective drawings are much easier to visualize and

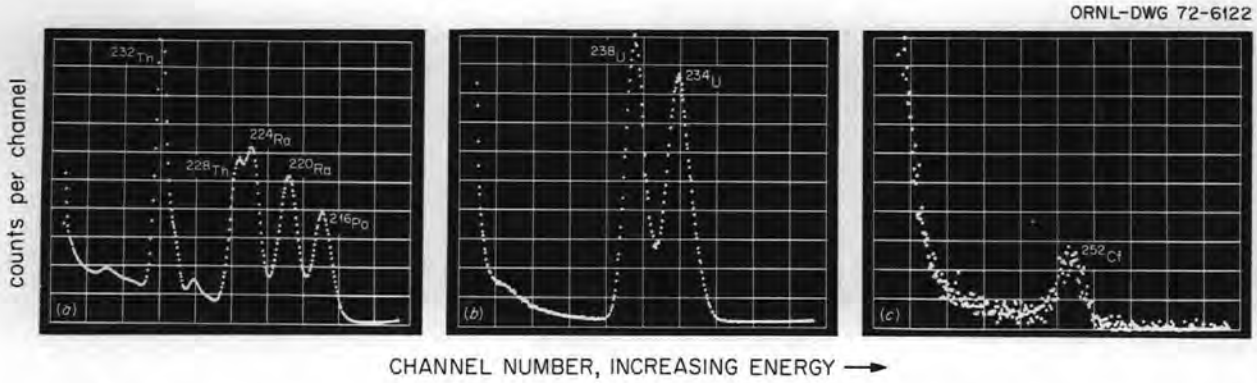

Fig. 8.6. High-resolution alpha liquid scintillation spectra. (a) ^{232}Th and four of the daughters (^{232}Th, 4.0 MeV; ^{228}Th, 5.4 MeV; ^{224}Ra, 5.7 MeV; ^{220}Ra, 6.3 MeV; and ^{216}Po, 6.8 MeV) in its natural decay chain show the present energy resolution ability of our system. (b) Natural uranium shows the normal ratio of ^{238}U (4.19 MeV) and ^{234}U (4.79 MeV); the peak for ^{235}U (4.39 MeV) can be found between these two peaks by computer analysis. (c) Alpha activity detected in routine urinalysis monitoring was identified by this method as ^{252}Cf, energy near 6.1 MeV, at a count rate of 2.2 dis/min.

interpret for complicated plots. We have developed a simple and effective method for producing true-perspective representations, especially suited to plots where much of the significant information can be placed in a series of parallel planes (cross sections).[24] Figure 5.1 of Sect. 5.5 was prepared by this method. A separate computer *x-y* plot for each value of *z* was photographed and enlarged on 8- by 10-in. transparency film. These were mounted on sheets of rigid clear plastic, supported at the proper *z*-spacing in a slotted wooden base. This array was photographed, after careful choice of the best camera angle and distance, and the figure was completed by adding the varying-*z* lines, legends, etc., to a tracing of the photograph. More than one view could have been presented if useful for clarity or shift of emphasis; stereo pairs could also be made.

8.7 LANTHANIDE AND ACTINIDE HYDROXIDES

Information on the relative basicities of Am, Cm, and the trivalent lanthanides[25] was presented at the Ninth Rare Earth Research Conference.[26]

Further study was made of the anomalous stoichiometry observed in titrations of salts of these elements with sodium hydroxide solutions. Stoichiometry varies with the element; in the extreme cases, complete precipitation of the metal can be attained with as little as 70% of the theoretical amount of base from chloride and nitrate solutions and as little as 55% from sulfate solutions. Analyses of supernatant samarium chloride and sulfate solutions at different stages of titration indicated that the ratios of these anions to metal in the precipitate decreased as titration proceeded, although a detectable amount of chloride or sulfate was always present in the precipitate, even with a large excess of base. The subsequent approach toward equilibrium continued for many days. The indefiniteness of composition of the precipitate precludes calculation of solubility products.

8.8 KINETICS OF METAL-ION EXTRACTIONS

The search has continued for an analytical method suitable for following the kinetics of aluminum extractions. Spark-source mass spectrometry appeared promising but failed because aluminum impurities in the electrodes caused significant errors at the low sample levels. Measurements in a part of the range of interest were obtained with aluminon (ammonium aurin tricarboxylate) in a microcolorimetric method giving fairly good precision down to 0.01 mg of aluminum.

Within the precision of the colorimetric method, the kinetics of aluminum extraction from $HClO_4$–$NaClO_4$ solutions by di(2-ethylhexyl)phosphoric acid (HDEHP) in *n*-octane are first order with respect to the aqueous aluminum concentration. The rate constant $k = -d[\mathrm{Al}]/[\mathrm{Al}]dt$ varied inversely with perchloric acid concentration from 0.0036 cm/min at 0.01 *M* H^+ to 0.00184 cm/min at 0.02 *M* H^+ (0.1 *M* HDEHP, aqueous ionic strength = 2, 25°C). This nearly matches the kinetics behavior of iron(III) in extraction by 0.01 *M* HDEHP (other conditions being identical), and is about 40% as fast as the iron extractions by 0.1 *M* HDEHP.[27] A much greater difference between iron and aluminum extraction rates by HDEHP from sulfate solutions was previously indicated by process development tests;[28] however, this may reflect different effects of sulfate complexing on the extraction rates of the two metal ions.

We have started a study of kinetics in the photochemical reduction of uranyl ion, with and without simultaneous extraction of the uranous ion produced. Tests without extraction, using ethanol as substrate and light of a wavelength near the low-energy limit of the uranyl absorption, showed an initial rapid decrease in the rate of uranium(IV) production, followed by a longer period in which the rate approximated first order with respect to uranyl concentration, independent of both the initial uranyl concentration over a range of low concentrations and the (large) excess of ethanol. The initial brief period of changing rate is tentatively attributed to a rapid buildup of uranium(V) intermediate product, followed shortly by its conversion to uranium(IV) with resulting competitive absorption of the incident light and a correspondingly lowered rate of uranium(V)

24. W. J. McDowell and W. N. Tillery, "A Photographic Method for Producing True-Perspective, Three-Dimensional Plots," *J. Chem. Ed.* (in press).

25. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971,* ORNL-4682, p. 177.

26. Boyd Weaver and R. R. Shoun, "Basicities of Trivalent Actinides and Lanthanides and Solubilities of Their Hydroxides," *Proceedings of the 9th Rare Earth Research Conference, Blacksburg, Va., Oct. 1971,* CONF-711001, p. 322.

27. J. W. Roddy, C. F. Coleman, and Sumio Arai, "Mechanism of the Slow Extraction of Iron(III) from Acid Perchlorate Solutions by Di(2-ethylhexyl)phosphoric Acid in *n*-Octane," *J. Inorg. Nucl. Chem.* 33, 1099 (1971).

28. C. F. Coleman and J. W. Roddy, "Kinetics of Metal Extraction by Organophosphorus Acids," *Solvent Extraction Revs.* 1, 63 (1971); rate constants calculated from data in C. A. Blake et al., *The Extraction and Recovery of Uranium (and Vanadium) from Acid Liquors with Di(2-ethylhexyl)phosphoric Acid and Some Other Organophosphorus Acids,* ORNL-1903 (June 1955).

formation. If this is correct, the subsequent seemingly first-order rate must actually be much more complicated, and this expectation is borne out by the appearance of complex behavior in preliminary tests with simultaneous extraction of the uranium(IV).

8.9 AGGREGATION AND ACTIVITY COEFFICIENTS IN SOLVENT PHASES

A previous investigation of the nonideality of solutions of 4-*sec*-butyl-2-(α-methylbenzyl)phenol (BAMP)[29] was extended to obtain more complete physicochemical data, determine the nature of intermolecular association, and elucidate the possibility of intramolecular hydrogen bonding. The abstract of a paper to be submitted to the *Journal of Inorganic and Nuclear Chemistry* follows:

"Investigation of Intermolecular Association of 4-*sec*-Butyl-2-(α-methylbenzyl)phenol (BAMBP) by Use of Dielectric and Isopiestic Measurements," by J. W. Roddy and C. F. Coleman. *Abstract*: The association of the cesium extractant 4-*sec*-butyl-2-(α-methylbenzyl)phenol (BAMBP) in *n*-hexane was investigated by means of isopiestic, dielectric constant, density, refractive index, and viscosity measurements at concentrations up to 6.8 *m*, and equilibrium constants describing this behavior in terms of association were determined for the concentration range of 0-2.8 *m*. The Kirkwood correlation factor and stoichiometric activity coefficients were also calculated. The results indicate that BAMBP associates to form dimers and pentamers in such orientations as to maintain a nearly constant resultant dipole moment, with formation concentration quotients $\log Q_{12} = 0.51$ and $\log Q_{15} = 1.67$.

29. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1964*, ORNL-3627, p. 206.

The osmotic coefficients of the *n*-hexane solutions are summarized by the equation

$$\phi = 0.3047 - 0.00853\, m_{\mathrm{BAMBP}} + 0.18884/(m_{\mathrm{BAMBP}} + 0.2716)\,,$$

and the resulting stoichiometric activity coefficients (i.e., ignoring aggregation) are summarized by the equation

$$\ln \gamma = 0.18884/(m_{\mathrm{BAMBP}} + 0.2716) - 0.6953 \ln (m_{\mathrm{BAMBP}} + 0.2716) - 0.01706\, m_{\mathrm{BAMBP}} - 1.6016\,.$$

Physicochemical properties of the solutions are listed in Table 8.1.

For use in the foregoing study, the osmotic coefficients of dry *n*-hexane solutions of tri-*n*-octylamine at concentrations up to 2.4 *m* were determined by direct and differential vapor pressure measurements at 20°C. The TOA deviated from ideality by 5% at 0.1 *m* and 34% at 1 *m*. The results are fitted by the equation

$$\phi = -0.3455 + 0.06854\, m_{\mathrm{TOA}} + 2.818/(m_{\mathrm{TOA}} + 2.0944)$$

with a standard deviation of fitting of 0.0067. Thus TOA in dry *n*-hexane is added to our growing list of "calibrated" reference solutes for isopiestic and dynamic vapor pressure osmometry in organic solvents.

Table 8.1. Physicochemical properties of BAMBP[a] and its *n*-hexane solutions at 25°C

Mole fraction BAMBP	Molality	Density (g/cm³)	Kinematic viscosity, η_k (cSt)	Viscosity[b] index, η_c (ml/g)	Refractive index	Dielectric constant
0	0	0.6550	0.456		1.3725	1.8874
0.0286	0.342	0.6756	0.503	1.92	1.3850	1.9748
0.0588	0.725	0.6952	0.568	2.26	1.3964	2.0765
0.0906	1.156	0.7143	0.656	2.70	1.4077	2.1833
0.1240	1.643	0.7345	0.767	3.15	1.4187	2.2685
0.1593	2.199	0.7542	0.896	3.56	1.4338	2.4046
0.1966	2.840	0.7739	1.109	4.40	1.4470	2.4868
0.2360	3.585	0.7940	1.387	5.38	1.4552	2.6455
0.2784	4.477	0.8129	1.715	6.37	1.4630	2.7473
0.3237	5.55	0.8315	2.184	7.77	1.4702	2.8725
0.3711	6.85	0.8516	2.98	10.19	1.4772	2.9703
1		1.004	400		1.5570	4.2066

[a]4-*sec*-Butyl-2-(α-methylbenzyl)phenol, C_4H_9-C_6H_3(OH)-CH(CH_3)C_6H_5, mol. wt 254.4.

[b]Viscosity index $\eta_c = (\eta_{k,\mathrm{soln}} - \eta_{k,\mathrm{solv}})/(\eta_{k,\mathrm{solv}})$(g/ml). Extrapolation of the viscosity index to $m = 0$ gives the intrinsic viscosity = 1.5 ml/g.

9. Chemical Applications of Nuclear Explosives

The purpose of this program is to conduct research and development in selected areas of the Plowshare Program. During the past year, studies were made of (1) the behavior of radionuclides in natural-gas storage reservoirs, and (2) the disposal of tritiated water solutions that are generated in gas stimulation and gas storage applications.

9.1 NATURAL-GAS STORAGE

The formation of storage reservoirs for natural gas by contained nuclear detonations in impermeable formations such as salt or Lewis shale has been proposed. We are investigating the potential contamination of the stored natural gas by radionuclides (especially tritium) that are released in the detonation and are studying methods for decontaminating the chimney prior to gas storage.

Most or all of the tritium is expected to be present as tritiated water. Results of recent tests[1,2] confirmed earlier indications[3] that exchange between tritiated water and the stored gas would be essentially negligible but that the gas would be contaminated with water vapor. In these tests, methane was stored in small pressure vessels for periods of up to 40 days with Lewis shale that had been contaminated with tritiated water. Although the tritium concentration in the water was more than 300 times that estimated[4] to be present in the shale chimney after use of a low-tritium-yield device, the methane contained barely detectable amounts of tritium. The gas contained tritiated water in amounts approximately corresponding to saturation of the gas with water vapor at the initial storage conditions. The amount of tritiated water would be greatly reduced by dehydration of the gas upon removal from storage. Natural gas is usually sold with a water vapor content no higher than 7 lb/MMscf (MMscf = million standard cubic feet = million cubic feet at 1 atm and 60°F); this corresponds to a tritium concentration of 0.034 pCi/ml at the expected chimney conditions.

Results of our laboratory tests[1,2] indicate that a major fraction of the tritiated water could be removed from the system by purging it with air prior to gas storage. Up to 90% of the tritiated water was removed from contaminated shale at a temperature of 90°C, but the rate of removal was slow and large volumes of purge air were required at this temperature. Purging could be more efficient in an actual system since the temperature of the chimney might be expected to be considerably higher than 90°C.

9.2 DISPOSAL OF TRITIATED WATER

The volume of tritiated water removed from the storage chimney, whether by dehydrating the gas or by purging the chimney, would be large; a chimney formed by detonation of a 24-kiloton device would contain more than 400,000 gal.[4] Large volumes of tritiated water are also produced in gas stimulation applications. A safe and adequate method for disposing of the tritiated water is needed. We have started an evaluation, relative to feasibility, safety, and cost, of various methods that might be used. These include evaporation from ponds, evaporation through a stack, discharge to streams, tank storage, and disposal in deep wells. In addition, the possibility of concentrating the tritiated water by isotopic separation methods, followed by disposal of the concentrate, is being considered; however, this approach appears to be prohibitively expensive.

The proposed Rio Blanco gas stimulation project[5] is being used as a model for water production. This

1. W. D. Arnold and D. J. Crouse, *Chemical Applications of Nuclear Explosions (CANE): Progress Report for April 1 to June 30, 1970*, ORNL-TM-3541 (September 1971).
2. W. D. Arnold and D. J. Crouse, *Chemical Applications of Nuclear Explosions (CANE): Progress Report for January 1 to March 31, 1971*, ORNL-TM-3480 (July 1971).
3. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 186.
4. W. D. Arnold and D. J. Crouse, *Chemical Applications of Nuclear Explosions (CANE): Progress Report for July 1 to December 31, 1971*, ORNL-TM-3760 (March 1972).
5. CER Geonuclear Corp., *Project Rio Blanco Demonstration Program*, PNE-RB-15 (January 1971).

involves detonation of three 30-kiloton explosives in a single well to stimulate gas production from formations as deep as 7000 ft. Assuming successful stimulation, about 26,000 MMscf of gas will be produced from the well in 25 years. We estimate that the chimney will contain about 4 million gal of dilute tritiated water (~0.15 μCi/ml) and that most of this water will be removed in the gas that is produced in the first year. Much less water will be produced annually in subsequent operation of the well, and its contamination level may be low enough to make special disposal unnecessary.

10. Biochemical Technology

MACROMOLECULAR SEPARATIONS

10.1 PURIFICATION OF CALF LIVER TRANSFER RIBONUCLEIC ACIDS

Procedures for the isolation and purification of nine calf liver tRNAs were developed during this report period. The phenylalanine and serine tRNAs were first separated from crude calf liver tRNA, prepared as described previously,[1] by BD-cellulose chromatography. This separation involved adsorbing the crude tRNA, dissolved in an aqueous buffer, on a BD-cellulose column and eluting the bulk of the tRNAs with 0.9 *M* NaCl, using a batch technique. The more tightly bound phenylalanine and serine tRNAs were then removed with 2.0 *M* NaCl–25 vol % ethanol. These two tRNAs were subsequently separated from each other by gradient elution from an RPC-5 column, and further purified by passage through a DEAE–Sephadex A-50 column. The two new reversed-phase chromatographic systems,[2] designated RPC-5 and RPC-6, gave excellent resolution of these tRNAs.

The remainder of the tRNAs, which were contained in the 0.9 *M* NaCl aqueous effluent from the BD-cellulose column, were diluted and readsorbed on the same column at a lower NaCl concentration. A mixture of three isoaccepting species of leucine tRNA and one lysine tRNA was isolated by using batch elution techniques similar to those discussed above. The four tRNAs in this mixture were separated from each other by gradient elution from an RPC-5 column; then selected fractions were rechromatographed on an RPC-6 column and further purified on a DEAE–Sephadex A-50 column to yield purified leucine and lysine tRNAs.

An aspartic acid tRNA, a threonine tRNA, and an arginine tRNA were isolated from the second BD-cellulose column effluent and then purified by gradient elution, first from an RPC-6 column and then from an RPC-5 column. Each tRNA was further purified on a DEAE–Sephadex A-50 column.

The amino-acid-accepting activities of the tRNAs in the crude mixture and in the purified products are given in Table 10.1. Each of the tRNA products was tested to identify the specific isoacceptor by the technique of cochromatographing a mixed sample of [^{3}H] aminoacylated crude tRNA and [^{14}C] aminoacylated product tRNA on the recently developed RPC-5 minicolumns.[3] The amino acid acceptance of the products ranged from about 734 to 1443 picomoles/A_{260} unit. Assuming that a value of 1400 picomoles/A_{260} unit represents pure tRNA, the purity of these products ranged from 50 to 100%. End-group analyses are being made to obtain a direct measurement of the purity.

It should be possible to isolate and purify additional tRNAs from the remaining tRNA mixture by altering chromatographic column operating conditions such as pH, temperature, magnesium concentrations, etc. Scale-up of the flowsheet could be easily achieved to prepare larger quantities of purified tRNAs as desired.

10.2 SEPARATION OF RIBOSOMAL RIBONUCLEIC ACIDS

Reversed-phase chromatography has previously been used for the separation and preparation of milligram quantities of 16S and 23S *E. coli* ribosomal ribonucleic acids (rRNAs).[4] By making refinements in the apparatus and techniques and by using polychlorotrifluoroethylene (Plaskon) as the support for the extractant, we have successfully adapted the method to the separation of microgram quantities of tRNAs and 5S, 16S, and 23S rRNAs from *E. coli* in 30 to 90 min.[5] The short

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1972,* pp. 187–89.
2. R. L. Pearson, J. F. Weiss, and A. D. Kelmers, *Biochim. Biophys. Acta* **228,** 770 (1971).
3. A. D. Kelmers and D. E. Heatherly, *Anal. Biochem.* **44,** 486 (1971).
4. B. Z. Egan, J. E. Caton, and A. D. Kelmers, *Biochem.* **10,** 1890 (1971).
5. B. Z. Egan and A. D. Kelmers, *Fed. Proc.* **30,** 1101 (1971); B. Z. Egan and A. D. Kelmers, *Prep. Biochem.* (in press).

Table 10.1. Summary of data obtained in the purification of calf liver transfer ribonucleic acids

tRNA	Amino acid acceptance (picomoles/A_{260})		Recovery (%)	Sequence of chromatographic steps
	Crude	Purified		
Phe	26	1386	13	BD, RPC-5, A-50
Ser 3	56	1124	11	BD, RPC-5, A-50
Leu 2		1166	10	BD, BD, RPC-5, RPC-6
Leu 4	69	758		BD, BD, RPC-5, RPC-6, A-50
Leu 5		1117		BD, BD, RPC-5, RPC-6, A-50
Lys 2	46	1324	12	BD, BD, RPC-5, RPC-6
Asp 2	83	1443	14	BD, BD, RPC-6, RPC-5
Thr	46	735	7	BD, BD, RPC-6, RPC-5, A-50
Arg 2	59	1067		BD, BD, RPC-6, RPC-5, A-50

separation time, increased sensitivity, and increased resolution are advantages over conventional gel electrophoresis and ultracentrifuge methods.

Small (0.63- by 30-cm) reversed-phase chromatographic columns were used for the rapid separation of 16S and 23S rRNAs from *E. coli.* The sensitivity of this system allows the use of a much smaller sample than is required by other methods. Figure 10.1 shows a chromatogram obtained with a sample of about 0.1 A_{260} unit (about 5 μg) of RNA. Good resolution of the 16S and 23S rRNAs was obtained in about 30 min with a 30-ml linear elution gradient having an NaCl concentration that increased from 0.60 to 1.2 *M*. Under the conditions used for this run, smaller RNAs were eluted near the void volume of the column. Although we have not determined the minimum time in which the separation can be achieved, the analysis time could probably be reduced to less than 30 min if desired. Doubling the flow rate (to 2 ml/min) did not adversely affect the separation.

Figure 10.2 shows a chromatogram obtained for a sample containing both low-molecular-weight RNAs, including tRNAs, and high-molecular-weight rRNAs obtained from *E. coli* Q13 ribosomes. Thus, RNAs ranging from tRNAs (4S) to 23S can be resolved in a single chromatographic run in about 90 min, and the sample can be easily recovered. Effects of various solution components on RNA behavior can also be studied.

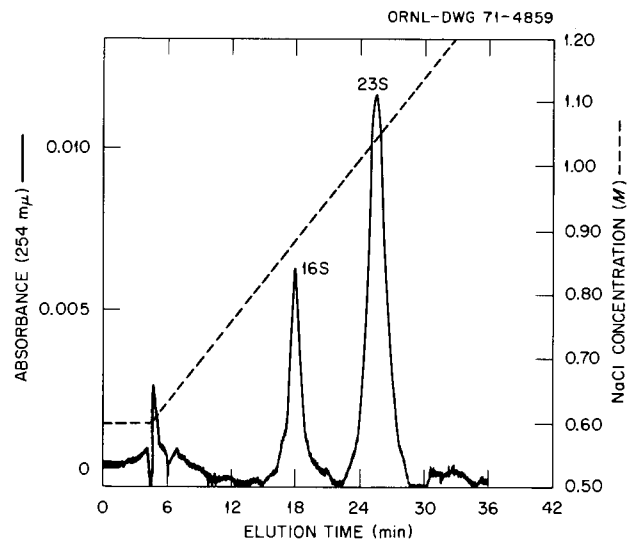

Fig. 10.1. Chromatogram of 0.1 A_{260} unit of *E. coli* Q13 ribosomal RNA. Column: 0.63 cm in diameter by 30 cm long; temperature: 25°C; eluent: 0.05 *M* tris-HCl, pH 7.3, 0.01 *M* $MgCl_2$, NaCl concentration as shown; flow rate: 1.0 ml/min.

10.3 SEPARATION OF OLIGONUCLEOTIDES

Methods commonly used for the preparation, separation, and characterization of oligonucleotides include: (1) column chromatography using DEAE-cellulose, DEAE-Sephadex, and ion exchange; (2) paper chromatography and paper electrophoresis; and (3) thin-layer chromatography. The biggest disadvantage shared by most of these methods is the length of time required to achieve useful separations. A typical chromatographic run utilizing DEAE-cellulose or DEAE-Sephadex for separating oligonucleotides, obtained by enzymatic digestion of tRNAs, requires 3 to 5 days. The limited capacities of thin-layer chromatography and paper chromatography present an additional disadvantage.

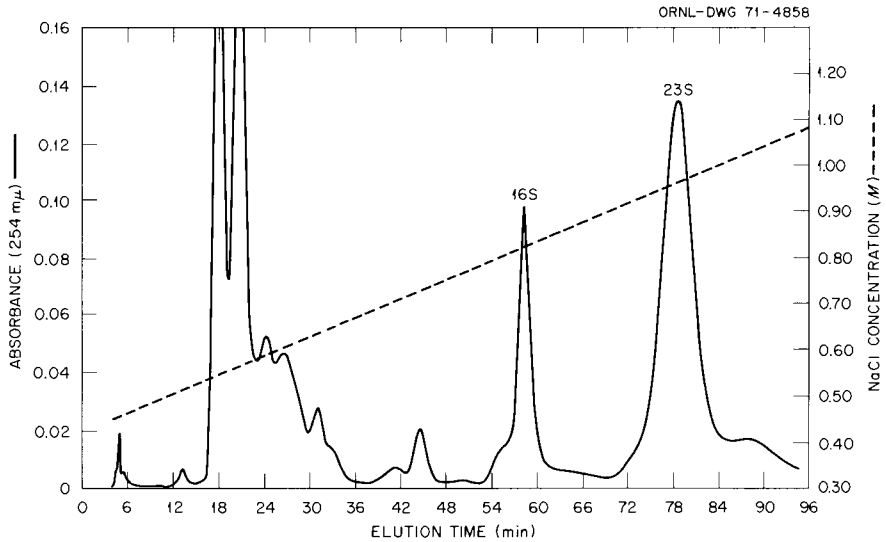

Fig. 10.2. Chromatogram of about 2.3 A_{260} units of a mixture of tRNAs and rRNAs. Column and conditions used are the same as those for Fig. 10.1.

Using reversed-phase chromatography, we have been able to obtain good fractionation of RNAs ranging from tRNAs to rRNAs (Sect. 10.2). We have now adapted this technique to the separation of oligonucleotides from ribonuclease A and ribonuclease T_1 digests of both specific and mixed tRNAs and of rRNAs. By taking advantage of differences in the sizes and the ion exchange properties of the oligonucleotides, this method offers the following advantages: (1) it provides excellent resolution; (2) it requires less time than other methods; (3) the separated products can be readily recovered; and (4) it is applicable to microgram as well as gram quantities of material.

Oligonucleotide patterns obtained from reversed-phase chromatography of enzymatic digests of $tRNA_1^{fMet}$, $tRNA_3^{fMet}$, $tRNA^{Val}$, $tRNA^{Phe}$, and $tRNA^{Glu}$ (*E. coli*) have been compared. The resolution obtainable in 3 to 4 hr was found to be approximately equivalent to that afforded by DEAE-cellulose chromatography only after a 4-day run.

Reversed-phase chromatography of well-characterized T_1 fragments of a $tRNA^{Glu}$, obtained from Dr. S. H. Chang of Louisiana State University, has shown the elution order to be similar to that obtained on DEAE columns. We have simplified the eluent so that the material corresponding to the effluent peaks can be concentrated by direct lyophilization, thereby eliminating the desalting step usually required prior to concentration and characterization.

Use of the improved separation method will allow more rapid structural determinations of RNAs to be made with smaller quantities of material. This will facilitate correlations of structural features with biological function, since structural areas of interest can be quickly identified. The method is expected to be especially applicable to mammalian RNAs, including those obtained from human tissues.

10.4 PURIFICATION OF MESSENGER RIBONUCLEIC ACIDS

Messenger ribonucleic acids (mRNAs) transmit the genetic information to direct the synthesis of specific proteins. This information is stored in the DNA in the nucleus and then, when needed, is transcribed into the mRNA. The mRNA, in turn, is "read" or translated on the ribosomes, and the appropriate amino acids from aminoacylated tRNAs are joined to form the protein. Much less is known about mRNAs than DNA or tRNAs since mRNAs are only transiently present in cells in small quantities. Purified samples of mRNAs will be required before many types of biochemical and biophysical investigations can be undertaken. Existing methods for recovering mRNAs rely on centrifugation, which lacks adequate resolution to separate various mRNAs, or gel electrophoresis, which is limited to only small quantities of tracer-labeled mRNAs.

Bacteriophage mRNAs were selected for the initial investigations to develop methods for the purification of mRNAs since the source material, phage-infected *E. coli,* can be obtained in any desired quantity, and since a simple and dependable assay was available for phage

lysozyme mRNA, the mRNA that directs the synthesis of the enzyme lysozyme that lyses, or breaks, the infected *E. coli* cell membrane to release the newly synthesized phage. The assay involves the in vitro translation of the mRNA in an incubation with various cofactors and then, in a second incubation, measurement of the activity of the lysozyme formed in vitro by the rate of lysis of *E. coli* substrate.

A new method was developed for the recovery of crude RNA from the phage-infected *E. coli* since published methods yielded very impure preparations containing large quantities of DNA as well as RNA. The steps in the new flowsheet are: growth of *E. coli* B on enriched media, infection with a multiplicity of phage T7, rapid harvesting of the infected cells prior to lysis, dispersion in a detergent-bentonite aqueous solution, double phenol extraction steps, ethanol precipitation, dissolution in tris buffer solution, deoxyribonuclease treatment, ethanol precipitation, air-drying of the solids, dissolution in H_2O and dialysis, and storage in

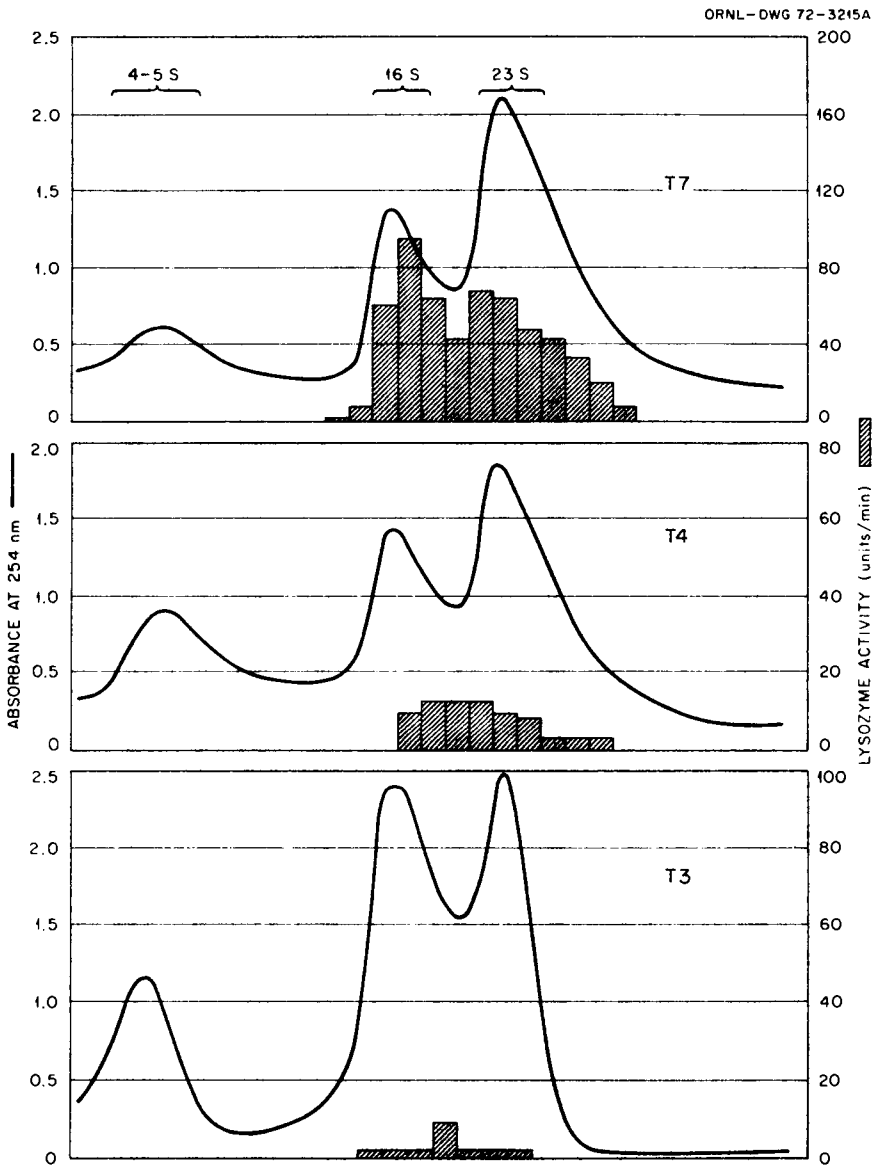

Fig. 10.3. Glycerol gradient fractionation of RNA from phage-infected *E. coli*. *E. coli* B was infected with phage T3 or T7, and *E. coli* D-10 with phage T4; the RNA was recovered as described. The RNA was layered on a 9 to 36% glycerol gradient (containing 0.001 *M* $MgCl_2$ and 0.01 *M* tris, pH 7), and centrifuged at 27,000 rpm for 19 hr in a Spinco SW 27 rotor. The gradient fractions were precipitated with ethanol, dialyzed vs H_2O, and assayed for lysozyme mRNA activity.

liquid nitrogen. In a recent experiment, 61 g of *E. coli* B was grown and 730 mg of crude RNA was obtained. The crude RNA contained less than 2% of the lysozyme mRNA.

A series of experiments was undertaken to estimate the size of the lysozyme mRNA from phages T3, T4, and T7. High-speed centrifugation of the crude RNA preparation in a glycerol gradient was used to resolve the RNAs. The results (see Fig. 10.3) show that the predominant classes of RNAs were resolved according to size. The 4–5S RNA class, which contains the tRNAs, and the two ribosomal RNAs, 16S and 23S, comprise the bulk of the RNA material. The lysozyme mRNA, located by the in vitro assay, does not form a sharp peak and appears to be between 16S and 23S in size. This size, which is much larger than the minimum required to code for lysozyme, suggests that the mRNA may be either polycistronic (codes for more than one protein) or redundant (contains repeating lysozyme mRNA units). In either case, the unexpectedly large size may complicate potential purification methods.

Reversed-phase chromatography is being evaluated as a method for purifying the lysozyme mRNA. In preliminary experiments, the lysozyme mRNA has proved to be stable. It can be bound to the column and then eluted by various solutions. Experiments are now under way to elute the lysozyme mRNA as a defined chromatographic peak and to attempt to obtain it in a purified form.

10.5 ENGINEERING INSTRUMENTATION

A retroreflective turbidimeter was developed to automatically and continuously assay the cell concentration in a fermenter by measuring the turbidity of the solution as a function of the light scattered at 180° to the incident light. The device consisted of a bifurcated fiber optic light pipe with its distal end inserted into a flow cell through which the material to be analyzed passed. A light source on one proximal branch of the light pipe illuminated the sample stream; light backscattered from particulates in the stream reentered the light pipe and was returned to a photodetector on the other proximal branch of the light pipe. A signal conditioning system connected to the optical head by a cable provided gain and zero adjustment so that the output signal could be made directly proportional to the *E. coli* cell concentration of the sample stream.

The turbidimeter was calibrated under static conditions by plugging the flow inlet and exit, and introducing solutions containing various concentrations of *E. coli* K-12 MO in the top part of the flow cell. No significant settling of the *E. coli* cells occurred during the time required to record the turbidimeter response as a function of cell concentration for two concentration ranges. The turbidimeter response vs Klett colorimeter readings at 660 mμ for the same samples was essentially linear for the range 0 to 200 Klett units except for a slight unexplained deviation between 150 and 200 Klett units. The response of the turbidimeter was then set to cover the range of 0 to 1400 Klett units. Again, the response was linear except for the unexplained change in slope near the concentration of 200 Klett units.

The turbidimeter was then connected to the 350-liter fermenter, and the fermentation mixture was pumped through the flow cell. The cell was automatically washed every 10 min with high-pressure water. The fermenter concentration was continuously recorded as a function of time. The fermenter was inoculated with 1 liter of *E. coli* K-12 MO, and growth was continued until the fermenter was cooled and the cells were harvested. Separate samples were withdrawn from the fermenter at hourly intervals, and the cell concentration was measured with the Klett colorimeter for comparison with the on-line turbidimeter. Again, a linear response with concentration was demonstrated for the turbidimeter.

This turbidimeter should be generally useful for continuously measuring and recording the concentration of suspended solids in a variety of solutions, for example, waste water streams, suspensions of ores in metallurgical extraction processes, concentrations of dispersed sols in colored solutions, etc., as well as fermentation media.

10.6 DISTRIBUTION OF PURIFIED *E. COLI* TRANSFER RIBONUCLEIC ACIDS

The distribution of samples of purified tRNAs from *E. coli* K-12 MO to interested scientists throughout the world has continued. The large-scale processing required to prepare these samples has been completed, and a summary of the results has been submitted for publication.[6] Requests have been received at a diminished but steady rate for the two tRNAs still on hand, formylmethionine and glutamic acid. One hundred three shipments, containing a total of 2.4 g of purified tRNAs, were made during this report period.

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6. H. O. Weeren and A. D. Ryon, *Development of a Process for the Separation and Purification of Ten tRNAs from E. coli K-12 MO,* ORNL-TM-3704 (May 1972); H. O. Weeren, A. D. Ryon, and A. D. Kelmers, *Biotech. Bioeng.* (in press).

It is interesting to note that our efforts to arouse interest in commercial production of purified *E. coli* tRNAs have been rewarded. The large-scale purification has been assumed by Biolabs, Beverly, Massachusetts. This company plans to utilize the methods developed at ORNL to make available several purified tRNAs through commercial suppliers.

10.7 PURIFICATION OF ERYTHROPOIETIN

The long-term goal of this project is the preparation of milligram quantities of erythropoietin (Epo) for evaluation in clinical testing for the potential relief of anemia due to renal failure and for clinical analysis to determine its structure and composition. The existing methods for the purification of Epo are not suitable for preparatory-scale operations; many purification steps are involved, and recovery is very low. Thus, the initial activities on this project must involve research and development to establish a simplified flowsheet that will provide high yields of purified product. Plasma from sheep made anemic with phenylhydrazine was selected as the source of Epo.

The in vivo polycythemic exhypoxic mouse assay was selected as the method for measuring Epo activity. This method is more sensitive than the in vivo fasted rat assay. (In vitro immunological or hemagglutination assays are not generally accepted as being fully reliable.) A controlled-atmosphere chamber capable of holding up to 240 mice was constructed for use in studies of the method. It was maintained at atmospheric pressure, and the oxygen content was reduced to 9% by blending compressed air and nitrogen. The assay procedure involved placing the mice in the chamber for 11 days and then returning them to normal air for 3 days to render them polycythemic and to inhibit endogenous Epo activity. The mice were then injected with the test sample on day 3 and with ^{59}Fe on day 5; the ^{59}Fe in the red blood cells was counted on day 7. C_3BF_1/CUM mice were used in the initial experiments. International Standard Epo was used to calibrate a plasma standard, and a semilog curve of ^{59}Fe incorporation vs International Units (I.U.) of Epo was constructed. Problems were encountered with the high background caused by high ^{59}Fe incorporation in saline (blank) samples. In experiments made with several other strains of mice, much lower blank values were obtained with the $B_6D_2F_1$/CUM strain; thus these mice are currently being used in the assay. This improvement has allowed more accurate results to be obtained for solutions having lower Epo concentrations. The standard deviation of the assay was ±18% of the average.

Thirty-nine sheep were treated at the rate of four per week to provide the plasma that was used in these experiments. The sheep were made anemic with calculated doses of phenylhydrazine, and the blood was recovered, following anesthetization, by making an incision in the jugular vein and collecting the blood by aspiration. Simultaneously, Ringer's lactate solution containing 5% gelatin was infused. About 4 liters of blood could be recovered before the heart stopped; this is approximately twice the yield per kilogram of sheep previously reported. A total of 113 liters of blood containing 370,000 I.U. of Epo activity (equivalent to approximately 42 mg of pure Epo) was obtained.

The blood obtained from the sheep was promptly cooled, centrifuged to recover the plasma, and then dialyzed against distilled H_2O until the conductivity was 2000 micromhos/cm or less. The Epo was then recovered from DEAE-cellulose by a procedure combining batch and gradient elution techniques. Results showed that all the Epo was bound to the column at pH 4.5, in contrast to earlier reports that up to 50% was not bound. The activity of Step I Epo ranged from 0.5 to 2.0 I.U. per A_{280} unit, an increase of 10- to 40-fold over the plasma concentration. Currently, we have on hand a total of 140,000 I.U. of Step I Epo.

A series of smaller-scale DEAE-cellulose tests was carried out to determine the loading capacity for Epo. Recovery of all the Epo was found to be possible even when the volume of DEAE-cellulose was reduced tenfold. This, then, permits a tenfold reduction in the eluent volume. These two factors substantially reduce the time required for the DEAE-cellulose step.

HIGH-RESOLUTION ANALYTICAL SYSTEMS

It is apparent that, in the future, most diseases will be studied, diagnosed, and treated on a molecular level. The hundreds of the molecular constituents of body fluids can be used as indicators of body function or malfunction. However, to take advantage of this approach in the clinical laboratory, it will be necessary to have automated, high-resolution analytical systems to determine large numbers of the molecular constituents in body fluids. Several different liquid chromatographic systems are being developed for this purpose.

To date, two analytical systems have been developed through the prototype phase and are being evaluated at other laboratories; other systems are in the preliminary stage of development. Many interesting and useful experimental results have been obtained with these advanced analytical systems.

10.8 ENGINEERING DEVELOPMENT

Second-generation prototype analyzers for UV-absorbing and carbohydrate constituents of human body fluids have been designed and built, and modifications to facilitate operation are in progress. Fourteen prototype systems of the UV- and carbohydrate analyzers are now in use in various laboratories in this country and in England.

The primary developmental efforts have been directed toward design, demonstration, and testing of a dual-column UV-analyzer system; further development of a detector for organic acids and other oxidizable compounds; and evaluation of several other separation systems that are potentially useful for high-resolution analyses of body fluids.

Dual-column chromatography. Several dual-column chromatographs for analyzing the UV-absorbing constituents of body fluids and other complex biochemical mixtures are now operating routinely.[7-9] These chromatographs were developed to demonstrate the feasibility and desirability of multicolumn operation for increasing sample throughput of high-resolution analytical systems. In this system, two columns are operated in parallel using dual sample introduction and eluate monitoring, but only a single elution system.

The dual-column arrangement allows a direct comparison to be made between separated constitutents of two samples, thus making possible an entirely new concept, differential chromatography.[10] The results of the two different analyses can be compared graphically either by observing the two chromatograms (see Fig. 10.4) or electronically by recording the differential signal from the two UV-monitors.

New systems. We are developing a column monitoring system in which a fluorescent material is generated by the addition of a reagent stream to the column eluate.[7,8,11] This system, which can detect organic acids and other oxidizable organic compounds, relies upon the reduction of reagent cerium(IV) to the fluorescent cerium(III). The cerium reagent solution is mixed continuously with the column eluate, and the reaction mixture is monitored by a flow fluorometer (Fig. 10.5). When coupled with an anion exchange separation system such as that used in the UV-analyzer, the monitor will have application in analyzing for organic acids and other oxidizable organic compounds. A flow fluorometer operating with a primary light source at 254 nm and measuring the secondary emission at 360 nm is being developed for this purpose. More than 50 chromatographic peaks can be detected with this monitoring system when used with the separation system in the UV-analyzer.

A high-pressure chromatographic separation system is being developed for the determination of various indole derivatives in physiologic fluids.[7,8,12] A coupled-column configuration (Fig. 10.6) is employed in which a 0.22-cm-diam by 25-cm-long jacketed, stainless steel anion exchange column is connected directly to a 0.22-cm-diam by 50-cm-long jacketed, stainless steel cation exchange column. The indole compounds are eluted from the column at 60°C with an ammonium acetate–acetic acid buffer that is 4 *M* in ammonia and 5.8 *M* in total acetate. A flow spectrophotofluorometer with a primary light source of 292 nm and measurement of secondary emission at 330 nm is used as the detector. Preliminary results show that the system is capable of providing base-line separation between 5-hydroxytryptophan, tryptophan, 5-hydroxyindoleacetic acid, serotonin, indoleacetic acid, and tryptamine in the 50- to 100-ng range (see Fig. 10.7).

At present, the analysis of drugs of abuse and their metabolites in body fluids commands high priority in the fields of forensic toxicology and clinical chemistry.[13] The common drugs of abuse may be generally classified as: (1) narcotics and analgesics, including heroin, morphine, codeine, meperidine, propoxyphene, and methadone; (2) sympathomimetics, including amphetamine and methamphetamine; (3) hypnotics and sedatives including barbiturates, glutethimide, and phenothiazines; and (4) hallucinogens including LSD, marijuana, and mescaline. Two classes of analyses are

7. N. G. Anderson et al., *The Molecular Anatomy (MAN) Program. First Semiannual Progress Report, March 1, 1971–August 31, 1971*, ORNL-4733 (1971).

8. N. G. Anderson et al., *The Molecular Anatomy (MAN) Program. Second Semiannual Progress Report, September 1, 1971–February 29, 1972*, ORNL-4771 (1972).

9. W. W. Pitt, C. D. Scott, and G. Jones, "Simultaneous Multicolumn Operation of the UV-Analyzer for Body Fluids," *Clin. Chem.* (in press).

10. C. D. Scott and W. W. Pitt, "Differential Chromatography Using Dual, Coupled Parallel Columns," presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., Apr. 10, 1972.

11. S. Katz and W. W. Pitt, "A New Versatile and Sensitive Monitoring System for Liquid Chromatography: Cerate Oxidation and Fluorescence Measurement," *Anal. Lett.* 5(3), 169 (1972).

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

13. E. S. Veseu and G. T. Passananti, "Utility of Clinical Chemical Determinations of Drug Concentrations in Biological Fluids," *Clin. Chem.* 17, 851 (1971).

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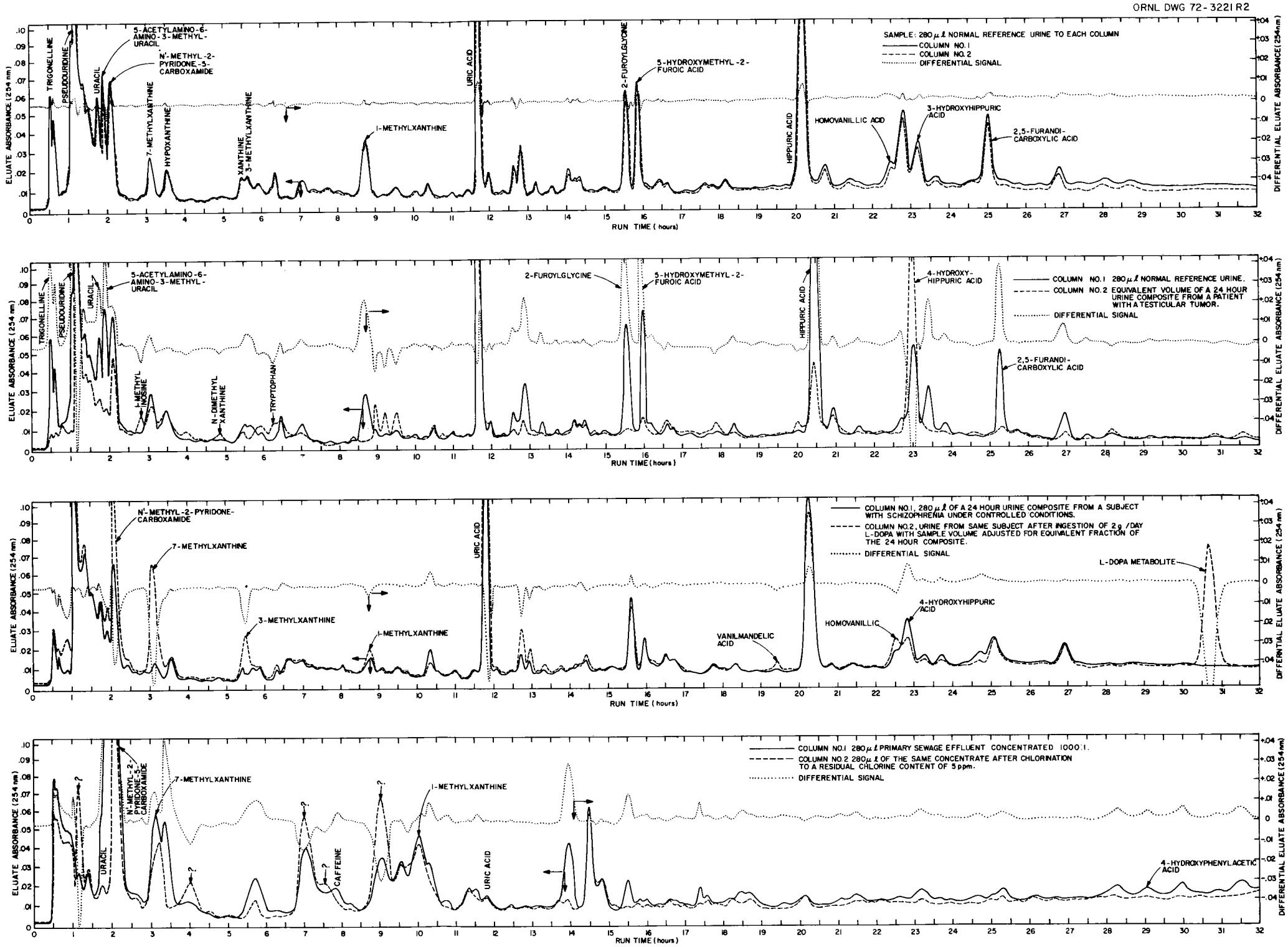

Fig. 10.4. Chromatograms from dual-column operation in the differential mode. Operating conditions: columns, 0.45 cm diam by 150 cm long; resin, 12- to 15-μ-diam Aminex A-27; eluent, ammonium acetate–acetic acid buffer, pH 4.4, varying in acetate concentration from 0.01 to 6 *M;* eluent flow rate, 10 ml/hr; temperature, ambient to 60°C at 8 hr.

needed: (1) a means of rapid mass screening, and (2) a more quantitative method for confirmative analysis and biochemical studies. The latter type of analysis may be achieved by automated adsorption chromatography using an inorganic oxide as the sorbent and an organic liquid as the eluent.

We have made what is apparently the first attempt to use silica sorbents in a column for separating drugs. Results showed that pentobarbital and phenobarbital are well separated in less than 15 min on a 0.45-cm-diam by 50-cm-long column containing a pellicular silica sorbent, using chloroform as the eluent. UV-

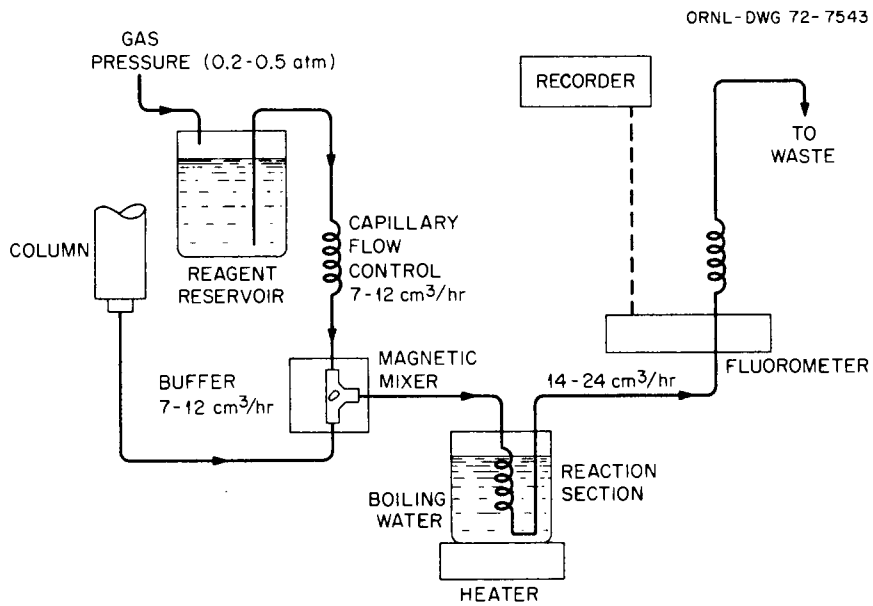

Fig. 10.5. Cerate oxidative column monitor for organic acids and other oxidizable organic compounds.

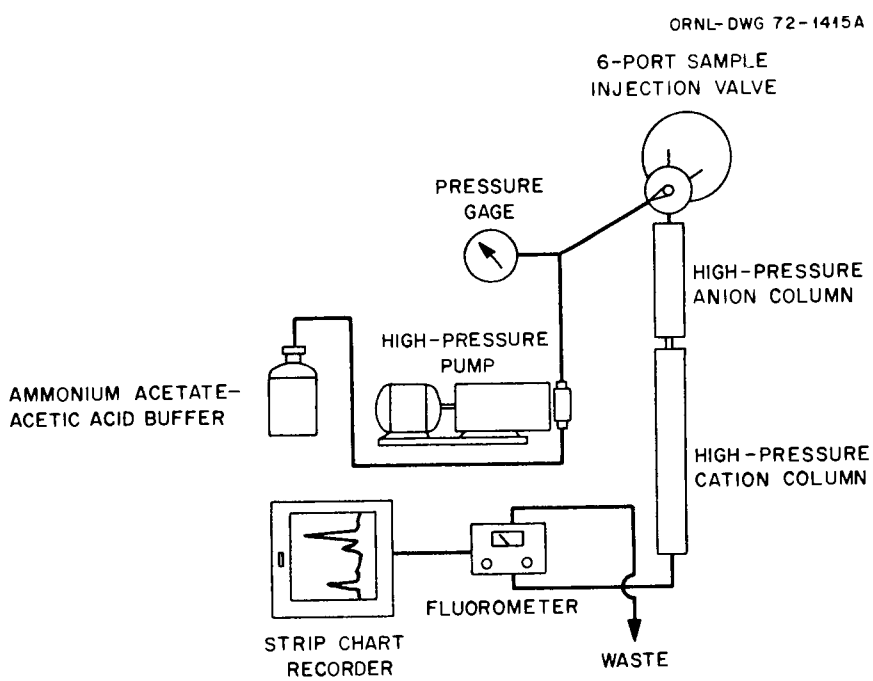

Fig. 10.6. Coupled-column chromatographic system for separation and quantification of indoles in physiologic fluids.

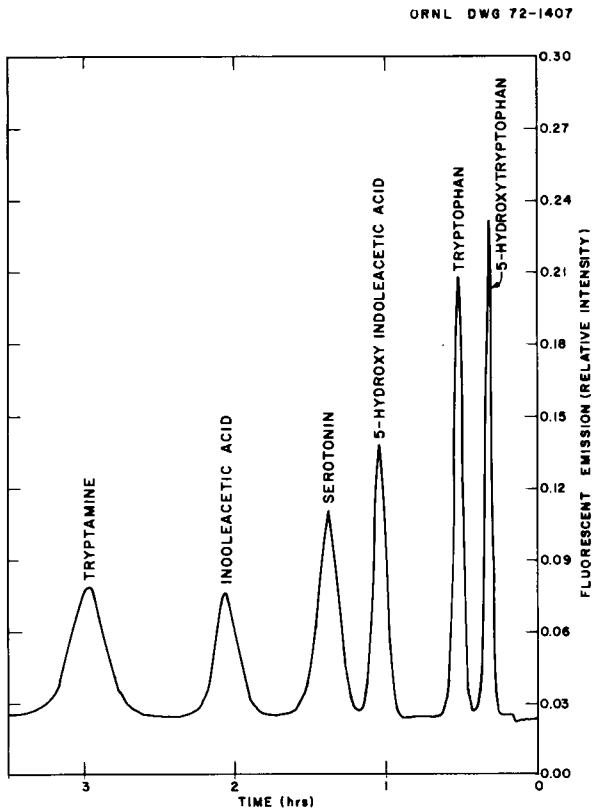

Fig. 10.7. Separation of a series of reference indole compounds, using the coupled-column system.

photometry was used to monitor the separation.[8] We have also shown that a porous silica sorbent (36–75 μ), deactivated with 10% water, will separate pentobarbital and phenobarbital successfully in a 0.45-cm-diam by 50-cm-long column, using chloroform (50% saturated with water) as the eluent. The retention times are noticeably longer, resulting in an increased analysis time; however, the increased capacity of this type of sorbent is a decided advantage. Zirconia prepared by the ORNL Sol Gel process is also being evaluated for this type of separation, and other drugs will be examined in future work.

10.9 APPLICATIONS AND EXPERIMENTAL RESULTS

Over 100 body fluid constituents separated by the high-resolution liquid chromatographic systems have now been isolated and identified by spectral, chromatographic, and chemical means.[7,8,14] Most of the work with pathologic fluid samples is done in cooperation with other laboratories. Major recent findings of these collaborative programs include: (1) presence of abnormal amounts of 3,4-dihydroxyphenylpropionic acid in urine during pregnancy; (2) absence of hippuric acid excretion in Lesch Nyhan syndrome treated with allopurinol; (3) abnormal levels of orotidine and orotic acid after allopurinol therapy; (4) excess 7- and 3-methylxanthine and vanilloylglycine in ataxia telangiectasia; (5) excess uracil and uridine in acquired orotic aciduria; (6) excretion of excess sucrose and fructose in congenital galactosemia; (7) abnormal levels of nicotinamide-N^1-oxide after nicotinic acid or nicotinamide therapy; (8) increased excretion of uracil, hypoxanthine, and xanthine after cancer radiation therapy; (9) abnormal levels of excretion for cytidine, N-methyl-5,6-dihydroxyindole, and N-methyl-3,5,6-trihydroxyindole in schizophrenia; and (10) alteration

14. J. E. Mrochek and W. T. Rainey, "Identification and Biochemical Significance of Substituted Furans in Human Urine," *Clin. Chem.* (in press).

Table 10.2. Methylated purine bases and nucleosides excreted at abnormal levels by six cancer patients

Type of cancer	Methylated base or nucleoside[a]
Malignant melanoma	N^2-Dimethylguanine N^2-Dimethylguanosine 7-Methylguanine[b] 1-Methylinosine
Ovarian cancer	1-Methylinosine 7-Methylguanine N^2-Dimethylguanine[c]
Cell sarcoma	N^2-Dimethylguanine N^2-Dimethylguanosine 7-Methylinosine
Embryonic neoplasm	N^2-Dimethylguanine N^2-Dimethylguanosine 1-Methylinosine
Ovarian cancer	1-Methylinosine N^2-Dimethylguanine N^2-Dimethylguanosine
Hodgkin's disease	N^2-Dimethylguanine N^2-Dimethylguanosine[c] 1-Methylinosine[c]

[a]Some of these compounds were tentatively identified by elution position and UV-spectral appearance.

[b]7-Methylguanine has been identified in urinary concentrates of normal subjects; however, the amount excreted by cancer patients seems elevated.

[c]Presence is questionable.

in the pattern of sugars excreted in response to drug ingestion.

One of the most significant findings has been that associated with the determination of biochemical markers of cancer. Physiologic body fluid samples from patients with 13 types of malignancies (obtained from Dr. T. P. Waalkes of the National Cancer Institute) have been analyzed on the UV-analyzer. The results showed that the urine from subjects with six different types of cancer contained abnormal amounts of several specific methylated bases and ribosides (see Table 10.2).

Another interesting finding has been the presence of substituted furans in urine samples obtained from both normal subjects and subjects with cancer. Three of the major chromatographic peaks observed in most urine samples have been identified as 5-hydroxymethyl-2-furoic acid, 2-furoylglycine, and 2,5-furandicarboxylic acid.[14] A related compound, 5-hydroxymethyl-2-furoyglycine, was also identified in the urine of a leukemia patient who was excreting an abnormal amount of the free acid. The compound 5-hydroxymethyl-2-furoic acid and its glycine conjugate have not, to our knowledge, been previously reported in human urine, and the excretion of 2-furoylglycine and 2,5-furandicarboxylic acid by all humans is not generally recognized. The four identified compounds seem to be biochemically interrelated, and a mechanism for their formation from uronic acids can be postulated.

WATER POLLUTION STUDIES

The continuing discharge of stable organic compounds in sewage effluents to surface waters and the buildup of organic constituents by recycle constitute a serious threat to our nation's water quality. Furthermore, as water requirements increase, water contamination will become more extensive and additional processing steps may become necessary to permit immediate reuse of the process effluents (e.g., sanitary sewage plant effluents). Most of the techniques used for analyzing sewage effluents are nonspecific and often indirect and, in general, do not provide sufficient information for developing advanced processing steps. The high-resolution analytical systems previously developed for the analysis of the molecular constituents of physiologic fluids (see Sect. 10.8) can provide reliable measurement of many of the refractory organic compounds present in sewage effluents and other polluted waters at microgram-per-liter levels. Such analytical systems are now being adapted for use in this field.

During the first year of this program, we demonstrated that at least 50 to 100 specific refractory organic compounds are present in effluents from municipal sewage treatment plants at microgram-per-liter levels and that many more compounds are present at higher concentrations in effluents from industrial sewage treatment plants.[15,16] A modified UV-analyzer was used in this work. During the second year (i.e., this report period), the primary emphasis has been centered on identifying separated compounds found in the sewage effluents. Modifications of the high-resolution chromatographic systems and of other measurement tools were made. A study has also been initiated to determine the effects of chlorinating sewage plant effluents that contain organic contaminants.

10.10 ANALYTICAL SYSTEMS

Advances made relative to analytical systems fall into three principal categories: (1) development of an oxidative detector for liquid chromatography; (2) development of a sensitive device for monitoring oxygen demand; and (3) the use of parallel columns in the UV-analyzer. The oxidative detector and the use of parallel columns in the UV-analyzer were discussed in Sect. 10.8; however, the development of a sensitive oxygen demand monitor has specific application in the water pollution program.

This system is being developed for continuous monitoring of the total content of oxidizable substances in the water supply. It is based on the principles of the cerate-fluorescence detector reported in Sect. 10.8. In this system, a small side stream of the water supply (7 to 12 ml/hr) is withdrawn continuously and mixed with ceric reagent, as described previously (see Sect. 10.8). The reaction mixture is heated at 100°C for 5 min as it progresses through coiled tubing suspended in a boiling water bath, and is then monitored by a flow fluorometer. As in the organic acid monitor, the cerium is reduced by oxidizable organics, after which it can be monitored by fluorometry. The ceric reagent system in the perchlorate form gave results comparable to those obtained with conventional methods in the oxygen

15. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 212.

16. S. Katz et al., "The Determination of Stable Organic Compounds in Waste Effluents at μg/liter Levels by Automatic High-Resolution Ion Exchange Chromatography," *Water Research* (in press).

demand range of 24 mg/liter.[17] Conventional methods include batch operations that can require several hours.

10.11 EXPERIMENTAL RESULTS

Identification of pollutants. The major effort of the experimental program has been to identify the individual molecular contaminants found in sewage plant effluents. Toward this end, 11 "domestic" sewage plant samples were collected, concentrated (~1000-fold), and separated on preparative-scale anion-exchange chromatographic systems for both UV-absorbing constituents and carbohydrates. Seven of these samples were primary sewage plant effluents, while four were secondary sewage plant effluents. Some of the effluents were chlorinated, either at the sewage plant or in the laboratory.

The identities of 24 organic compounds in primary effluent samples and seven compounds in secondary effluent samples were established (Table 10.3).[15,16] Where possible, the UV-absorbing compounds were also quantified. Of special interest was copper(II) acetate, which was found in some of the fractions of chlorinated sewage effluents. The presence of this compound, which was indicated by the blue color of the eluate and later confirmed by mass spectroscopic analysis, was surprising. We have postulated that its formation occurs via reaction of ionic copper in the sewage effluent with the acetate ion in the ion exchange column eluent. However, we are unable to explain why it is present only in chlorinated sewage effluents.

Effects of chlorination. Little definitive information is available concerning the potentially hazardous practice of chlorinating sewage effluent streams and other process streams prior to their use or return to the water supply. However, there is concern that this operation could result in chlorination of some of the organic pollutants, thus generating more-hazardous pollutants. A study to determine whether such chlorinated organic compounds are produced during the chlorination process is now under way.

Preliminary results are now available from three sanitary sewage effluent samples that were chlorinated to different residual chlorine levels prior to concentration for analysis by the UV-analyzer. Chlorination was accomplished by bubbling chlorine gas through the samples. Obvious differences were observed in the chromatographic results for nonchlorinated and those for samples chlorinated either in the laboratory (see lower chromatogram in Fig. 10.4) or in routine field treatments. Residual chlorine contents of 2 to 5 ppm were experienced in these tests. These differences included the apparent reduction or removal of some molecular contaminants and the generation of additional contaminants as indicated by changes in the chromatograms.

In an attempt to further study these effects, the radioisotope ^{36}Cl was used as a tracer in the chlorine gas for some of the laboratory chlorination experiments. The presence of ^{36}Cl activity in chromatographic fractions other than those containing chloride ion would be a strong indication that some compounds in the sewage effluent samples were being chlorinated, and identification efforts could be concentrated on these fractions.

A primary sewage plant effluent was chlorinated with ^{36}Cl-tagged chlorine to a chlorine residual of 5 ppm and then concentrated 570-fold. Analysis of this concentrate on a dual-column UV-analyzer resulted in 37 radioactive chromatographic peaks, 6 of which were correlated with UV-absorbing peaks. A radioactivity balance on the chromatographed sample revealed that approximately 99% of the ^{36}Cl was contained in a single peak (probably the chloride ion) and 0.6% was distributed throughout the other 36 peaks; the remainder was found to be adsorbed on the anion exchange resin of the pre-column. Identification efforts are now being concentrated on the six largest chromatographic peaks containing radioactive chlorine.

MINIATURIZED FAST ANALYZER

A Fast Analyzer, designated the Mark I Gravity Zero (GØ) Analyzer, has been designed and fabricated for evaluation as a clinical chemistry analytical module for potential use in the NASA Skylab and the Orbiting Laboratory.

Miniaturized analyzer. The Mark I GØ Analyzer is an integrated, miniature system that occupies only about 1 ft^3 of space and has been demonstrated to be completely compatible with the hardware and the software of the existing GeMSAEC computer system. It has a 17-place rotor (a reference cuvet plus 16 cuvets filled with sample) that spins through a stationary photometer consisting of a miniature photomultiplier tube, a quartz-iodine lamp, and interference filters (Fig.

17. W. A. Moore, F. J. Ludzack, and C. C. Ruchhoft, "Determination of Oxygen-Consumed Values of Organic Wastes," *Anal. Chem.* **23**, 1972 (1951).

Table 10.3. Identification of molecular constituents in concentrates of domestic sewage plant effluents

Compound	Identification Method[a]	Concentration (μg/liter)	Elution Position (ml)
	Primary Effluent		
Maltose	AC, GC		8
N^1-methyl-4-pyridone-3-carboxamide	AC, UV, GC	10	14
Uracil	AC, CC, UV, GC, MS	40	18
5-Acetylamino-6-amino-3-methyluracil	AC, CC, UV, GC	140	20
N^1-methyl-2-pyridone-5-carboxamide	AC, CC, UV, GC	20	21
Thymine	AC, CC, GC	~7	29
Xanthine	AC, CC, UC, GC	70	55
Caffeine	AC, CC, UV	~10	67
Guanosine	AC, CC, UV, GC, MS	50	76
1-Methylxanthine	AC, CC, UV	70	82
4-Hydroxyphenylacetic acid	AC, UV, GC, MS	190	235
3-Hydroxybenzoic acid	AC, GC, MS	~40	295
3-Hydroxyphenylpropionic acid	AC, GC, MS	~20	295
3-Hydroxyphenylhydracrylic acid[b]	AC, UV, GC, MS	10	205
o-Phthalic acid[c]	AC, UV, MS	200	315
Theobromine	AC, CC		29
7-Methylxanthine	AC, CC	~90	29
1,7-Dimethylxanthine	AC, CC		64
3-Methylxanthine	AC, CC		64
Uric acid	AC, GC, MS	20	106
Benzoic acid	AC, GC, MS		260
Phenylacetic acid[d]	AC, GC	~10	230
Indican[b]	AC, GC, F	~2	315
Copper(II) acetate	MS		60
	Secondary Effluent		
Uracil	AC, CC, UV	30	18
5-Acetylamino-6-amino-3-methyluracil	AC, CC, UV	30	20
1-Methylinosine	AC, CC, UV	80	29
Inosine	AC, CC, UV	20	29
7-Methylxanthine	AC, CC, UV	5	29
1-Methylxanthine	AC, GC	6	82
1,7-Dimethylxanthine	AC, CC, UV	~6	64

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

[b]Effluent chlorinated to 2.0 ppm chlorine residual, orthotolidine.

[c]Effluent from the Mill Creek Sewage Plant, Cincinnati, Ohio.

[d]Effluent chlorinated to 85 ppm chlorine, total.

PHOTO 2093-71A

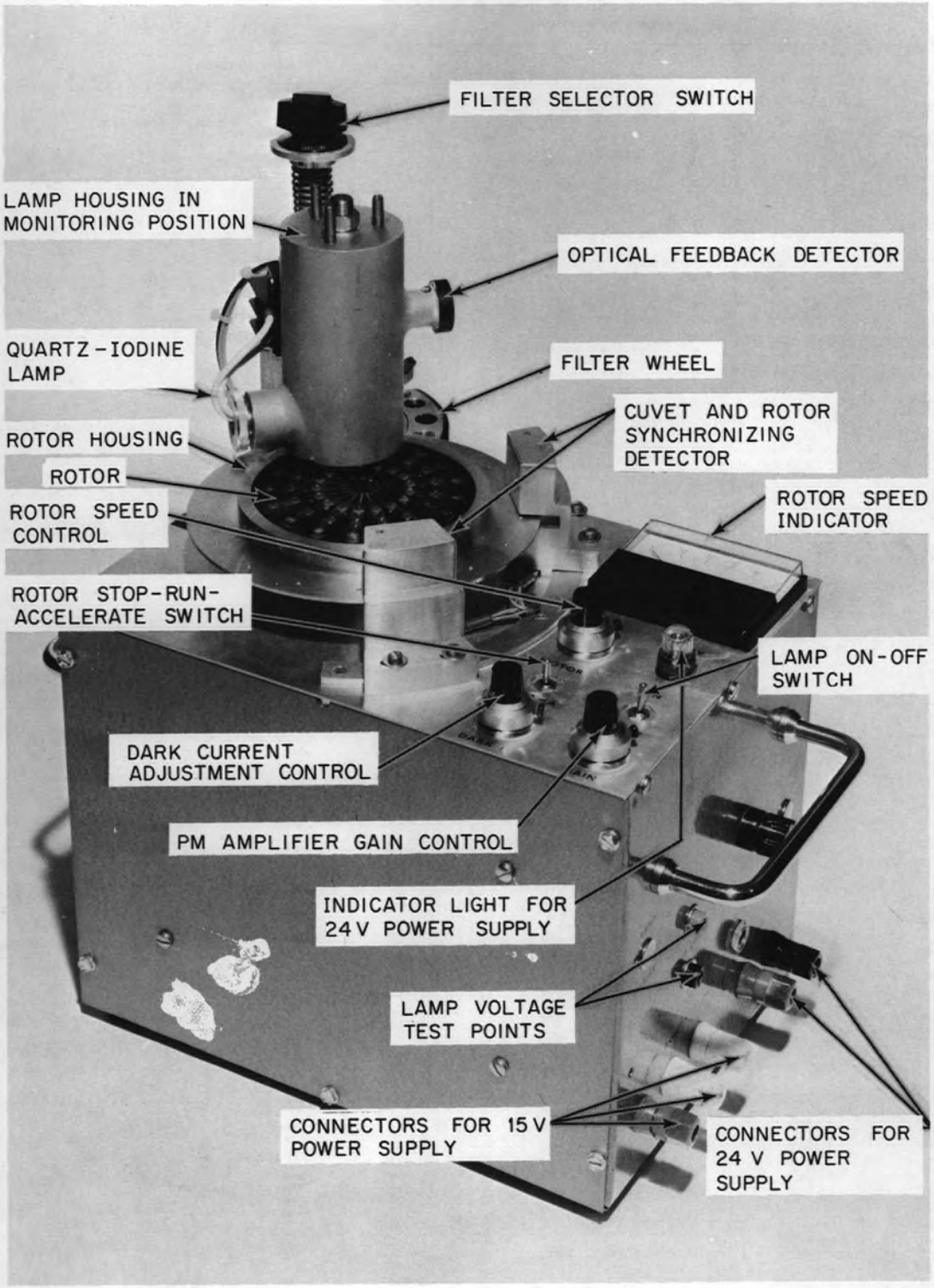

Fig. 10.8. Miniature Mark I GØ Analyzer.

10.8).[7,8,18-20] During operation it is possible to monitor the light transmittance of each cuvet at 100-msec intervals.

Multicuvet rotors that will ultimately be totally enclosed for easy disposal have also been designed and fabricated. The unassembled rotors consist of three parts: a central body made of black acrylic plastic, and two cover windows fabricated from ultraviolet-transmitting (UVT) acrylic plastic. The rotors are assembled by gluing the individual components with an epoxy adhesive. The rotors developed to date include multifunctional devices into which samples and reagents can be loaded either discretely or dynamically and specialized devices that are capable of accepting and processing samples of whole blood (Fig. 10.9).[21] The design goal is disposable rotors, probably fabricated from acrylic plastic, that will contain prepackaged reagents. Preliminary studies have indicated that conventional molding techniques can be used.

Chemical and operational parameters for several of the desired assays have been determined using plastic rotors in conjunction with the Mark I GØ Analyzer. These include analyses for albumin, ammonia, bilirubin, blood urea nitrogen, calcium, glucose, inorganic phosphate, total protein, uric acid, alkaline phosphatase, CPK, LDH, SGOT, and SGPT. The sizes of the serum samples used in these analyses range from 1 to 5 μl each.

A mechanical data printer has been designed and fabricated as an inexpensive and relatively fail-safe backup to the computerized data system.[22] The meas-

18. N. G. Anderson et al., "Feasibility of Miniaturization of a Fast Analyzer," *Anal. Lett.* **5**(3), 153 (1972).

19. C. A. Burtis et al., "Development of a Miniature Fast Analyzer," *Clin. Chem.* (in press).

20. C. A. Burtis et al., *Gravity Zero (GØ) Analytical Clinical Laboratory System Annual Progress Report for the Period April 1, 1971 to March 31, 1972,* ORNL-TM-3792 (1972).

21. C. D. Scott and J. C. Mailen, "Dynamic Introduction of Whole Blood Samples into Fast Analyzers," *Clin. Chem.* (in press).

22. W. F. Johnson et al., "Development of a Portable Data Processor with a Mechanical Data Output for Use with a Miniature Fast Analyzer," *Clin. Chem.* (in press).

ORNL PHOTO 0503-72A

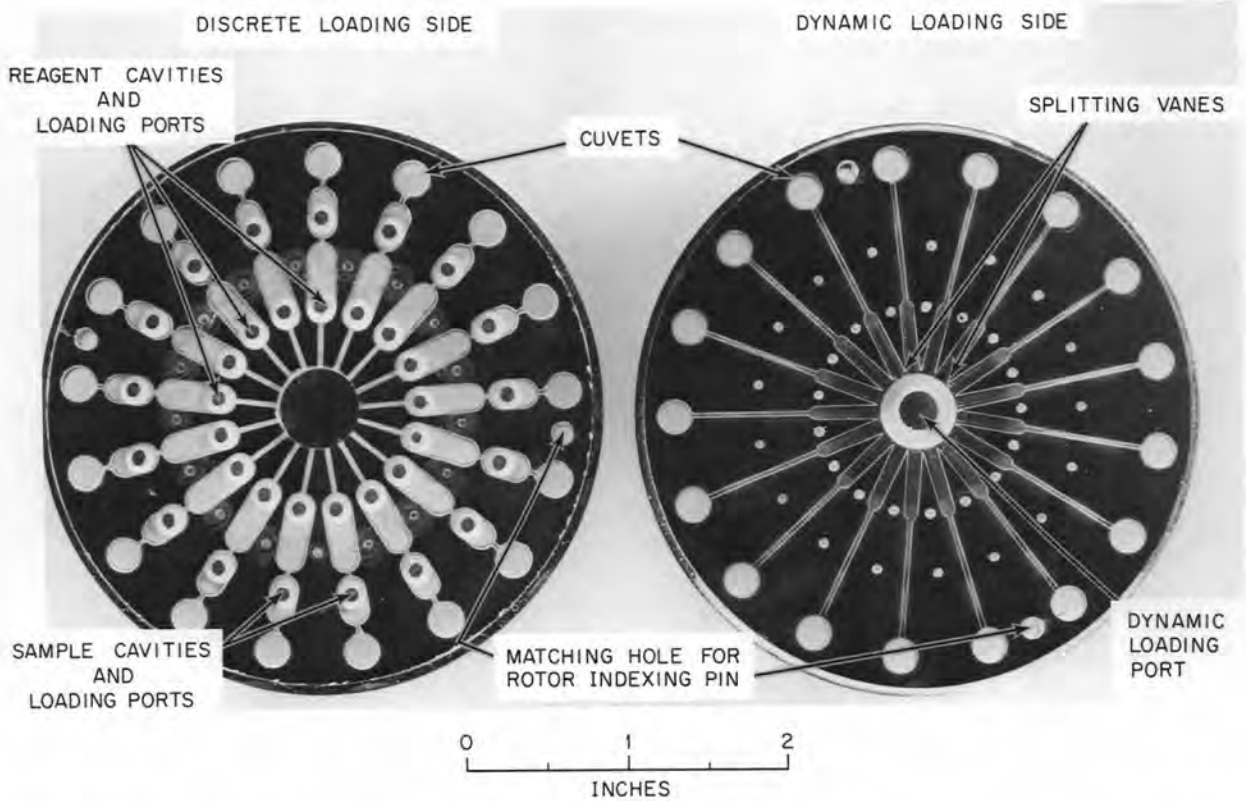

Fig. 10.9. Plastic rotor fabricated from UVT acrylic with provisions for discrete loading of samples and reagents on one side and dynamic loading on the other side.

ured light absorbance of the solution contained in each cuvet is printed as a dot on an IBM paper card (i.e., one dot per cuvet). By successive scans, a measure of the absorbance change per unit time can be obtained; thus, both end-point and kinetic enzyme analyses are possible with the printer. Preliminary tests have shown that this device is capable of a linear response over a useful range. Problems that are unique to space applications and that affect the design of a useful system have also been taken into consideration. These include methods for obtaining the initial sample, making dilutions, and preparing serum or plasma.

11. Spectrophotometric Studies of Solutions of Lanthanides and Actinides

11.1 STUDIES OF PLUTONIUM(IV) POLYMER

The data from studies on the formation of Pu(IV) polymer at four acidities over the range 0.04 to 0.1 *M* HNO_3 and at temperatures of 25, 50, and 75°C have been analyzed, and the results have been reported in three papers submitted to the *Journal of Inorganic and Nuclear Chemistry*. The abstracts follow:

"Plutonium Polymerization: I. A Spectrophotometric Study of the Polymerization of Plutonium(IV)," by D. A. Costanzo, R. E. Biggers, and J. T. Bell. *Abstract:* Standard spectra of the Pu species have been observed and then used in the calculations of the distribution of Pu(III), (IV), (V), VI, and polymeric Pu(IV) in solutions containing ~0.009 *M* total Pu at initial acidities of 0.1, 0.075, 0.06, and 0.04 *M* HNO_3, and at 25, 50, and 75°C. The distributions of the Pu species are given for the four acidities at 25°C, and the distributions are given for the initial acidity of 0.075 *M* HNO_3 at 25, 50, and 75°C.

In these studies the polymer is not formed when the initial acidity is 0.1 *M* and the temperature is 25°C, but the degree of polymerization continuously increases at the lower acidities and is almost quantitative when the initial acidity is 0.04 *M*. The effect of an increasing temperature is to increase the rate of polymerization at the expense of the ionic Pu species. The amount of polymer formed at 75°C is ~3.5 times as great as the amount at 25°C when the initial acidity is 0.075 *M*.

"Plutonium Polymerization: II. Kinetics of the Plutonium Polymerization," by J. T. Bell, D. A. Costanzo, and R. E. Biggers. *Abstract:* Experimental data for the distribution of Pu(III), Pu(IV), Pu(V), Pu(VI), and Pu(IV) polymer have been used to calculate the rates of polymerization of Pu(IV). The rate of formation of Pu(IV) polymer is proportional to the first power of the Pu(IV) concentration and to the inverse square of the acidity as long as the solution contains a detectable amount of Pu(IV). When the concentration of Pu(IV) is not detectable, the rate of polymerization is proportional to the product of the square roots of the Pu(V) and (III) concentrations. When the concentrations of both the Pu(IV) and (III) are not detectable, the rate of polymerization is proportional to the product of the squares of the Pu(V) and the acid concentrations and to the inverse first power of the Pu(VI) concentration.

"Plutonium Polymerization: III. The Nitrate Precipitation of Pu(IV) Polymer," by J. T. Bell, C. F. Coleman, D. A. Costanzo, and R. E. Biggers. *Abstract:* The precipitation of aged Pu(IV) polymer by HNO_3, $LiNO_3$, $Al(NO_3)_3$, and $NaNO_3$ has been observed. With the exception of $LiNO_3$, the precipitation of 0.00678 *M* Pu(IV) polymer was independent of the source of NO_3^-, and the maximum amount of precipitated polymer occurred at 1.8 *M* NO_3^-. Further addition of NO_3^- redissolved the polymer. The nitrate precipitation of Pu(IV) polymer has been analyzed according to the solubility product principle and has been found to closely resemble a solubility product mechanism. The solubility product for the aged Pu(IV) polymer nitrate was determined to be 0.0049, and the formation quotient for the soluble Pu(IV) polymer nitrate complex was determined to be 0.026.

11.2 SPECTRAL STUDIES OF THE ACTINIDES

The photoreduction of the uranyl ion is being investigated, with interest centered on the reducing agents and on the quantum yields of both U(V) and U(IV) in various media and at various wavelengths. The medium containing the uranyl ions determines the positions and intensities of the absorption bands, and might influence the quantum yields and the reactivity with various reducing agents. The effects of two sulfate media are shown in comparison with a perchlorate medium[1] in Table 11.1. The effects of SO_4^{2-} on the uranyl "hot bands"[2] are also given in Table 11.1. These effects closely correspond, as to be expected, to the effects on the adjacent absorption bands.

The uranyl spectrum in 4 *M* sulfate medium, from 3500 to 5200 Å, has been resolved by computer fitting into the constituent overlapping Gaussian bands (Fig. 11.1).

1. J. T. Bell and R. E. Biggers, "The Absorption Spectrum of the Uranyl Ion in Perchlorate Media. Part I. Mathematical Resolution of the Overlapping Band Structure and Studies of Environmental Effects," *J. Mol. Spectrosc.* **18**, 247 (1965).

2. J. T. Bell, "New Absorption Bands for the Uranyl Ion," *J. Mol. Spectrosc.* **41**, 409 (1972).

Table 11.1. Effects of two sulfate media relative to a perchlorate medium on the uranyl ion absorption band positions and molar absorptivities

A. Band positions (Å)			B. Molar absorptivities		
0.01 M UO_2^{2+}	0.288 M UO_2^{2+}		0.01 M UO_2^{2+}	0.288 M UO_2^{2+}	
ClO_4^-	1 M SO_4^{2-}	4 M SO_4^{2-}	ClO_4^-	1 M SO_4^{2-}	4 M SO_4^{2-}
5310[a]		5355[a]	$\sim 10^{-4}$		$>10^{-4}$
5077[a]		5120[a]	0.007		0.018
4859	4889	4900	0.295	0.68	0.83
4688	4715	4735	0.852	2.87	3.66
4533	4555	4575	1.23	4.06	5.02
4271	4295	4308	5.92	11.03	11.96
4146	4190	4202	7.73	13.48	14.20
4028	4085	4105	6.97	11.90	12.17
3701	3728	3732	2.72	3.42	3.36
3605	3615	3625	2.93	3.60	3.53

[a]"Hot bands."

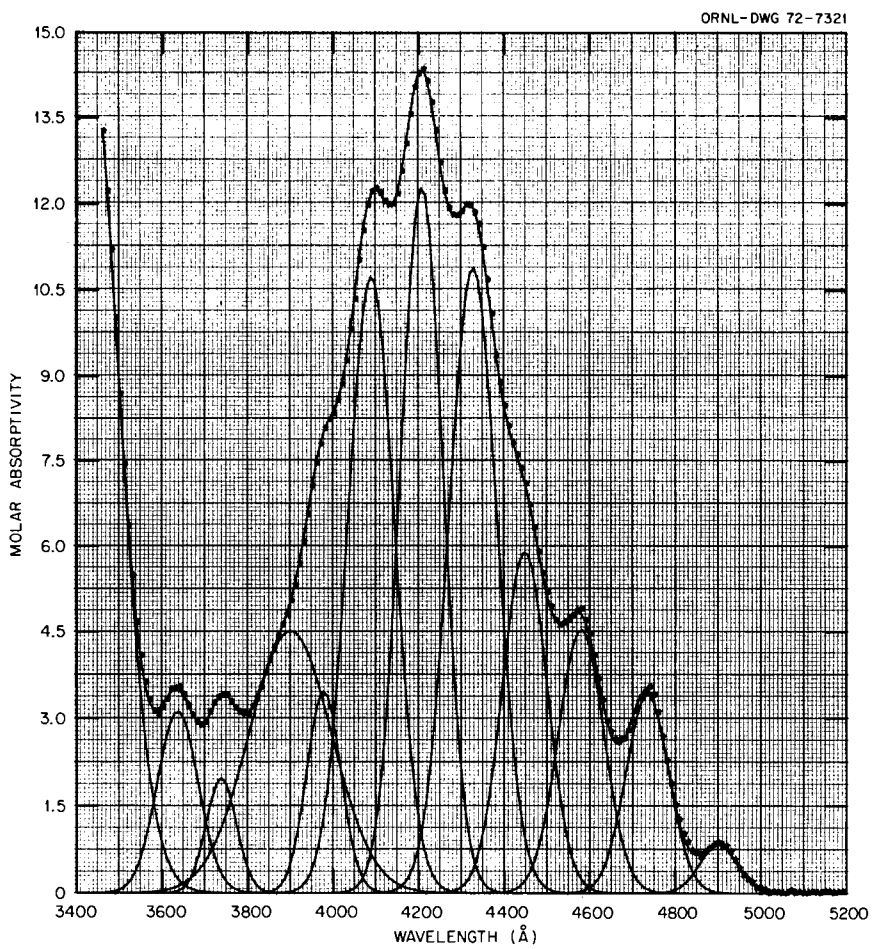

Fig. 11.1. Comparison of the experimental and the nonlinear least-squares calculated spectrum of 0.5188 M UO_2SO_4 in 3.490 M H_2SO_4 solution, showing the resolved Gaussian bands. Cell pathlength, 0.1996 cm. Points, experimental; lines, calculated.

11.3 PROTONIC WAVE FUNCTIONS AND SPECTRA

The studies on the multiplet theory of symmetric wave functions, the angular dependence of the vibrational and rotational excitations that occur when an electron is photoejected from a molecule, and the theory of photoejection of protons from hydrides were completed, and the results were published.[3-5]

A calculation of the ground-state wave function of DH^+ is in progress. This wave function will be "exact" in the sense that it will include the distance between the proton and electron in the same way as the interelectronic distance was included in the helium wave function by Hylleraas.[6] Calculation of the protonic and electronic structures of light monohydrides using the method described previously[7] is also in progress. Preliminary work has been done on a program to calculate numerical Dirac-Fock wave functions for actinide hydrides.

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3. I. L. Thomas, "Multiplet Theory for Symmetric Wave Functions," *Phys. Rev.* **A4**, 2120 (1971).
4. I. L. Thomas, "Angular Dependence of the Vibrational and Rotational Excitations Seen in Photoelectron Spectroscopy," *Phys. Rev.* **A4**, 457 (1971).
5. I. L. Thomas, "Photoprotonic Effect in Hydrides," *Phys. Rev.* **A5**, 1104 (1972).
6. E. A. Hylleraas, *Z. Physik* **54**, 347 (1929).
7. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1970*, ORNL-4572, p. 235.

12. Preparation and Properties of Actinide Oxides

12.1 OXIDATION-REDUCTION STUDIES OF URANIUM-PLUTONIUM OXIDES

A fundamental study of the oxidation behavior of unirradiated $(U,Pu)O_2$ fuels was undertaken to better understand the factors that affect the voloxidation process.[1] The experiments were designed for collaboration with hot-cell studies on the pulverization of irradiated fuel and the release of volatile fission products upon oxidation. Earlier work[2] indicated that the Pu/M ratio of the fuel was an important variable in the process. Subsequent experiments on unirradiated $(U,Pu)O_2$ fuel specimens have led to the conclusion that the oxidation with resulting pulverization of homogeneous mixtures is dependent on several variables such as the Pu/M ratio, the ceramic quality of the specimen, and its physical size.

The Pu/M ratio of the fuel was found to be the most important variable since it limited the amount of oxidation that could be obtained under a set of oxidizing conditions. From thermogravimetric studies, it was found that samples with Pu/M ratios of $\leqslant 0.20$ oxidized in two steps. The first step corresponded to an intermediate product with O/M = 2.3, which further oxidized to give a product with O/M = 2.6. X-ray diffraction analyses of the oxidized materials indicated only cubic M_4O_9 and orthorhombic M_3O_{8-y} phases for the final products. When the Pu/M ratio was $\geqslant 0.25$, oxidation beyond the cubic M_4O_9 phase did not occur, except when the oxidation was carried out with high-pressure oxygen (600°C, 500-psi oxygen). Since pulverization of the ceramic fuel occurs as a result of the formation of the orthorhombic M_3O_{8-y} phase from a cubic phase (due to the increase in the unit cell volume of the crystal matrix), samples that did not oxidize beyond the M_4O_9 composition did not pulverize.

The ceramic quality and the physical size of the $(U,Pu)O_2$ specimens were found to be important in the pulverization process when the Pu/M ratio was $\geqslant 0.20$. High ceramic quality (high density, low porosity, well-defined grains) and large size impaired the rate and the relative ease of reaching the equilibrium O/M ratio set by the Pu/M ratio.

Studies were also undertaken to characterize the physical changes that occurred during the oxidation. Measurements by x-ray line broadening techniques showed that the crystallite sizes of the starting materials and the oxidized products were essentially the same, ranging from 1000 to 2000 Å in diameter. From BET surface area measurements on the oxidized powders, the particle size in the products was calculated to be on the order of 1 to 10 μ. The conclusion reached from these results and from electron microscopy was that the oxidation process pulverized the ceramic bodies (pellets or microspheres) by fracturing the material along the grain boundaries. Therefore, the particles comprising the pulverized product were aggregates of the individual crystallites, and the maximum amount of pulverization occurred when the ceramic was completely reduced to the individual grains. Thus, if the volatile fission products in irradiated fuels were to collect both at the grain boundaries and in voids inside the grains, pulverization of the fuel by oxidation would release only the fission products located at the grain boundaries. The volatile fission products that did not readily diffuse through the oxide would then be released in the subsequent dissolution step. This mechanism is in accord with hot-cell studies on irradiated fuels.[1]

Although the above-mentioned variables have been shown to affect oxidation of $(U,Pu)O_2$ fuel specimens, the data obtained from unirradiated fuels should not be applied directly to irradiated fuels. The effects of restructuring, uranium migration, and radiation damage are important variables. For example, the restructuring that occurs during irradiation can lead to both grain

1. J. H. Goode (compiler and editor), *Voloxidation – Volatile Fission Product Removal from LMFBR Fuels*, ORNL-TM-3723 (in press).

2. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 49.

growth and cracking, and the migration of uranium can produce phases with different Pu/M ratios. Thus these factors are expected to affect the behavior of the irradiated fuel on oxidation and need to be evaluated.

12.2 DEVELOPMENT OF THE UO_2-PuO_2 SOL-GEL PROCESS

Laboratory work to develop a solvent extraction process for the preparation of mixed UO_2-PuO_2 sol[3] was continued. Emphasis was centered on solvent extraction since this type of process should be readily amenable to scale-up and to the remote operations necessary for fabricating LMFBR recycle plutonium into reactor fuel. In the process selected for study, CUSP-prepared urania sol is mixed in the proper proportions with an APEX-prepared low-nitrate plutonia sol. Low-nitrate plutonia sols can be prepared by the APEX process when the primary crystallites in the sol are arranged in aggregated micelle structures, which result in rapid denitration and crystallite growth when the sols are taken to dryness and heated. The resulting low-nitrate sols can be used to prepare mixed UO_2-PuO_2 sols with greatly improved shelf lives or to prepare pure plutonia microspheres. During this report period, development efforts were concentrated on the thermal denitration behavior of APEX sols and on certain variables that affect the aggregated structure.

In addition to temperature, two other variables – concentration of decomposition gases and concentration of water vapor – were found to greatly affect thermal denitration behavior when a plutonia sol with the appropriate aggregated micelle structure is taken to dryness and heated. Denitration rates are a function of the atmosphere in the baking chamber. This was demonstrated by comparing heating a sol in a stagnant atmosphere with heating in an atmosphere in which evolved gases were removed continuously by a dry air sweep through the baking chamber. When the air sweep was used, less than 15 min at 230°C was required to obtain a final sol of adequately low nitrate, whereas approximately 50 min was required for material heated in a stagnant atmosphere. When argon, nitrogen, or oxygen was used as the sweep gas, similar results were obtained, suggesting that the increased denitration rate is due to the removal of gaseous decomposition products rather than an interaction of the solids with the sweep gas.

3. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 149.

It was also found that the presence of water vapor has a serious adverse effect on denitration behavior. Crystallites from high-nitrate plutonia sols prepared by any method undergo two growth mechanisms during thermal denitration at elevated temperatures. One is crystallite growth, which is desired; the other is irreversible, random aggregation of crystallites, which is undesirable because in a severe case it leads to the production of large particles that will not resuspend to form a sol. The effect of water vapor is illustrated in Fig. 12.1, which shows a thermal denitration curve that was obtained when dry argon was used as the sweep gas through the baking chamber. In this experiment, the conversion to 60-Å crystallites occurred in 20 min or less; however, sol obtained after the solids were heated for 4 hr was still very dark green, which indicated that very little aggregation into large particles had occurred. The two data points indicated by squares were obtained in a second experiment in which the argon sweep gas was bubbled through a water trap at 25°C to introduce water vapor. The sol was very light green after 20 min, indicating the presence of large particles, and the solids could not be resuspended after 30 min of heating. This demonstrates the rather startling effect of moisture in promoting undesirable secondary aggregation.

The aggregated micelle structure is obtained by seeding, in which a portion of a normally prepared high-nitrate sol is added to feed solution during the initial extraction of a subsequent sol preparation. In

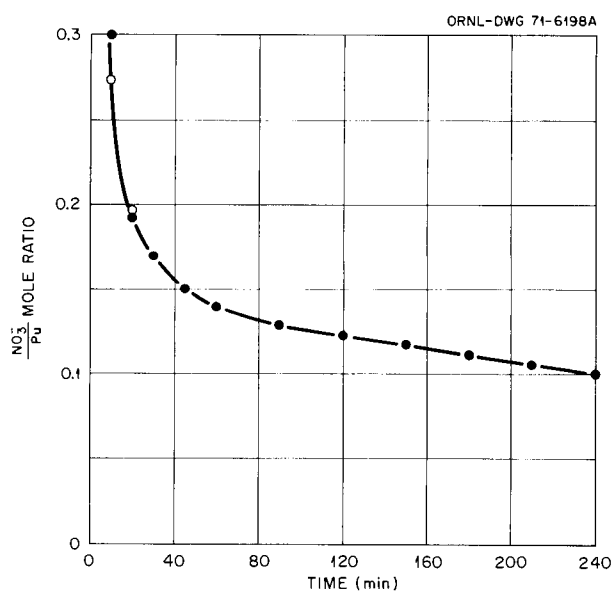

Fig. 12.1. Effect of water vapor on the thermal denitration of dried plutonia sol at 230°C. Under dry argon (●), solids were resuspended after 240 min; under moist argon (○), solids were not resuspendible after 30 min.

continued studies of this effect it was found that aggregation occurs when the NO_3^-/Pu mole ratio of the feed is reduced from 4.6 to 3.0, and the extraction time during this period is critical. Complete aggregation is obtained if an extraction time of 1.5 hr is used; however, if this time is reduced to 1 hr by extracting at a faster rate, less than half of the material will aggregate. It is significant that crystallite aggregation actually relates to contact time between the seed polymer and the feed in this critical region rather than to extraction rates per se. This was demonstrated in a series of experiments in which the total contact time was maintained at 1.5 hr. Comparable results were obtained by slow continuous extraction, intermittent extraction at a more rapid extraction rate, and a long hold period followed by rapid continuous extraction.

Additional details of the work will be available as follows: M. H. Lloyd and O. K. Tallent, "A New Solvent Extraction Process for Preparation of PuO_2 Sols," to be presented at the Eighteenth Annual Meeting of the American Nuclear Society, June 18–22, 1972, and to be submitted for publication in *Nuclear Technology*.

12.3 THORIA DESINTERING STUDIES[4]

Experiments with thoria to determine the causes of desintering[5] were completed. Results of these experiments established that nitrogen moves in and out of thoria sol-gel dense sinters at 1800°C, the temperature where denitration occurs. After being fired in air, the ThO_2 contains nitrogen. If refired in vacuum, it loses the nitrogen; then, if refired in air again, it reabsorbs nitrogen. This contradicts a usual belief that the porosity of desintering is caused by pressure of trapped gas such as nitrogen. A paper has been prepared for publication in the *Journal of the American Ceramic Society*. The abstract follows:

"Desintering of Thoria," by C. S. Morgan, K. H. McCorkle, and C. V. Powell. *Abstract:* Sintered ThO_2 powder compacts will sometimes undergo a density loss and become more porous if held at high temperature for a sufficient time. ThO_2 sol-gel sintered to 99% of theoretical density at 1200°C will undergo a steady bulk density decrease at 1800°C with the density falling below 90% T.D. after about 15 hours. Gas release measurements from desintered ThO_2 specimens annealed in air or in vacuum indicate that gases move through the material rather freely at 1800°C, suggesting that loss of density may not be a gas pressure effect. The extent of desintering was decreased by firing in argon and vacuum and by the addition of small quantities of other oxides.

12.4 PREPARATION OF CARBIDES AND CARBONITRIDES

Carbothermic preparations. The feasibility of preparing uranium, uranium-plutonium, and plutonium carbides and carbonitrides from colloidal solutions of the reactants has been demonstrated on a laboratory scale. Past efforts in this area have been previously reported.[6] The procedure employs a colloidal MO_2+C mixture, prepared from UO_2 and/or PuO_2 sols and carbon black, to obtain homogeneous mixtures of the reactants in the form of powders, shards, or microspheres. The solid oxide-carbon mixture is then converted to the desired product by heating to 1500–1700°C in an appropriate atmosphere.

Although the preparation of carbides and carbonitrides via a carbothermic reduction of the oxide presents some problems in obtaining a pure, single-phase product, the method is favored economically and the products may be suitable for reactor fuels. The exact specifications required for these fuels need to be determined in future irradiation studies.

Studies made to date have shown that it is possible to prepare an essentially single-phase monocarbide or carbonitride (by x-ray diffraction) from $(U,Pu)O_2$+C mixtures by selectively choosing the C/M ratio and the atmosphere used during the conversion step. Pu/M ratios $\leq$0.25 were used in all the studies. The oxygen contents of the products have been as low as 200 ppm and can routinely be kept below 1000 ppm. Theoretically, a monophase carbonitride can be produced from an MO_2+C mixture with a C/M ratio as low as 2.2; however, experience has shown that a longer conversion time is required when the ratio is less than 2.5, and the products generally have an oxygen content of greater than 1000 ppm. By choosing a C/M ratio of 2.5 to 2.8 for preparing the (U,Pu) carbonitrides, these problems have been avoided while still maintaining some flexibility in the carbon content.

Preparation of a single-phase plutonium monocarbide from a PuO_2+C mixture has been experimentally more difficult than for the corresponding preparation in the (U,Pu) system. This difficulty arises because Pu_2C_3 is thermodynamically more stable than PuC. Most of the PuC products that have been prepared contained small

4. Work done in cooperation with C. S. Morgan, Metals and Ceramics Division, and G. L. Powell, Y-12 Plant.

5. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 218.

6. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 224.

quantities of Pu_2C_3 (by x-ray diffraction). Preparation of a single-phase plutonium carbonitride requires that the C/M ratio in the reactants be 2.0 to 2.2; and, as in the (U,Pu) system, the carbothermic reduction does not proceed as well as when higher ratios are used. The oxygen contents of both the plutonium monocarbide and carbonitride preparations were routinely higher than found for the (U,Pu) counterparts, and ranged from 2000 to 6000 ppm. The higher values may reflect, in part, the higher susceptibility of the plutonium products to oxygen and water contaminants.

Examination of the (U,Pu) and Pu carbides and carbonitrides by metallography and mercury porosimetry has shown that microspheres of 85 to 95% of theoretical density can be prepared by the single conversion-sintering procedure. Shards were found to have a slightly lower density, probably resulting from the porosity induced in the gel fragments during their formation and retained throughout the conversion-sintering step.

Kinetics of carbide and carbonitride syntheses.[7] Kinetics models were developed to identify the important variables in both the hydrogen and the C-CO-CO_2 reduction of uranium-plutonium mixed oxides to produce substoichiometric oxide fuels. These models are being used to aid work on LMFBR oxide fuels at ORNL and at several other installations. The derivation and the description of the models have been published.[8]

Results of a further study of the kinetics in the U-C-O-N system at 1700°C have been submitted for publication in the *Journal of the American Ceramic Society.* The abstract follows:

"Kinetics of the UO_2-C-N_2 Reaction at 1700°C," by T. B. Lindemer. *Abstract:* The reaction of UO_2 with carbon in the presence of nitrogen has been studied at 1700°C to determine the mechanism and rate of the formation of the carbonitride products. The formation of uranium carbonitride at specific oxygen and nitrogen chemical potentials is accomplished via two typical sequential reactions: $UO_2(s) + 0.67\ C(s) + 0.225\ N_2(g) \rightarrow UO_{1.33}N_{0.45}(s) + 0.67\ CO(g)$ and $UO_{1.33}NO_{0.45}(s) + 1.58\ C(s) + 0.375\ N_2(g) \rightarrow UC_{0.25}N_{0.75}(s) + 1.33\ CO(g)$. The presence of nitrogen in the UO_2-C-N_2 reaction permitted a gas-phase transport of reactants and products by HCN that was not observed in an otherwise equivalent study of the UO_2-C reaction. The first reaction is completed in a short time and can be controlled by a gas-phase transport of carbon by HCN; the second reaction proceeds as soon as there is oxynitride available and is eventually controlled by solid-state diffusion. The reaction rates and product composition were dependent on the N_2 and CO pressures imposed on the system.

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7. Work done by T. B. Lindemer, Metals and Ceramics Division.

8. T. B. Lindemer and R. A. Bradley, "Kinetic Models for the Synthesis of $(U,Pu)O_{2-y}$ by Hydrogen-Reduction and Carbothermic Techniques," *J. Nucl. Mater.* 41, 293–302 (1971).

13. Surface and Interface Properties in Heterogeneous Systems

13.1 ISOTOPE ENRICHMENT BY (n,γ) REACTIONS IN MOLECULAR SIEVES

Measurements of the isotopic enrichment resulting from irradiation of lanthanide-exchanged zeolites[1] have been extended to much higher neutron exposures, and the results indicate a decrease in enrichment factors in the exposure range that is expected to cause significant crystal structure damage from fast neutrons. The implication of these experiments is that some actinide isotopes of interest can probably be produced at an enrichment severalfold greater than would be possible by conventional irradiations.

In several irradiations of PrX (praseodymium-exchanged Linde X) zeolite in the Oak Ridge Research Reactor (ORR) at fluences of 10^{16} to 2×10^{17} thermal neutrons/cm^2, the yield of the neutron capture product, ^{242}Pr, was 56 to 66% and the enrichment factor varied from about 70 to 120. At a fluence of 5×10^{18} neutrons/cm^2 the yield was still 50%, but the enrichment factor dropped to 24. In two experiments in which the fluence was near 10^{20} neutrons/cm^2, the yield decreased to about 20% and the enrichment factor was only 4. Results of these experiments show that both the yield and the enrichment factor decreased in the neutron exposure range of interest for producing useful actinide isotopes, 5×10^{19} to 10^{21} neutrons/cm^2.

Since the ORR irradiation facilities have a rather high ratio of fast to thermal neutrons, the deterioration in enrichment occurred in the expected region, based on displacement of a significant fraction of the atoms from their crystal lattice positions by fast-neutron collisions. In general, thermal neutrons cause the reaction leading to the desired separation, and fast neutrons cause damage that destroys this separation. The facility currently being installed in the outer reflector region of the High Flux Isotope Reactor (HFIR) will have a much lower ratio of fast to thermal neutrons; thus, higher exposures may be possible before serious damage occurs. Additional irradiation tests are planned for this facility, using actinide-exchanged as well as lanthanide-exchanged zeolites.

1. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, p. 174.

13.2 OXIDATION OF COLLOIDAL URANIA

Investigation of the oxidation of urania sols was continued in studies concerning the rate of sorption of oxygen, oxidation with hydrogen peroxide, and moving boundary electrophoresis of partially oxidized sols. A 100% crystalline 1.0 *M* urania sol (LS-23) that had been prepared by the CUSP process,[2,3] was used in these studies. Sol LS-23 contained 13% U(VI) and was composed of spherical micelles about 300 Å in diameter, which, in turn, consisted of agglomerates of crystallites having an average size of 40 Å as measured by x-ray diffraction.

Results of previous studies on the rate of sorption of O_2 by 1 *M* CUSP sols at room temperature under pure O_2 at 1 atm pressure indicated an initial linear rate of O_2 sorption and a sharp decrease in rate when a total U(VI) content of 17 to 18% was attained, interpreted as representing the completion of oxidation of the urania surfaces.[4] Results of the work carried out during this report period, using approximately the same experimental arrangement for O_2 sorption and conditions similar to those used in the previous studies, confirm the sharp decrease in rate but indicate that its cause is a sudden and reproducible increase in the viscosity of the sol rather than a limitation of oxidation to the surface of the 40-Å crystallites. In the experiments with the

2. J. P. McBride, K. H. McCorkle, W. L. Pattison, and B. C. Finney, "The CUSP Process for Preparing Concentrated Crystalline Urania Sols by Solvent Extraction," *Nucl. Technol.* 13, 148 (1972).

3. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1969*, ORNL-4422, p. 203.

4. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1970*, ORNL-4572, p. 243.

LS-23 sol, aliquots of the sol thickened sufficiently to hinder stirring as the total U(VI) content approached 17 to 18%; on further oxidation, they regained much of their fluidity but showed evidence of some thixotropy. With adequate stirring (or with dilute sols, to decrease the effect of viscosity), the oxygen sorption curves up to 86% U(VI) were smoothed out to the continuous parabolic type often encountered in the oxidation of metals.

Conductivity changes observed during the oxidation of portions of the LS-23 sol with both oxygen and hydrogen peroxide were similar, attaining a minimum as the total U(VI) content reached 17 to 18%. The thickening noted above was observed in each case. Hence, it would appear that oxidation with either oxidant yielded the same result for equivalent stoichiometries.

The electrophoretic properties of partially oxidized 0.02 *M* urania sols were examined by moving boundary studies. These sols were prepared by diluting 2-ml aliquots of sol LS-23 to 100 ml with an HNO_3 solution (0.018 *M*) having about the same conductivity as the sol and containing predetermined amounts of hydrogen peroxide. The experiments were carried out at 20°C using a standard Tiselius cell and a Beckman Model H Electrophoresis-Diffusion apparatus.[5] The displacement of the boundaries in both descending and ascending legs of the Tiselius cell were linear with time. As is customary, the rate of displacement of the descending boundary was used to calculate the zeta potentials, which are shown in Fig. 13.1 as a function of the U(VI) content of the sols.

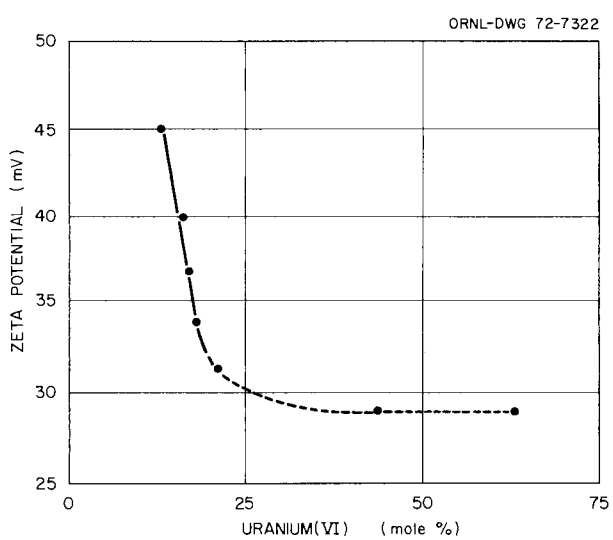

Fig. 13.1. Zeta potential of urania sol as a function of uranium(VI) content. Sol LS-23 was diluted to 0.02 *M* and oxidized by the controlled addition of hydrogen peroxide.

The diluted sols had lower conductivities and, in general, higher pH's than sol LS-23, the relative change increasing with increasing U(VI) content. At least part of this change resulted from the dissolution of a fraction of the uranium in the sol as shown by analysis of the intermicellar liquids. Hence, the zeta potentials shown in Fig. 13.1 are not necessarily those which would be obtained in concentrated sols of the same U(VI) contents, and the relationship between them remains to be established. It should be noted, however, that concentrated sols with U(VI) contents of 25% or greater are relatively unstable, and this would be predicted from the present data. It should be noted, also, that the thickening observed in the O_2 sorption experiments with LS-23 occurred at a U(VI) content of 17 to 18%, where the present data would indicate a zeta potential midway between the highest and lowest values. This is not inconsistent with the theory of oriented flocculation of Thomas and McCorkle,[6] which predicts a region of viscous behavior in sols at zeta potentials well above the value where the sols are unstable.

13.3 THEORETICAL MODEL OF COLLOIDAL INTERACTION

The work on the theory of oriented flocculation was completed and summarized for publication.[6] While this work explained the flocculation of metal oxide sols adequately, it could not describe the detailed nature of the interaction of two colloidal particles. A model aimed primarily at the description of this interaction has been derived. In this model the charge distribution about a colloidal particle and the potential arising from the surface charge on the particle are described by linear combinations of functions of the form

$$r^{l-1}S_{lm}(\theta,\phi)\,,$$

where r is the distance from the particle and $S_{lm}(\theta,\phi)$ is a real spherical harmonic. If ρ_1 and V_1 represent the charge distribution and potential of one colloidal particle and ρ_2 and V_2 represent the charge distribution

5. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1967,* ORNL-4145, p. 287; *May 31, 1968,* ORNL-4272, p. 238; *May 31, 1969,* ORNL-4422, p. 312.

6. I. L. Thomas and K. H. McCorkle, "Theory of Oriented Flocculation," *J. Colloid Interface Sci.* **36**, 110 (1971).

and potential of the other, the energy of interaction (neglecting all kinetic energies) is:

$$W = \iint \rho_1 \frac{1}{r_{12}} \rho_2 \, dv_1 dv_2 - \int \rho_1 V_1 \, dv_1 - \int \rho_1 V_2 \, dv_1 - \int \rho_2 V_2 \, dv_2 - \int \rho_2 V_1 \, dv_2 + a^2 b^2 \iint \sigma_1 \frac{1}{r_{12}} \sigma_2 \, ds_1 ds_2 ,$$

where r_{12} is the distance between two elements of charge; dv_i is the volume element; a and b are the radii of particles 1 and 2, respectively; σ_i is the surface charge; and ds_i is the surface element. The energy, W, is minimized by varying the coefficients in the expansions of ρ_1, ρ_2, V_1, V_2, σ_1, and σ_2 for various values of R, the distance between the colloidal particles.

From this study we will find how the charge distributions change as the particles approach each other and where the charge concentrates.

14. Chemical Engineering Research

The Chemical Engineering Research Program consists of several studies which are generally pertinent to the applied programs of the Chemical Technology Division; however, the studies are carried out in a more fundamental manner than that usually employed in applied programs. The areas of study may arise from needs for fundamental information in existing applied programs or from new ideas, which frequently mature into applied programs.

14.1 THORIUM ANION EXCHANGE WITH VERY SMALL RESIN PARTICLES

The use of small resin particles has proved to be beneficial in ion exchange processes for separating both biological and inorganic materials. The advantages accrue from improved kinetics and flow patterns (e.g., less channeling and smaller mixing cells). However, applications of small resin particles (<400 mesh) have generally been limited to small-scale processes such as laboratory separations.

During this report period, a study of the applicability of small resin particles (10 to 50 μ) to large-scale processes was initiated. The first system to be investigated was the anion exchange process used for concentrating and purifying plutonium nitrate. This process involves very slow diffusion rates in the resin particles, resulting in diffuse loading fronts and requiring long columns. If a sharply defined loading front could be obtained, the columns could be shortened and operated on a rapid load-elution cycle. Also, oxidation and radiation damage to the resin would be reduced and the higher pressure gradients characteristic of columns containing small particles would be more effective in removing gases that often form in plutonium nitrate columns.

Thorium was used as a "stand-in" for plutonium in the initial experiments. Small-scale loading experiments were performed with several resins smaller than 400 mesh. These resins were carefully sized by elutriation, and the diameters of samples were measured by a Coulter counter as well as optically (from photographs). The results obtained by the two methods failed to agree, but the optical measurements are considered to be more reliable.

The objective of the loading experiments was to develop a method for predicting breakthrough curves for columns of any size. The model selected for evaluation, rate control by particle diffusion resistance, was an obvious choice. The principal simplification was the selection of a single, constant particle diffusion coefficient. The anion exchange process involves counterdiffusion of nitrate and one or more thorium (plutonium) ions and simultaneous dehydration of the resin. The effective interdiffusion coefficients could be evaluated either in loading experiments or by elution of a narrow band of thorium from the column (i.e., by spreading of the band). Because of the complex phenomena that occur during loading, we chose to make measurements under conditions that closely simulate the loading procedure of interest.

The equations describing sorption in a bed with a constant particle diffusion coefficient and a constant distribution coefficient (conditions closely approximated in these experiments) have been developed by Rosen.[1,2] By making additional calculations, we expanded his results and replotted them in the more convenient form shown in Fig. 14.1. Two points are read from the breakthrough curve: $t_{0.3}$, the time for the breakthrough concentration to reach three-tenths of the inlet concentration, and $t_{0.7}$, the time for the outlet concentration to reach seven-tenths of the inlet concentration. The dimensionless diffusion coefficient, X, is plotted as a function of $(t_{0.7} - t_{0.3})/t_{0.7}$ in Fig. 14.1. Here,

$$X = \frac{3DKZ}{mvb^2},$$

D = particle diffusion coefficient,

K = distribution coefficient,

1. J. B. Rosen, *J. Chem. Phys.* **20**, 387 (1952).
2. J. B. Rosen, *Ind. Eng. Chem.* **46**, 1590 (1954).

Z = length of the bed,

m = column void fraction,

v = superficial velocity of particle through the bed,

b = radius of resin particles.

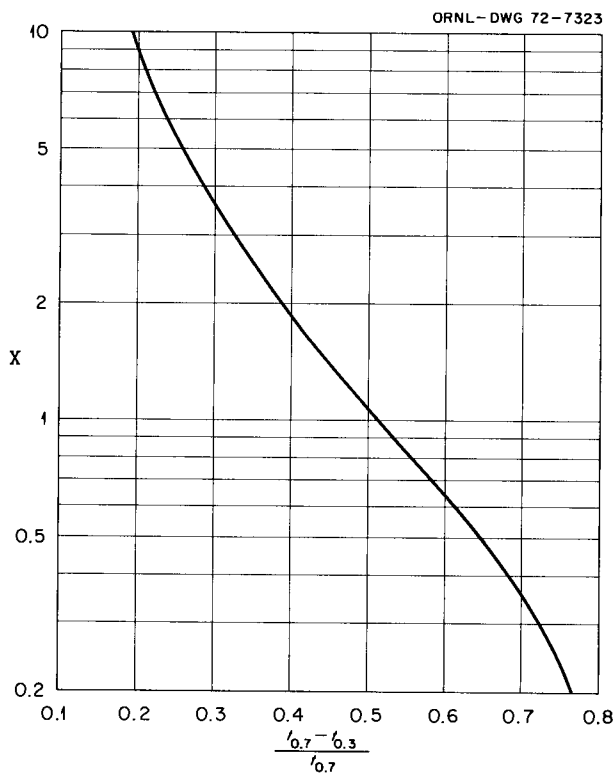

Fig. 14.1. Determination of particle diffusion coefficient.

Once the diffusion coefficient has been determined, the experimental results can be compared with the theoretical breakthrough curve. A typical comparison is shown in Fig. 14.2. Although the fit is reasonably good, the experimental data fall noticeably below the curve for a short period after initial breakthrough (at the first signs of breakthrough). This can probably be attributed to dehydration of the resin and hence to lower diffusion coefficients as loading progresses. The usefulness of the method lies in its capability for predicting the effects of liquid flow rate, resin size, and column height. Particle diffusion coefficients have been evaluated with different resins, resin sizes, and flow rates. Results show that these coefficients are independent of flow rate for any particular resin, indicating that the effects of flow rate are adequately predicted. With Dowex 1-X8 resin, there is an apparent decrease in the measured diffusion coefficient as the resin size decreases. Such a decrease could stem from variations in the resins used and/or from uncertainties in the smaller resin size measurements. In general, experimental agreement with the model is adequate and simple procedures have been developed to predict the behavior of larger columns on this basis.

The effects of other resin properties have also been evaluated. As expected, the diffusion coefficient decreases markedly with increasing cross-linkage. A few experiments were made with two macroreticular resins (Amberlite IRA-900 and -938), which are relatively large particles formed from very small particles. It was hypothesized that diffusion would be relatively rapid in the space between the small subparticles and that the mass transfer behavior would be comparable to that of

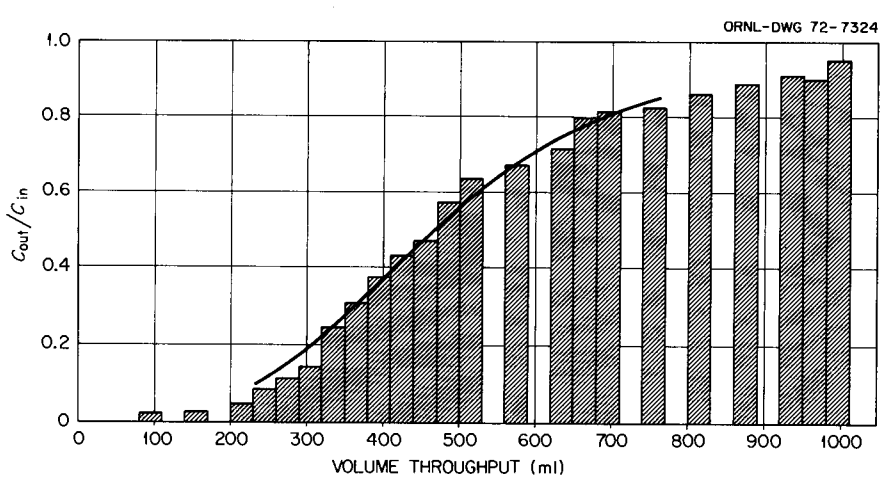

Fig. 14.2. Breakthrough curve obtained for 44-μ-diam Dowex 1-X8 resin. Conditions: liquid flow rate, 1 cm/sec; temperature, 40°C; diffusion coefficient, 2.1×10^{-10} cm^2/sec.

resin of the subparticle size, while the pressure drop would be comparable to that of resin of the overall particle size. Relative to mass transfer, neither resin performed as well as Dowex 1-X8, but the results were much better than one would expect from 16- to 20-mesh Dowex 1.

Because large-scale applications of small-particle resins may initially be limited by resin supply, irregularly shaped resins obtained by grinding larger resins were tested. (Of course, once the demand for small resin is well established, spherical resins will probably become available in any desired quantity.) Large (16 to 20 mesh) resin was "ground" in a blender and carefully sized by elutriation. The resulting product gave breakthrough curves and pressure drops similar to spherical resins of comparable size (approximately 30 μ). The yield of a particular size fraction depends on the grinding technique, but no attempt has been made to explore this variable. These experiments were intended only to demonstrate the potential usefulness of nonspherical resins.

14.2 MULTICOMPONENT MASS TRANSFER IN ELECTROLYTE SYSTEMS

Calculations of the rates of mass transfer between two fluids are usually made in terms of mass transfer resistances on one side, or both sides, of the interface. This type of approach is often inappropriate in multicomponent systems or in systems where the transferring components (e.g., ions) are electrically charged because the mass transfer coefficient is a complex function of concentrations and concentration gradients, which are, in turn, a function of position in the column.

Previously, we described a calculational procedure for predicting mass transfer rates for any number of ions (the procedure is programmed for up to ten ions) transferring between an electrolyte and a nonelectrolyte.[3] Calculations have now been made under a variety of conditions to evaluate the effects of parameters such as equilibria, diffusion coefficients, and concentrations. The procedure appears to be useful both for quantitative evaluations of transfer rates and, in many cases, simply for determining whether the electrical charges will significantly affect the transfer rate.

During the past report period, the calculational procedure was extended to describe the behavior of entire countercurrent columns. Again, up to ten components can be treated. The calculation time is a function of the particular column design; however, for all practical conditions under which the system has been tested, the calculation times are modest.

14.3 MASS TRANSFER OF WATER FROM SOL DROPLETS

During the preparation of sol-gel microspheres, aqueous sol droplets must be fluidized in an organic phase until enough water is extracted to cause gelation. The rate of mass transfer has been investigated by fluidizing a single water or thoria sol droplet in a partially miscible alcohol and measuring the diameter of the droplet as a function of time. With rigid aqueous drops (i.e., a surfactant present in the organic phase), the sphere Reynolds number was varied from 0.2 to 30; with fully circulating water drops (i.e., no surfactant in the organic phase), the sphere Reynolds number was varied from 1 to 13. Mass transfer coefficient expressions were derived and confirmed experimentally for both rigid and fully circulating aqueous drops. For fluidized rigid drops, the mass transfer coefficient is proportional to the product of the mass diffusivity raised to the two-thirds power and the density difference of the droplet and solvent raised to the one-third power, divided by the viscosity of the solvent raised to the one-third power. For fluidized, fully circulating drops, the mass transfer coefficient is proportional to the product of the drop diameter raised to the one-half power, the mass diffusivity, and the droplet and solvent density difference, divided by the viscosity of the droplet.

To check the assumed parabolic velocity profile, the fluidizing characteristics of 15 solid spheres were measured in both the tapered Plexiglas column and a straight glass tube with a diameter of 0.250 in. The densities of the solid spheres ranged from 1.1 to 4.0 g/cc, and the ratios of sphere diameter to column diameter varied from 0.06 to 0.38. The fluidizing velocities measured in the tapered column agreed with the maximum approach velocities measured in the straight tube with an average error of ±3%. This suggests that mass transfer rates predicted from this study can be applied to large fluidized systems.

14.4 PRODUCTION OF SOL-GEL MICROSPHERES OF SMALL UNIFORM SIZE

The use of transverse vibrations to break liquid jets into small uniform droplets suitable for producing small microspheres was investigated. The formation of water droplets was studied both in air and in 2-ethyl-1-hexa-

3. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, pp. 237–39.

nol (2EH) at frequencies from 60 to 2000 Hz. An attempt was made to form droplets at ultrasonic frequencies, but the available equipment was not capable of producing consistent drop sizes. Regions of frequency and amplitude that yield one, two, or more drops per cycle were outlined. Stable one and two drop formations per cycle could only be obtained at frequencies near the natural instabilities of the jet, and no stable formation of uniform drops smaller in diameter than the jet nozzle opening was observed. Uniform drops as small as 340 μ were formed from a single 254-μ nozzle in 2EH at flow rates up to 5.73 cc/min. These conditions would allow reasonable production rates for solid microspheres less than 100 μ in diameter. The exact size of the microspheres could be adjusted over a limited range by controlling the concentration of the sol.

At very high amplitudes, several smaller drops may be formed per cycle; twelve or more drops per cycle were observed. The drops formed at any position in the cycle are uniform in size but will not necessarily be the same size as those formed at another position in the cycle. Thus, this mode of operation produces a discrete (not continuous) distribution of small drops. The operation is not as stable under these conditions as under conditions where one or two drops are produced per cycle; slight changes in amplitude or water flow rate will cause the number of drops formed per cycle (and thus the size distribution) to vary.

14.5 CHEMICAL ENGINEERING RESEARCH STUDIES RELATED TO MSR PROCESSING

Continuous salt purification. Difficulties were encountered after 11 iron fluoride reduction runs had been carried out[4] for study of the reduction of FeF_2 in molten fluoride salt (72-14.4-13.6 mole % LiF-BeF_2-ThF_4) by countercurrent flow of hydrogen and molten salt in a column packed with $^1/_4$-in. Raschig rings. These difficulties, which stemmed from salt leaks and plugged lines, necessitated opening the system to the atmosphere. Following a maintenance period, the flow capacity of the column was found to be reduced to about 10% of the original flow capacity, presumably because oxide had accumulated in the system. Treatment of salt in the column with an H_2-HF mixture only reduced the restriction slightly. In order to obtain more accurate reduction data under the imposed condition of low flow rates, the iron concentration was increased from about 100 ppm to 1000 ppm and five additional runs were made. To further improve analytical accuracy, the sample size was increased from 1 g to 4 g and the nickel samplers were replaced with copper tools to minimize possible iron contamination during removal of the sample.

After these runs had been completed, the column was removed and cut into sections for examination. A heavy deposit of nickel near the top of the column and a near-uniform deposit of iron on the packing were noted.[5] The column that was installed to replace the old one was packed with $^1/_4$-in. Raschig rings having a $^1/_{32}$-in. wall thickness instead of the $^1/_{16}$-in. wall thickness used initially. This new column operated very smoothly at flow rates three times the maximum possible with the previous column. Data from the first three reduction runs indicated that a smaller fraction of the FeF_2 was being reduced per run than in the old column, and the average variation in the colorimetric analysis (±3.9%) was larger than the fractional reduction of FeF_2 per run (1.8%). For this reason, ^{59}Fe tracer was added to the salt. With the tracer, the average variation in the colorimetric analysis was only ±1.8% during the succeeding 14 reduction runs in which the average extent of reduction was 4.8% per run. The average mass transfer coefficient, *ka*, in the new column was 7.8×10^{-6} mole/cm^3·sec as compared with 32×10^{-6} mole/cm^3·sec in the initial column before it became restricted and 2.7×10^{-6} mole/cm^3·sec in the initial column after it became restricted.

Data on salt holdup in the packed column during countercurrent flow of argon and molten salt (72.0-14.4-13.6 mole % LiF-BeF_2-ThF_4) at 700°C were also obtained. The salt holdup increased linearly with increasing salt flow rate, from about 5% of the column void volume at 100 cm^3/min to about 11% at 500 cm^3/min.

Hydrodynamics of countercurrent flow in packed columns. The hydrodynamics of countercurrent flow of fluids with high densities and a high density difference has been studied to obtain data for the design of solvent extraction columns using liquid metals and molten salts. Existing correlations based on solvent-water systems have been shown to be inappropriate for liquid-metal–molten-salt systems. In the previous report, we presented experimental data for packed columns using mercury-water and mercury-glycerin solutions, and a correlation for use with high-density systems was developed from these results.

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4. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971*, ORNL-4682, pp. 37–38.

5. R. B. Lindauer et al., *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, pp. 226–28.

Recent efforts have been directed at studying the effect of density difference more systematically in order to develop correlations that will apply to systems with either low- or high-density differences. Measurements of pressure drop, dispersed-phase holdup, and flooding rates have been made with countercurrent flow of water and relatively dense organic liquids, carbon tetrachloride (density, 1.6 g/cm^3) and dibromomethane (density, 2.5 g/cm^3). The results indicate that the superficial slip velocity at flow conditions below flooding is essentially a constant, as observed in previous studies with mercury and water. The data are being combined with earlier data and with literature values to produce a general correlation.

14.6 RECOVERY OF TRITIUM FROM BLANKETS OF CONTROLLED THERMONUCLEAR REACTORS

Controlled thermonuclear reactors operating with deuterium-tritium fusion will require an economical supply of tritium. This can be achieved by breeding tritium in a blanket of lithium metal or possibly a lithium-beryllium fluoride salt surrounding the plasma region. Only one neutron is produced per fusion; thus neutron multiplication (n,$2n$) must also occur in order to achieve a practical breeding system. Potential methods for recovering bred tritium from the blankets or coolant systems of fusion reactors have been reviewed and evaluated. The efficiency of the recovery system or the maximum permitted concentration may be set by inventory charges, hydrogen (tritium) embrittlement of the niobium structural materials, or release rates to the environment. The most restrictive requirement for the removal system will be prevention of an unacceptably large release of tritium to the environment. Diffusion of tritium through walls of heat exchangers into the steam turbine system is the most serious problem because containment of tritium that reaches the steam system appears to be impractical. This study was made with a standard release rate of 4 Ci/day for a 2800-MW(e) system, which is in accordance with estimates of future tritium release regulations; however, the effects of other regulations, both more and less restrictive, were taken into account. The ORNL reference design, featuring a potassium coolant and a "topping" turbine coupled to a conventional steam turbine system, was used as the basis for this study. Alternative systems that use a helium coolant and, possibly, gas turbines were also considered.

Two recovery methods appear to be promising. The tritium can be recovered by cold traps in the potassium system. However, unless a sorbent (e.g., yttrium) is used in the cold trap, reduction of the release rate to 4 Ci/day by this method does not appear feasible; in addition, the cold traps would be too large to be economical. Nevertheless, traps filled with sorbent do appear to be economical and promising. The development of more effective tritium barriers on the coolant-steam heat exchanger could alter this conclusion.

Tritium can also be recovered by intentionally allowing it to diffuse through very permeable metal surfaces, probably palladium-coated niobium, into a slightly oxidizing atmosphere. When the metal surface is located in the high-temperature lithium system and the potassium-steam heat exchanger is coated with a less permeable material such as tungsten, removal to the recovery system is strongly favored over loss to the steam system; and the required additional capital costs for tritium recovery appear to be acceptable.

Neither gas sparging nor distillation is expected to be an economical recovery process. At the low tritium concentrations required to prevent leakage of more than 4 Ci/day, binary distillation or sparging will not generate a lithium-free product.

A development program to further evaluate and demonstrate recovery methods has been outlined. The emphasis will be directed at metal window systems and cold traps with sorbents. This program will be coordinated with power system design studies and with appropriate materials support work or consultations.

15. Reactor Evaluation Studies

This program, which is a joint effort with the ORNL Reactor Division, has the primary purpose of assisting the USAEC to evaluate the technical and economic feasibility of various nuclear power concepts being developed, or being considered for development, under the U.S. civilian power program. Work in this Division during the past year was devoted primarily to the development of systems analysis models for electric utility systems in cooperation with other members of the Joint Utility Planning Study Group (Tennessee Valley Authority, Commonwealth Edison Company, Westinghouse Atomic Development Corporation, Massachusetts Institute of Technology, and ORNL).

15.1 PROBABILISTIC SIMULATION OF POWER SYSTEMS

The technique of probabilistic simulation has aroused widespread interest throughout the electric power industry. In cooperation with other members of the Joint Utility Planning Study Group, we have developed the computer program SIMUL, a probabilistic model for estimating the operating cost of an electric power generating system.[1] Basically, the probabilistic simulation technique develops the cost of operating an electricity generating system over an extended period of time by forecasting the power to be generated by each plant. Information supplied by the user includes the system load duration curve, loading order of units, generating unit characteristics, and limitations on the energy to be supplied by hydroelectric or other energy-limited units. The major advantage of the technique is its capability for simulating the effects of random events such as unit forced outages. Older methods did not adequately take into account the probability of such events, and thus gave results that differed considerably from those experienced in practice. SIMUL has been applied to an actual system by workers at Commonwealth Edison Company, who report it to be far superior to the methods previously used.

15.2 POWER SYSTEMS INTEGRATION MODEL

With the exception of the nuclear core simulator, the basic systems integration model ORSIM has been completed and is operational. This code simulates the operation of a power system consisting of fossil, hydroelectric, pumped storage, and nuclear plants over a period of about 3 to 5 years. Calendar refueling dates for the nuclear units are supplied in advance by the user. For each nuclear refueling schedule, ORSIM determines an approximately optimal plan of operation for the system, including maintenance schedules for nonnuclear units and monthly energy deliveries for all plants in the system.

ORSIM permits the user to make economic comparisons of various alternative nuclear refueling schedules. For each schedule, ORSIM generates a near-optimal operating plan and a total discounted operating cost for the system. The user can then determine which refueling schedule is most suitable when cost, reliability, and other system criteria are taken into consideration.

Energy deliveries of the various units within each month are determined by SIMUL. Monthly allocations of energy from hydroelectric plants and energy-limited nuclear fuel cycles, if any, are determined by dynamic programming in such a way as to minimize the total discounted system cost over the desired planning period.

In the present stage of development of the code, incremental and levelized average nuclear fuel costs for various cycle energies are provided as input. The Joint Utility Planning Study Group plans to develop a nuclear core simulator which will calculate reactor mass data (materials charged and discharged) for given cycle energies. This subprogram, when combined with a nuclear fuel cycle cost code, can be inserted into the

1. D. S. Joy and R. T. Jenkins, *A Probabilistic Model for Estimating the Operating Cost of an Electric Generating System,* ORNL-TM-3549 (October 1971).

model to provide a more realistic representation of the nuclear costs.

15.3 FUEL CYCLE COST CODE

The fuel cycle cost code REFCO was briefly mentioned in the previous annual report.[2] This code calculates nuclear fuel cycle costs by the discounted cash flow procedure. Continuous discounting is used, so that each cash expenditure is discounted from the precise time at which it occurs. In addition to increased speed, continuous discounting has the advantage that the effects of small changes in the timing of fuel cycle events can be accurately evaluated. The original version of the code was designed for light-water reactors operating on the enriched uranium fuel cycle.[3] A new version is now available which can be applied to fast breeder reactors and to light-water reactors using either the enriched uranium or the recycle plutonium fuel cycle.[4] Levelized fuel cycle costs are calculated for each cycle of operation, both individually and cumulatively. The calculation includes federal income taxes, state income and revenue taxes, local property taxes, and property insurance on the fuel. Tax rates and other economic parameters, such as rates of return on debt and equity, are supplied by the user.

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2. *Chem. Technol. Div. Annu. Progr. Rep. Mar. 31, 1971,* ORNL-4682, p. 241.

3. R. Salmon, *Two Computer Codes for Calculating the Fuel Cycle Cost of a Nuclear Power Reactor,* ORNL-4695 (August 1971).

4. R. Salmon, *User's Manual for REFCO, a Discounted Cash Flow Code for Calculating Nuclear Fuel Cycle Costs,* ORNL-TM-3709 (April 1972).

16. Miscellaneous Programs

16.1 QUALITY ASSURANCE PROGRAM

Oak Ridge National Laboratory formally adopted a quality assurance program in August 1970 with the promulgation of Standard Practice Procedure 39. The objective of this program is to ensure that a material, component, system, or facility will perform satisfactorily through the application of planned and systematic actions. Responsibility for the overall program rests with the Quality Assurance Director. Quality Assurance Coordinators (QACs) situated in the various Divisions report to the Quality Assurance Director.

The following method is used to keep the QAC informed of events having QA implications within the Chemical Technology Division. When a new experiment or project (or revisions thereto) is considered, the Project Leader (or Principal Experimenter or Project Engineer) must inform the QAC by completing and submitting a quality assurance checklist such as that shown in Appendix I of QA-CT-1-101, "Guide for the Selection of Quality Level." The QAC, with the concurrence of the Project Leader, then assigns an appropriate quality level to the experiment or project. The QAC is also apprised of all purchase requests and newly opened work orders which serve to direct attention to developing projects.

The quality level assigned to a project depends on the severity of consequences expected if failure should occur; quality level I is the highest and quality level IV is the lowest. Most of the work in the Chemical Technology Division falls into quality level III. In this manner a trade-off between cost and benefit is achieved since a level higher than justified will unnecessarily increase the cost of a project, while a level lower than required would tend to relax some requirements that should be met.

Four quality assurance procedures were issued by the Chemical Technology Division during the year: (1) QA-CT-1-100, "Management and Planning," (2) QA-CT-1-101, "Guide for the Selection of Quality Level," (3) QA-CT-1-102, "Quality Assurance Program Plans," and (4) QA-CT-1-103, "Standard Quality Assurance Procedures for Quality Level III Projects in the Chemical Technology Division." Other procedures are in various stages of preparation.

Metal Transfer Experiment No. 3, which is being conducted in the Unit Operations Section, was audited by the Quality Assurance Director as part of a continuing program for screening various projects throughout the Laboratory. As a result of the audit, various changes in procedure were instigated in a move to request and maintain better records for this experiment.

Another quality assurance activity was the drafting of a "Quality Verification Plan for $^{233}UO_2$ Powder Fuel for the Light-Water Breeder Reactor Program" by the Pilot Plant. A companion effort to this was the compilation, by the Design Section, of a package of more than 400 drawings concerned with the $^{233}UO_2$ processing equipment. This package was sent to the customer as part of the Quality Assurance Program for the project.

16.2 EVALUATION OF THE RADIATION RESISTANCE OF SELECTED PROTECTIVE COATINGS (PAINTS)

Radiation tolerance tests of commercial protective coatings were continued in an effort to evaluate the potential uses of new formulations in nuclear facilities.

The comparative ratings of 54 protective coating systems show that the same generic systems (epoxies, modified phenolics, and urethanes) reported in prior tests have continued to exhibit superior radiation resistance properties when exposed to a gamma source in either air or demineralized water. Seventeen of these systems exhibited a radiation tolerance of $>3.0 \times 10^9$ rads in deionized water. Those irradiated in air showed a tolerance of $>1.0 \times 10^9$ rads; 16 were still satisfactory at 1.0×10^{10} rads, and another 33 have the potential of resisting 1.0×10^{10} rads (see Table 16.1). Each coating system tested is exposed until failure occurs or until a cumulative exposure of 1.0×10^{10} rads has been received. The tests are conducted at

Table 16.1. Gamma radiation resistance of several protective coatings

Radiation source: ^{60}Co with an intensity of 6×10^5 R/hr
Temperature: 40 to 50°C

Coating	Type	Manufacturer[a]	Substrate	Exposure[b] in Demineralized Water		Exposure in Air[b]	
				Dose (rads)	Effect[c]	Dose (rads)	Effect[c]
Q-Kote	Phenolic	1	Steel	3.4×10^9	A	1.0×10^{10}	B
Epoxy-Polyamide	Epoxy[d]	1	Steel	7.0×10^{9e}	C	1.0×10^{10}	B
			Concrete	3.4×10^9	C	1.0×10^{10}	C
Chem-Thane	Urethane	1	Steel	7.8×10^{9e}	C	1.0×10^{10}	B
			Concrete	1.0×10^{10}	C	1.0×10^{10}	B
Silicone-Alkyd	Alkyd		Concrete	1.0×10^8	D	1.0×10^{10}	B
68-139A (Epolon AE-7/Epolon Multi-Mil)	Epoxy	2	Concrete	1.5×10^9	A,E	1.0×10^{10}	B
68-139B (Vinyloid AE-98/Epolon Multi-Mil)	Vinyl	2	Concrete	2.0×10^9	C,D	1.0×10^{10}	B
68-139C (AE 14-69/Epolon)	Polyurethane	2	Concrete	5.1×10^9	C	$>7.9 \times 10^9$	
68-139D (AE 15-69/Epolon)	Polyester	2	Concrete	1.0×10^9	A,E	$>7.9 \times 10^9$	
Dur-A-Poxy No. 200	Epoxy	3	Steel	1.0×10^9	D	1.0×10^{10}	B
			Concrete	$>6.8 \times 10^9$		1.0×10^{10}	B
System-A (Engard Epoxy No. 437)	Epoxy	4	Steel	1.9×10^9	A,E	$>7.9 \times 10^9$	
System-D (Engard Epoxy No. 437)	Epoxy	4	Concrete	1.0×10^9	D	$>6.8 \times 10^9$	
System-B (Engard Epoxy No. 475)	Epoxy	4	Steel	2.9×10^9	D	$>7.9 \times 10^9$	
System-E (Engard Epoxy No. 475)	Epoxy	4	Concrete	2.5×10^9	E	$>6.9 \times 10^9$	
System-C (Engard Epoxy No. 480)	Epoxy	4	Steel	5.3×10^9	E	$>7.9 \times 10^9$	
System-F (Engard Epoxy No. 480)	Epoxy	4	Concrete	2.5×10^9	D	$>6.9 \times 10^9$	
Epoxy-Phenolic (Rust-Ban EP6846/EP6841)	Modified phenolic	5	Steel	4.5×10^9	C	1.0×10^{10}	B
			Concrete	3.3×10^9	C,D	1.0×10^{10}	B
Epoxy-Polyamide (Rust-Ban EX6671/EX6664)	Epoxy[d]	5	Steel	4.5×10^9	C	1.0×10^{10}	B,E
			Concrete	4.1×10^9	E	1.0×10^{10}	B
Epoxy-Polyamide (Rust-Ban EX6671/EX6664 and No. 191)	Epoxy[d]	5	Steel	4.9×10^9	D	1.0×10^{10}	B,E
No. 1 (Vinyl Y-5280/Y-5296, Y-5295, Y-5290)	Vinyl	6	Steel	4.8×10^8	D	4.0×10^9	E,F
No. 2 (Nu-Pon Y-5240, Y-5242/Glid-Zinc 103)	Epoxy	6	Steel	1.2×10^9	D	1.0×10^{10}	B
No. 3 (Nu-Pon Y-5240, Y-5242/EGL-69722)	Epoxy	6	Steel	4.8×10^9	A	1.0×10^{10}	B
No. 4 (Nu-Pon Y-5240, Y-5242/Chromate Primer)	Epoxy	6	Steel	1.2×10^9	D	1.0×10^{10}	B
No. 5 (Glid-Tile Y-5596/Nu-Pon Cote Y-5240)	Epoxy	6	Steel	4.8×10^8	D	1.0×10^{10}	B
No. 6 (Nu-Pon Y-5240, Y-5242/Nu-Pon Mastic Y-5256)	Epoxy	6	Steel	1.0×10^{10}	B	1.0×10^9	B
Nu-Pon Y-5240, Y-5242/Glid-Tile, Y-5512	Epoxy	6	Concrete	1.9×10^9	A,E	$>5.9 \times 10^9$	
Nu-Pon Y-5240, Y-5242/Nu-Pon Y-5256, Y-5257	Epoxy	6	Concrete	1.4×10^9	A,E	$>6.8 \times 10^9$	
Glid-Tile, Y-5597, Y-5596/Glid-Tile Y-5512	Epoxy	6	Concrete	8.6×10^8	A,F	$>7.4 \times 10^9$	
Water reducible enamel ELG-68144, ELG-68146 ELG-68145, ELG-68146 primer	Epoxy[f]	6	Concrete	5.0×10^8	D	2.4×10^9	D
Vinyl Y-5280/Y-5285/Y-5283	Vinyl	6	Concrete	3.6×10^8	D	4.4×10^9	A,F
Glamorglaze	Epoxy	7	Steel	2.4×10^9	E	$>6.8 \times 10^9$	
			Concrete	5.0×10^9	D	3.8×10^9	A,F
No. 200/No. 654 primer	Epoxy	7	Steel	2.4×10^9	E	$>6.8 \times 10^9$	
			Concrete	5.0×10^8	D	3.4×10^9	A,E,F
No. 201/NO. 654 primer	Epoxy	7	Steel	3.6×10^8	D	$>6.8 \times 10^9$	
No. 201/Acrylic Surfacer	Epoxy	7	Concrete	5.0×10^8	D	2.0×10^9	C
Vinyl No. 403/400/No. 25 primer	Vinyl	7	Steel	3.6×10^8	D	3.9×10^{9e}	A,F
	Vinyl	7	Concrete	5.0×10^8	D	2.5×10^{9e}	A,F
Bitumastic No. 300-M	Epoxy (coal tar)	7	Steel	5.4×10^9	B,D	$>6.8 \times 10^9$	
		7	Concrete	1.0×10^9	F	2.9×10^9	A,E,F
No. 800/810Torex/820 primer	Chlorinated rubber	7	Steel	3.6×10^8	D	$>6.8 \times 10^9$	
		7	Concrete	5.0×10^8	D,F	1.5×10^9	A,F
Organic zinc W/Phenoxy resin	Organic zinc	7	Steel	3.9×10^9	D	2.7×10^9	G
System-A (91-W-9/98-W-9)	Epoxy[f]	8	Steel	1.0×10^9	E	$>1.5 \times 10^9$	
System-3	Epoxy[f]	8	Concrete	1.7×10^9	E	$>1.5 \times 10^9$	
System X	Epoxy	8	Concrete	1.7×10^9	E	$>1.5 \times 10^9$	
System Y	Epoxy	8	Steel	1.0×10^9	E	$>1.5 \times 10^9$	
Sample-A	Polyester	9	Concrete	2.0×10^9	E	$>2.8 \times 10^9$	
Sample-B	Polyester	9	Concrete	2.0×10^9	E	$>2.8 \times 10^9$	
Sample-C	Polyester	9	Concrete	2.0×10^9	E	$>2.8 \times 10^9$	
Sample-1	Polyester	9	Steel			$>2.8 \times 10^9$	
Sample-2	Polyester	9	Steel			$>2.8 \times 10^9$	
Sample-3	Polyester	9	Steel			$>2.8 \times 10^9$	
Series-1 (DD-82/DD-82 primer)	Polyurethane	10	Concrete	2.3×10^9	D,F	$>8.9 \times 10^9$	
Series-2 (DD-82/DD-81 primer)	Polyurethane	10	1-Concrete	1.0×10^8	D,E	$>8.9 \times 10^9$	
			2-Concrete	2.3×10^9	D		
Series-3 (100% solids epoxy)	Epoxy	10	Concrete	1.0×10^8	E,F	$>8.9 \times 10^9$	
Series-4 (DD-82/HB epoxy primer)	Polyurethane	10	1-Concrete	6.0×10^9	D		
			2-Concrete	3.5×10^8	E,F	$>8.9 \times 10^9$	
System-7 (No. 520/Epoxy Primastic and ZP-200)	Epoxy	10	Concrete	6.0×10^9	D	$>7.9 \times 10^9$	
Plasite No. C-725	Epoxy	11	Steel	2.2×10^9	C	$>3.7 \times 10^9$	
Plasite No. 717	Epoxy	11	Steel	9.0×10^8	D	$>3.7 \times 10^9$	

[a]Manufacturer: (1) Chemline Div., Dixie Paint and Varnish Co., Inc.; (2) Con-Lux Paint Products, Inc.; (3) Dur-A-Flex, Inc., (4) Engard Coatings, Corp.; (5) Enjay Chemical Co.; (6) Glidden-Durkee Div. of SCM Corp.; (7) Koppers Co., Inc.; (8) Mobil Chemical Co.; (9) Farbenfabriken Bayer AG, Leverkusen, Germany; (10) Prufcoat Div., Grow Chem. Coatings Corp.; (11) Wisconsin Protective Coating Co.

[b]The coatings were inspected for radiation damage at various exposure levels ($\sim 1.0 \times 10^8$, 3.0×10^8, and each additional 5.0×10^8 rads exposure thereafter). The values listed represent the cumulative dose that had been received at the time adverse effects were observed. If no effects are entered and the cumulative dose is less than 1.0×10^{10} rads, the exposure test is continuing.

[c]Radiation effects: A, embrittlement; B, discolored and hardened; C, checking (surface cracking); D, blistered; E, chalked; F, loss of adhesion; G, "sweating".

[d]Polyamide-cured epoxy. (Cure unkown for other epoxies listed.)

[e]Earlier failure not detected. Appearance indicates that resistance is less than that given.

[f]Water-based epoxy.

temperatures ranging from 40 to 50°C in a ^{60}Co source having an average intensity of 6.0×10^5 R/hr.

16.3 RESOURCE STUDIES

The Chemical Technology Division continued to contribute to the Laboratory's interdivisional efforts on resource and energy analyses under the ORNL – National Science Foundation Environmental Program. Because the program sponsorship has shifted in the past year from the now defunct Office of Interdisciplinary Research Relevant to Problems of Society (IRRPOS) to the new Office of Research Applied to National Needs (RANN), the ORNL program has become increasingly oriented toward research and development. During the past year, H. E. Goeller and W. E. Clark worked full time and part time, respectively, on the program; M. E. Whatley served in an advisory capacity.

Studies on mercury pollution and its control were continued under W. E. Clark. The following three activities were pursued: (1) A review of the mercury recycle industry, which included the issuance of questionnaires to various companies in the business and an evaluation of returned queries. (2) A study of mercury flow at ORNL, aimed at improving recycle and minimizing losses to the environment. This effort is presently being extended to include a survey of mercury handling at other governmental installations and laboratories under the premise that it will be easier to convince industry to tighten mercury controls if the government leads the way. (3) Development of a mathematical model of the flow of mercury in the United States, including the economics of such flow. The model has been tested against past experience in order to develop a predictive model. M. R. Patterson of the ORNL Mathematics Panel has done most of this work.

In June 1971, H. E. Goeller and R. I. Van Hook (Environmental Science Division) attended a two-week Institute of Ecology (TIE) workshop funded by the National Science Foundation and held at the University of Wisconsin, Madison, to study worldwide ecological problems in preparation for the U.N. Conference on the Human Environment to be held in Stockholm in June 1972. Both of the ORNL attendees at the workshop contributed to the work on environmental effects of toxic materials; in addition, Goeller assisted in studies on the phosphorus biocycle. The results of the Madison workshop have been published by The Institute of Ecology in a book entitled "Man in the Living Environment."

In July 1971, H. E. Goeller became a member of Panel II of the Committee on the Study of Materials Science and Technology (COSMAT) sponsored jointly by NAS-NAE. The Committee was set up to make a critical study of materials science and engineering (MSE) as a discrete scientific discipline (as opposed to the separate fields of metallurgy, ceramics, petrochemicals, etc.); to review its past modus operandi and accomplishments; and to assess its future role in the scientific and engineering community. Goeller contributed the section on material resources, and opportunities for substitution and recycle. COSMAT will summarize its findings in a book, which is now in preparation and due to be issued by the end of this calendar year.

The major effort on resource analysis during the past year was the preparation of an interdisciplinary study of cadmium; this work is summarized in ORNL-NSF-EP-21, *Cadmium, the Dissipated Element.* The report attempts to cover all aspects of the cadmium pollution problem and to make recommendations for both research and development and legislative action for safeguarding the public from overexposure to this metal. The interdisciplinary study included consideration of the chemistry and physics of cadmium, past and future supply and demand, ecological and epidemiological effects, economics, and present legal aspects of control. Because cadmium is a by-product of zinc, the report also contains a considerable amount of material on zinc.

Work on "A Mineral Resource Primer," was continued. The primer is being written in a nontechnical form to provide a comprehensive review of nonrenewable resources and possibilities for substitution and recycle, for administrators and the general public. A paper entitled "The Ultimate Mineral Resource Situation" was prepared and presented at (1) the local A.I.Ch.E. fall symposium in September 1971, and (2) the Southeastern Regional meeting of the American Society for Engineering Education (ASEE) at the University of Tennessee in April 1972.

16.4 ENVIRONMENTAL IMPACT OF NUCLEAR POWER REACTORS AND CHEMICAL REPROCESSING PLANTS

The AEC is now required to examine the impact on the environment that will be caused by nuclear power reactors and chemical reprocessing plants. As a result of the July 23, 1971, "Calvert Cliffs" decision of Judge Skelly Wright, of the U.S. Court of Appeals for the

District of Columbia, these AEC environmental impact statements must (1) include evaluations of thermal, mechanical, and radiological effects; (2) consider alternatives to the use of nuclear power; (3) state the relationship between short-term uses of the environment and enhancement of long-term productivity; and (4) summarize the benefits vs the adverse effects. All the conclusions must be reached by evaluations made independently and must not be based on arguments by applicants for AEC licenses. The requirement to prepare such complex and detailed statements as an essential part of the reactor licensing procedure has created a critical situation.

The AEC has asked ORNL, ANL, and PNL (Pacific Northwest Laboratory) to assist in the preparation of the required environmental impact statements for about 100 nuclear power plants as quickly as possible. In addition to preparing initial drafts of about one-third of the impact statements, ORNL has been assigned three other tasks (described below): the "Source Term" Project, the Radiological Impact Project, and the Generic Reports Project. The Chemical Technology Division is actively participating in all phases of this work, supplying 21 people on a full- or part-time basis.

"Source term" project. The objective of this project is to supply the radiological source terms on which the environmental impact studies are based. The source terms are the concentrations and total annual amounts of radioactive isotopes in the gaseous and liquid wastes discharged to the environment. The work consists of making an engineering evaluation of the treatment systems for radioactive liquid and gaseous wastes at every nuclear power station applying for an operating license. The descriptions of the systems and the derived source terms are sent to the AEC in Washington for review before being passed on to the Environmental Impact Task Group for that particular reactor at one of the national laboratories. To date, 37 reactors have been evaluated.

Radiological impact project. A report entitled "Radiological Impact Study – Part 1: Cost of Radioactive Waste Treatment at Light Water Nuclear Power Reactors" was prepared to assist the AEC in quantifying the term "as low as practicable." This term is used in the Code of Federal Regulations – 10 CFR 50 and in a proposed amendment to 10 CFR 50, that is, Appendix I. The objective of the study was to determine the dollar cost required to reduce the radioactivity released in a series of cases ranging from relatively high release levels, using minimal waste treatment systems, to very low levels, using advanced, complex treatment systems. The most complex systems illustrate very low but not "zero" release of radionuclides in the liquid and gaseous effluents. Six conceptual cases for gaseous wastes and four for liquid wastes were studied for pressurized water reactors; similar cases were studied for boiling water reactors.

Generic reports project. Generic reports are being prepared on unit operations such as ion exchange, filtration of liquids, and concentration of wastes by evaporation in order to accumulate and document the latest information on the treatment of radioactive wastes at nuclear power plants. In addition, a report is being prepared that describes a computer code for calculating the concentrations of radionuclides in the primary coolant and various waste streams of both pressurized and boiling water reactors. The code uses current best estimates of such parameters as percentage of failed fuel, leak rate from primary to secondary coolant in steam generators, decontamination factors for treatment devices, partition factors for gaseous radionuclides, etc. Reports are also being prepared on the chemical and ecological effects of chlorine and other chemicals used in cooling towers.

Publications, Speeches, and Seminars

BIOCHEMICAL TECHNOLOGY

Burtis,[1] C. A., W. F. Johnson,[2] J. E. Attrill,[3] C. D. Scott, N. Cho,[1] and N. G. Anderson,[1] "Increased Rate of Analysis by Use of a 42-Cuvet GeMSAEC Fast Analyzer," *Clin. Chem.* **17**(8), 686–95 (1971).

Burtis,[1] C. A., W. F. Johnson,[2] C. D. Scott, and N. G. Anderson,[1] "Increase in the Rate of Sample Throughput by Use of a 42-Cuvet GeMSAEC Fast Analyzer," presented at the 23rd National Meeting of the American Association of Clinical Chemists, Seattle, Wash., Aug. 8–13, 1971.

Burtis,[1] C. A., W. F. Johnson,[2] C. D. Scott, J. E. Attrill,[3] and N. G. Anderson,[1] "Increase in the Rate of Sample Throughput by Use of a 42-Cuvette GeMSAEC Fast Analyzer," presented at the Spring Meeting, Southeast Section of the American Association of Clinical Chemists, Gatlinburg, Tenn., Apr. 23–24, 1971.

Burtis,[1] C. A., J. C. Mailen, W. F. Johnson,[2] C. D. Scott, and T. O. Tiffany,[1] "Miniaturization of a Fast Analyzer," presented at the Fourth Annual Symposium on Advanced Analytical Methods for the Clinical Laboratory, ORNL, Mar. 9–10, 1972.

Butts,[4] W. C., J. E. Mrochek, and D. S. Young,[5] "The Influence of Certain Components of a Chemically Defined Diet on Urinary Excretion of Ultraviolet-Absorbing Compounds," *Clin. Chem.* **17**, 956 (1971).

Chilcote, D. D., and J. E. Mrochek, "The Separation of Indole Compounds of Physiologic Interest by Liquid Chromatography," presented at the Fifteenth Conference on Analytical Chemistry in Nuclear Technology, Oak Ridge, Tenn., Oct. 12–14, 1971.

Chilcote, D. D., and J. E. Mrochek, "The Separation of Indole Compounds of Physiologic Interest by Liquid Chromatography," presented at the Fourth Annual Symposium on Advanced Analytical Methods for the Clinical Laboratory, ORNL, Mar. 9–10, 1972.

Chilcote, D. D., and J. E. Mrochek, "Use of Automatic Digital Data Acquisition and On-Line Computer Analysis in High-Resolution Liquid Chromatography," *Clin. Chem.* **17**(8), 751–56 (1971).

Chilcote, D. D., and C. D. Scott, "Use of a Small, Dedicated Computer with a High-Resolution Liquid Chromatograph," *Chem. Instrum.* **3**(2), 113–24 (1971).

Egan, B. Z., J. E. Caton,[3] and A. D. Kelmers, "Separation of *E. coli* Ribosomal RNAs by Reversed-Phase Chromatography," *Biochem.* **10**, 1890 (1971).

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1. MAN Program.
2. Instrumentation and Controls Division.
3. Analytical Chemistry Division.
4. University of Washington, Seattle.
5. Clinical Pathology Dept., Clinical Center, NIH, Bethesda, Md.

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SEMINARS

1971

April 23	Preparation of EBR-II Fuel:	
	Sphere-Pac Fuel	W. T. McDuffee
	Pellet Fuel	R. A. Bradley[13]
	Preparation of Argonne Sphere-Pac Fuel	W. T. McDuffee
May 13	Hydrodynamics in Packed Columns During Countercurrent Flow of Fluids Having a Large Density Difference	J. S. Watson
	Induction Heating Studies for Design of a Continuous Fluorinator	J. R. Hightower
November 17	Plutonium Polymer	J. T. Bell
November 24	Lanthanide and Actinide Hydrides and Metallides	J. W. Roddy
December 1	LWBR Support Program: Precipitation, Reduction, and Stabilization Parameters in the Production of $^{233}UO_2$	J. M. Leitnaker[13]
December 8	LWBR Support Program:	
	Flowsheet Development for ^{233}U Purification	R. H. Rainey
	Equipment Design for ^{233}U Purification in Building 3019	F. E. Harrington
December 15	Progress Report on Alpha Liquid Scintillation Counting	W. J. McDowell

1972

January 5	MSBR Metal Transfer Process Studies:	
	Distribution of Li and Bi Between Molten LiCl and Li-Bi Solutions	L. M. Ferris
	Solubilities of Thorium and Rare Earths in Liquid Li-Bi Solutions	F. J. Smith

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January 12	Development of the Metal Transfer Process for MSBR Processing	E. L. Youngblood
January 19	Rapid Ion Exchange Separations	D. O. Campbell
January 26	Precipitation of Protactinium Oxide from MSBR Fuel Salt	O. K. Tallent
February 2	Engineering Studies of Uranium Oxide Precipitation from MSBR Fuel Salt	M. J. Bell
February 9	Studies of the Unusual Oxidation States of Transplutonium Elements	R. D. Baybarz
February 16	LMFBR Fuel Processing: Hot-Cell Studies of Voloxidation and Dissolution	J. H. Goode
February 23	Lanthanide and Actinide Hydroxides	B. Weaver
March 1	LMFBR Fuel Transport: Cask Design Concepts and Status of Development	L. B. Shappert
March 8	Status of the TRU Program	J. E. Bigelow
March 15	HTGR Fuel Preparation:	
	Sol-Gel UO_2 Spheres	B. C. Finney
	Uranium Loading of Resin Beads	K. J. Notz and P. A. Haas
March 29	Analytical Capabilities of the Service Laboratories	W. R. Laing[3] D. A. Costanzo[3]

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