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Argonne National Laboratory

CHEMICAL ENGINEERING DIVISION
RESEARCH HIGHLIGHTS

May 1966-April 1967

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CHEMICAL ENGINEERING DIVISION
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May 1966-April 1967

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I. COMPACT PYROCHEMICAL PROCESSES

Research and development studies have continued on compact pyrochemical processes for the decontamination and recovery of spent reactor fuels. Because radiation-stable liquid metal and salt solvents are used in these processes, they can accommodate short-cooled, high-burnup fuels, thereby permitting rapid recycle of the fuel and a reduction in out-of-reactor inventory costs. Such processes appear to be particularly suited to compact plants located on or near a reactor site.

The concept of an integrated reactor and fuel processing facility (ANL-6766, p. 57) has been demonstrated successfully in Argonne's EBR-II reactor complex in Idaho. The melt refining process (ANL-6875, p. 8; ANL-7020, pp. 11 and 12), which was developed specifically for the enriched uranium alloy core in EBR-II, is currently in routine operation, processing about three 10-kg batches of highly irradiated fuel per week. This fuel is processed after as little as 15 days of cooling, and the reprocessed fuel has been returned to the reactor within 30 days after discharge.

Although the melt refining process is restricted to enriched uranium alloy fuel, it has provided valuable experience in the remote operation of typical pyrochemical process steps.

Development of an auxiliary process for the recovery of uranium from the residue (skull) in melt refining crucibles has been completed. The skull reclamation process and equipment for the recovery and purification of uranium residues in melt refining crucibles were described in the previous Highlights Report (ANL-7175, pp. 10-22). A final series of test runs has been completed (see ANL-7225). The development and satisfactory performance of the reduction furnace and the retorting furnace were achieved. Adaptation of the equipment to fully remote operation and installation in the Fuel Cycle Facility have been postponed.

The present trend in the development of fast breeder reactors is toward ceramic, i.e., oxide or carbide, fuels. The pyrochemical processes currently under development are therefore designed primarily for oxide and carbide fuels, although they can also accept metallic fuels. The use of oxidation-reduction reactions in liquid metal and salt solutions permits a much wider range of separations in the pyrochemical processes currently being developed than those which can be effected by melt refining-type processes.

In the past year, pyrochemical flowsheets incorporating a salt transport process for the separation of plutonium from uranium and fission products have been investigated. Salt transport separations are based upon the selective transfer of solutes between liquid metal solutions that are in contact with the same molten salt. The molten salt, which acts as the solute

carrier, can be cycled batchwise or continuously between the liquid metal solutions. With the proper choice of liquid metal solvents, salt transport processes offer the possibility of simple, efficient decontamination and recovery of uranium-plutonium fuels.

A. Conceptual Flowsheet for Pyrochemical Process for Fast Breeder Reactor Fuels

A conceptual pyrochemical process (Figure I-1) that is currently under investigation employs a salt transport step for the separation of plutonium from uranium and fission products. This process is designed to accommodate discharged core or blanket elements from fast breeder reactors employing oxide or carbide fuels. The same steps are used for core and blanket material, but the required processing rate would be two to three times higher for the blanket than for the core. The flowsheet in Figure I-1 is shown for oxide core or blanket fuel clad in stainless steel; with appropriate modifications, the process is applicable to carbide fuels.

Fig. I-1. Pyrochemical Process for Fast Breeder Reactor Fuels.
(Oxide core or blanket fuel clad in stainless steel)

The decladding step employs selective dissolution of the cladding in liquid zinc, followed by a separation of the oxide fuel from the waste zinc solution.

The oxide mixture from the decladding step is added to a molten NaCl-CaCl₂-MgCl₂ mixture, which is contacted with liquid copper-33 w/o magnesium alloy to reduce the oxides to metallic uranium and plutonium. In this step the alkali, alkaline earth and rare earth fission products, and the solid MgO formed as a by-product of the reduction reaction remain in

the waste salt. Krypton, xenon, and iodine are collected in a small volume of argon used as the cover gas. The uranium, plutonium, and noble and refractory metal fission products appear in the copper-magnesium alloy; the uranium is present as a precipitate and the plutonium is in solution. Two additional stages are incorporated into the reduction step--one in which the waste salt is contacted with the incoming batch of fresh copper-magnesium alloy to recover residual traces of plutonium, and one in which the copper-magnesium alloy product is contacted with the incoming batch of fresh salt for additional fission product removal.

The next step employs a salt transport procedure to separate plutonium from the uranium and fission products in the copper-magnesium alloy. This procedure consists of cycling a molten salt (e.g., 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl , m.p. 396°C) between the copper-magnesium (donor) alloy and a zinc-5 w/o magnesium (acceptor) alloy. Under these conditions plutonium transfers selectively and spontaneously to the zinc-magnesium alloy. The uranium and the fission products in the copper-magnesium alloy do not transfer at an appreciable rate because of the low solubility of uranium in the copper-magnesium alloy (~ 0.005 w/o at 600°C) and the low distribution coefficients of both uranium and the fission products. The plutonium is recovered from the acceptor alloy as a metallic product by vacuum distillation (retorting) to remove the zinc and magnesium.

The precipitated uranium is recovered by decanting the supernatant copper-magnesium alloy which contains most of the fission products and washing the uranium with liquid magnesium to remove residual copper and fission products.¹ The metallic uranium product is retorted to remove the adhering magnesium.

The products of the process are metallic plutonium and uranium which are recovered separately. Uranium is recycled to the blanket; uranium and plutonium are alloyed in the proper proportions for core fuel. In the case of an oxide (PuO_2 - UO_2) fuel, these products would first be converted to PuO_2 and U_3O_8 with oxygen, after which the PuO_2 - U_3O_8 mixture would be subjected to treatment with hydrogen to reduce the U_3O_8 to UO_2 .

To apply the salt transport process to a carbide fuel, the fuel would first be oxidized to produce an oxide feed to the reduction step. The metallic products would be converted to carbides, UC for the blanket and (U,Pu)C for the core, probably by reaction with a methane-hydrogen mixture in a fluid bed (see Sect. III-B-1).

¹Should greater decontamination of the uranium be required, the composition of the Cu-Mg donor alloy can then be changed to increase the uranium solubility so that the uranium can be transferred by means of a salt transport step to a high magnesium-low zinc acceptor alloy. The noble and refractory metal fission products remain behind in the Cu-Mg alloy.

B. Liquid Metal-Molten Salt Extractions

1. Chemical Basis

a. Distribution of Fuel Constituents between Liquid Metals and Molten Salts

Many of the separations in the pyrochemical processes currently under development are effected through differences in the distribution behavior of fuel constituents between liquid metals and molten salts. This technique is employed in the oxide reduction step of the current reference flowsheet (Figure I-1) where a chloride-salt mixture containing MgCl_2 is used to extract the alkali, alkaline earth, and rare earth fission products from plutonium and uranium in a liquid Cu-33 w/o Mg solution. Previously reported data (ANL-7175, pp. 33 and 34) have shown that large differences occur in the distribution coefficients ($K_d = \text{w/o in salt solution} / \text{w/o in metal solution}$) of cerium and plutonium between MgCl_2 and Cu-Mg alloys at 800°C . These data were used in recent work to calculate the number of extraction stages required for a satisfactory separation of rare earth fission products from plutonium and a high recovery of plutonium. The calculations indicate that only three or four stages are needed. Under these conditions, a 99.5% plutonium recovery requires that the plutonium extraction factor² not exceed about 0.07. Since there are practical limits on the salt-to-metal mass ratio that can be used, it is necessary to be able to vary the distribution coefficient; this may be achieved by varying either the MgCl_2 concentration of the salt phase or the magnesium content of the metal phase. However, when the compositions of the salt and metal phases are varied, the effect on the separation factor³ must also be considered.

The dependence of the distribution coefficient and separation factor on the compositions of the salt and metal phases may be derived quantitatively from a consideration of the chemical equilibria involved in these systems. For example, the distribution of plutonium between a molten salt which contains MgCl_2 and a liquid magnesium alloy is governed by the equilibrium reaction

The distribution coefficient of plutonium, D_{Pu} ,⁴ between the molten salt and the liquid alloy is defined by the equation

²To maintain a desired plutonium recovery for a given number of extraction stages, there is a plutonium extraction factor which must not be exceeded. Extraction Factor = SK_d/M , where S = mass of salt, K_d = distribution coefficient (w/o in salt/w/o in metal), and M = mass of metal.

³Separation factor of rare earths (R.E.) from Pu: S.F. = $K_d(\text{R.E.})/K_d(\text{Pu})$.

⁴For theoretical purposes, the distribution coefficient of an element, M , is more conveniently defined as $D = \text{m/o } \text{MCl}_x \text{ in salt solution} / \text{a/o } M \text{ in metal solution}$.

$$D_{\text{Pu}} = \frac{1}{K_a} \cdot \frac{\gamma_{\text{Pu}}}{a_{\text{Mg}}^{3/2}} \cdot \frac{a_{\text{MgCl}_2}^{3/2}}{\gamma_{\text{PuCl}_3}} \quad (2)$$

where $D_{\text{Pu}} = m/\text{o PuCl}_3 \text{ in salt} / a/\text{o Pu in alloy}$, K_a = thermodynamic (activity) equilibrium constant, γ_{Pu} = activity coefficient of Pu in the alloy, a_{Mg} = activity of Mg in the alloy, a_{MgCl_2} = activity of MgCl_2 in the salt, and γ_{PuCl_3} = activity coefficient of PuCl_3 in the salt. Thus, the distribution coefficient is a product of three factors:

- (1) $1/K_a$, which depends on the difference in the standard free energies of formation of MgCl_2 and PuCl_3
 $(-RT \ln K_a = \frac{3}{2} \Delta G_{\text{MgCl}_2}^{\circ} - \Delta G_{\text{PuCl}_3}^{\circ})$,
- (2) $\gamma_{\text{Pu}}/a_{\text{Mg}}^{3/2}$, which depends on the composition of the alloy, and
- (3) $a_{\text{MgCl}_2}^{3/2}/\gamma_{\text{PuCl}_3}$, which depends on the composition of the molten salt.

Because these thermodynamic quantities are temperature dependent, the distribution coefficient will also be temperature dependent.

b. Effect of Salt Composition on Separation Factor

The separation factor for two elements can be expressed, for theoretical purposes, in terms of the activity coefficients and activity equilibrium constants of the two elements. For the separation of cerium from plutonium, for example, the separation factor, Q , is expressed by the equation

$$Q = \frac{K_a (\text{Pu})}{K_a (\text{Ce})} \cdot \frac{\gamma_{\text{Ce}}}{\gamma_{\text{Pu}}} \cdot \frac{\gamma_{\text{PuCl}_3}}{\gamma_{\text{CeCl}_3}} \quad (3)$$

In order to achieve a required plutonium recovery, it may be necessary to use a system in which the plutonium distribution coefficient has a small value. From equation 2 it can be seen that the distribution coefficient can be decreased by lowering the activity of MgCl_2 in the molten salt, i.e., by lowering the concentration of MgCl_2 . However, the separation factor (equation 3) would be influenced by this change in salt composition because of its effect on the ratio of the activity coefficients. The magnitude of this effect was measured in a system of practical interest. Distribution coefficients of cerium, plutonium, and uranium between a molten salt mixture consisting

Fig. I-2. Dependence of Distribution Coefficients of Cerium, Plutonium, and Uranium on $MgCl_2$ Content of Salt in the System $MgCl_2$ - $NaCl$ - $CaCl_2$ / Cu -6.5 w/o Mg at $800^\circ C$

of equimolar $CaCl_2$ - $NaCl$ plus 1 to 100 m/o $MgCl_2$ and a liquid Cu -6.5 w/o Mg alloy⁵ were obtained at $800^\circ C$. The composition of the liquid metal phase was maintained constant.

As the $MgCl_2$ concentration of the salt phase was decreased, the distribution coefficients also decreased. This dependence on the $MgCl_2$ content of the salt phase is expected, since according to equation 2 the distribution coefficient is directly proportional to the three-halves power of the $MgCl_2$ activity in the salt. The $MgCl_2$ activity is the product of its concentration (m/o) and its activity coefficient in the molten salt. Consequently, the quantity $D/X_{MgCl_2}^{3/2}$ might be expected to depend far less on the $MgCl_2$ content of the salt than does D . This is seen in Figure I-2 where, based on the data obtained in the above experiment, $D/X_{MgCl_2}^{3/2}$ is plotted as a function of X_{MgCl_2} . Within the experimental scatter of the data it is found that the quantity $D/X_{MgCl_2}^{3/2}$ is constant for each of the three elements studied.

Therefore, since the separation factor is the ratio of two distribution coefficients, it is also independent of the $MgCl_2$ concentration in the salt phase. Thus, the results of this experiment indicate that the $MgCl_2$ content of the

salt phase may be adjusted to an appropriate value to obtain a particular distribution coefficient for plutonium without markedly affecting the separation factor.

c. Effect of Liquid Alloy Composition on Separation Factor

The alloy composition affects the separation factor through its influence on the ratio of the activity coefficients of the elements in the liquid alloy, as indicated in equation 3. Since this ratio varies widely as the composition of the liquid alloy is changed, many experimental data have

⁵Although a Cu -6.5 w/o Mg alloy is not employed in the reference flowsheet (Figure I-1), it has a potential application as a donor solvent in the purification of uranium by a salt transport procedure.

Fig. I-3. Praseodymium-Plutonium Separation Factors for Systems Using 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl Salt and Binary Magnesium Alloys at 600 and 800°C

been obtained on the effect of alloy composition on distribution coefficients. The separation factor was found to depend on the magnesium content of the liquid alloy, the metal(s) used to dilute the magnesium, and the temperature. The effects of these three factors are illustrated in Figure I-3, where the Pr/Pu separation factor is shown as a function of the magnesium content of the alloy phase for binary alloys of magnesium with copper, zinc, and cadmium at 600°C. The effect of temperature may be seen by comparing the curves for the Pr/Pu separation factor in the binary Cu-Mg system at 600° and 800°C. In all cases the salt phase was the ternary mixture 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl .

The experimental results shown in Figure I-3 for the variation of the separation factor of praseodymium from plutonium with magnesium content are in qualitative agreement with the predictions which may be made from the activity coefficients of praseodymium and plutonium in the four pure solvents, i.e., liquid magnesium, copper, zinc, and cadmium. Thus, the activity coefficient ratio $\gamma_{\text{Pr}}/\gamma_{\text{Pu}}$ at 600°C has the value 3.5×10^{-4} in liquid (supercooled) magnesium, 5.7×10^{-4} in liquid cadmium, 1.2×10^{-3} in liquid zinc, and approximately 1.7×10^{-2} in liquid (supercooled) copper. These values indicate that the separation factors in the pure metals should differ by the following factors: ~1.6 for magnesium and cadmium, ~3.4 for magnesium and zinc, and ~490 for magnesium and copper. These predicted values compare well with experimental values of about 1, 4, and 500 estimated by extrapolation of the data of Figure I-3.

2. Engineering Studies

a. Liquid Metal-Molten Salt Extractions

Investigations are being made of equipment and procedures for liquid metal-molten salt extractions in stirred vessels and in counter-current columns. Most of the development work has been on stirred vessels and associated equipment for batch processing and has been related to the EBR-II skull reclamation process (ANL-7175, p. 10) and the salt transport separation technique. Batch processing techniques are necessary where the materials of construction are difficult to fabricate and are advantageous

where few processing steps are required. On the other hand, continuous processing may prove advantageous for large-scale plants expected in the future. Continuous equipment generally needs less space, offers higher throughputs, and requires fewer manipulations than batch equipment.

An experimental program has been initiated for the systematic study of the kinetics of liquid metal-molten salt reductions and extractions in stirred vessels. This program will supplement the experience gained in the pilot-plant developmental experiments discussed in a later section (I-C-2) of this report. The objective of this work is to identify the mechanism of solute transfer.

Another small experimental effort has been maintained on the development of equipment and techniques for continuous pyrochemical processes (ANL-7175, pp. 34 and 35). This work has centered around the operation of a countercurrent, packed column at 500-600°C for the extraction of cerium between a Cd-Zn-Mg alloy and a MgCl_2 -NaCl-KCl salt. In preliminary experiments using unsteady-state techniques, the extraction rates were reasonably high and corresponded to a theoretical stage height of about 15 in. (ANL-7175, p. 35). This program includes some work on the development of pumps, valves, instrumentation, and other equipment necessary for continuous and semi-continuous operations.

A low-temperature column (Figure I-4), operated at 85 to 90°C with Wood's metal (m.p. 71°C) and water as the two phases, has been employed to assist in the design and operation of a high-temperature column and to provide basic information on the behavior of liquid-liquid systems that have a large density difference and a high interfacial tension. The pressure drop of the continuous phase (water) through the packed section and the limiting flow rates were determined in order to establish operating conditions for the high-temperature column. Present correlations of limiting flows, which are in agreement when applied to ordinary liquid systems, diverge when extrapolated to metal-water and metal-salt systems. It is hoped that a more general flooding correlation that is applicable to a wider range of fluid properties can be developed.

Measurements of the amount of discontinuous phase (metal) present in the column have been made by rapidly freezing the metal in the column. The fraction of the column void volume filled with metal was about 0.15 to 0.35; these values were dependent on the metal flow rate but almost independent of the water flow rate. The metal in the column appeared to collect in pools which grew to a critical size and then broke into small drops. Both the pools and the drops seemed to be in violent agitation. It is believed that the same flow pattern will exist in liquid metal-salt systems and the violent agitation and the re-formation of the drops will promote rapid mass transfer.

Fig. I-4. Apparatus for Studying the Hydrodynamic Behavior of Liquid Metal-Molten Salt Systems. To simulate such systems, water (continuous phase) and Wood's metal alloy (discontinuous phase; m.p. 71°C) are being used. The column, fabricated of glass pipe, was packed with $3/16$ -in. perforated metal saddles to a nominal height of 24 in.

b. Component Testing

Continuous extraction processes require equipment items such as pumps, valves, and devices to measure flow rate, pressure, and liquid level. To test some of these items, a component test loop was constructed and operated with a chloride salt mixture (50 m/o MgCl -30 m/o NaCl -20 m/o KCl) as the circulated fluid (ANL-7175, p. 40). The loop consisted of a centrifugal pump (obtained from Oak Ridge National Laboratory), a pressure sensor to measure the discharge pressure of the pump, a bellows-sealed valve to throttle the salt flow, an orifice flow meter to measure the flow rate, and a freeze valve to hold the salt in the loop. Except for the pump, which was made of INOR-8,⁶ the loop was made of type 304 stainless steel.

⁶INOR-8 is a nickel alloy containing 17 w/o Mo, 7 w/o Cr, and 5 w/o Fe.

The loop has been operated for a total of 1000 hours: 150 hr at 515°C, 550 hr at 550°C, and 300 hr at 600°C. The average flow rate of salt was 1 gpm, but flow rates up to 3 gpm were reached. The loop and its components performed satisfactorily. The salt in the loop was found to contain only small amounts of corrosion products (iron, nickel and chromium) and contaminants (oxygen and carbon).

C. Salt Transport Separations Process

1. Chemistry of Salt Transport Separations

The salt transport technique is based upon the selective transfer of solutes between two liquid metal alloy solutions (designated as the donor alloy and the acceptor alloy) that are in contact with the same molten salt. In the liquid metal-molten salt systems proposed for process use, all of the alloys contain the same reducing agent (Mg) and the salt phase contains the complementary oxidizing agent (MgCl_2). Initially, the donor alloy contains the metal to be purified as well as impurity metals (e.g., fission products). Generally, this alloy will also contain one or more solvent metals that are poorer reducing agents than magnesium. These solvent metals are used to adjust the thermodynamic activities of the metal to be purified, the impurity metals, and magnesium in the donor alloy. Initially, the acceptor alloy will contain magnesium and one or more solvent metals; the solvent metals are used to adjust the activities of magnesium and other solute metals in the acceptor alloy. Separation of the product metal from impurities can be achieved in two ways. In the first method, the product metal is transported to an acceptor alloy and the impurities are left behind in the donor alloy. In the other, the impurities are transported to an acceptor alloy and the product metal remains in the donor alloy. When two product metals, for example plutonium and uranium, are to be purified and separated, a proper choice of acceptor alloy compositions makes it possible to transport one of the product metals to one acceptor alloy and the other product metal to another acceptor alloy and to leave the impurities behind in the donor alloy.

In the salt transport process, a solute metal is transferred from a donor alloy to an acceptor alloy through a sequence of oxidation-reduction reactions. Thus, at the interface of the donor alloy and salt phase, the metal (e.g., plutonium) in the donor alloy dissolves in the salt phase:

The PuCl_3 -rich salt is then transferred from the region of the donor alloy to the region of the acceptor alloy where the PuCl_3 is reduced:

The overall reaction for the salt transport process is therefore:

When the transport is complete, the free energy change of reaction 6 will be zero, whence

$$\Delta G(\text{salt transport}) = 0 = \bar{G}_{\text{Pu(a)}} + 3/2 \bar{G}_{\text{Mg(d)}} - \bar{G}_{\text{Pu(d)}} - 3/2 \bar{G}_{\text{Mg(a)}} \quad (7)$$

where $\bar{G}$ refers to the partial molar free energies in the liquid donor, (d), or acceptor, (a), alloys. Thus, the salt transport will tend to make the values of the quantity $\bar{G}_{\text{Pu}} - 3/2 \bar{G}_{\text{Mg}}$ the same in each alloy. When the transfer is complete, the ratio of the atom fractions, x , of the solute in solution in each alloy is therefore expressed by the equation:

$$\frac{x_{\text{Pu(a)}}}{x_{\text{Pu(d)}}} = \frac{\gamma_{\text{Pu(d)}}}{\gamma_{\text{Pu(a)}}} \cdot \left[\frac{a_{\text{Mg(a)}}}{a_{\text{Mg(d)}}} \right]^{3/2} \quad (8)$$

By an appropriate choice of donor and acceptor alloy compositions, the thermodynamic properties of the solutes in the alloys can be fixed to provide the desired separations through selective transport of the various solutes.

When the transport step is complete, the concentration of the solute in the salt over the donor and acceptor alloys is the same; therefore, the ratio of the contents of the two alloys may be represented by

$$\frac{\text{w/o Pu in solution in acceptor alloy}}{\text{w/o Pu in solution in donor alloy}} = \frac{K_{\text{Pu(a)}}}{K_{\text{Pu(d)}}} \quad (9)$$

where $K_{\text{Pu(a)}}$ and $K_{\text{Pu(d)}}$ are the distribution coefficients of plutonium between the salt phase and acceptor alloy and the salt phase and donor alloy, respectively.

The above discussion is based upon equilibrium considerations only, as represented by equations 8 and 9. In the practical case, the rate of transfer of a solute may be very low if it has a low extraction factor or a low solubility in the donor alloy. These effects are sufficiently pronounced for the noble and refractory metal fission products and for other impurities (e.g., copper) that these materials do not undergo significant transfer from the donor alloy and can thereby be separated from plutonium or uranium.

During the past year, chemical studies in support of the salt transport purification and separations of plutonium and uranium have been

conducted. Solubility measurements were obtained for the following liquid alloy systems: (1) plutonium, uranium, zirconium, cerium, niobium, and molybdenum in Cu-Mg alloys that were being considered as donor alloys, (2) plutonium and uranium in Zn-Mg alloys that were being considered as acceptor alloys, and (3) plutonium, uranium, and cerium in Mg-Zn-Cd alloys that were also being considered as acceptor alloys. Distribution coefficients were determined for the following liquid metal-molten salt systems: (1) plutonium and uranium between representative salt mixtures and Cu-Mg or Zn-Mg alloys, (2) plutonium, uranium, and cerium between Mg-Zn-Cd alloys and 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl , and (3) neptunium between liquid metal and molten salt systems tentatively chosen for the reference flowsheet (Figure I-1) to aid in the determination of the path that neptunium will follow in the process. Liquid copper-cadmium-magnesium alloys were also investigated as potential donor alloys.

Laboratory-scale experiments related to salt transport separations have been carried out. In one of these experiments conducted at 600°C , plutonium was selectively transferred from a liquid Cu-33 w/o Mg donor alloy containing a U-20 w/o Pu alloy through a molten 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl salt to a liquid Zn-10 w/o Mg alloy. The combined uranium-plutonium content of the donor alloy amounted to about 20 w/o. At the temperature of the experiment, uranium is very insoluble in the donor alloy whereas plutonium is soluble. The measured final concentrations of plutonium in solution in the donor and acceptor alloys and the transport salt were in excellent agreement with calculated concentration values based on experimentally determined distribution coefficients and solubilities in the metal phase. At the end of the experiment, 99.5% of the plutonium charged to the donor alloy had transported to the acceptor alloy whereas only 1.9% of the uranium charged had transported. Since the initial Pu/U ratio in the donor alloy was 0.25 and the final ratio in the plutonium-rich acceptor alloy was 13.3, a satisfactory concentration of plutonium relative to uranium was obtained.

2. Engineering Studies of Salt Transport Separations

Recently completed experiments on the engineering development of salt transport separations have been of an exploratory nature and have had the following objectives: (1) to demonstrate the engineering feasibility of salt transport separations, (2) to provide a basis for the further development of equipment and techniques, and (3) to determine the fission product decontamination obtainable by this method.

All experiments (five in the series) were conducted in pilot-plant equipment originally used in the studies of the EBR-II skull reclamation process (ANL-6875, p. 20). Since this facility was not designed for experimentation with plutonium, the experiments were restricted to the study of uranium transport. A schematic diagram of the equipment is given in Figure I-5.

Fig. I-5. Schematic Diagram of Salt Transport Equipment

charge of liquid MgCl_2 . Prior to each salt transfer, the salt and metal phases were mixed for 4 to 5 min to promote chemical equilibration and allowed to separate by settling for 5 to 10 min. After the uranium transfer to the acceptor alloy was about 99% complete, the supernatant acceptor alloy was separated from the precipitated uranium, and the uranium product was washed with Mg-30 w/o Zn for additional removal of soluble noble and refractory metals. Following separation of the wash solution, the uranium product was dissolved in a Zn-13 w/o Mg solution which was then retorted to evaporate the zinc and magnesium for recovery of the uranium.

The results of the last experiment (run USTP-5) are given in Figure I-6, in which the uranium recovery is shown as a function of the number of cycles completed. The uranium transferred at a constant rate until the fifth cycle when the last of the uranium precipitate in the Cu-Mg alloy had dissolved. The transfer rate then decreased steadily, and a uranium recovery of about 99% (process objective) was achieved after a total of 27 cycles. A similar behavior had been observed in the preceding four runs. Considerably fewer cycles would be required in a full-scale processing plant, since most of the uranium transfer would occur at the maximum possible rate and

Fig. I-6. Rate of Uranium Recovery in Salt Transport Experiment USTP-5

System: Cu-Mg/ MgCl_2 /Zn-Mg
 Donor Alloy: Cu-5 w/o Mg
 Acceptor Alloy: Mg-35 w/o Zn
 Salt: 100% MgCl_2

the diminishing rate period would be minimized. The overall removals of fission product elements were as follows: zirconium, 99.7%; molybdenum, 99.9%; palladium, 99.99%; ruthenium, 99.99%; and niobium, 99.9999%.

The small volumes (~20 liters) of the tungsten crucibles used limited the rate of uranium transport. If 100-liter vessels were to be used, 99% of a 10-kg charge of uranium could be transported in less than 10 cycles, which would require a period of less than 4 hr. Calculated uranium transfer rates (for a saturated donor alloy) as functions of solution volume and cycle frequency for the batch transfer method are shown in Figure I-7. Figure I-8 gives theoretical uranium transfer rates as functions of solution volume and salt circulation rate (based on the available kinetic data) for the case of continuous salt circulation between two liquid metal alloys (assuming vigorous mixing of the salt with each alloy). In this case, the transfer rates are higher than those calculated for equivalent batch-contact systems.

Since these experiments have successfully demonstrated the feasibility of salt transport separations on a pilot-plant scale, equipment has been constructed for a series of plutonium transport experiments using the batch-transfer method (Figure I-9). Other steps in the reference flow-sheet (Figure I-1) will also be tested in this equipment. These will include oxide reduction, uranium purification and product recovery, and plutonium product retorting. Preliminary testing of the equipment (without plutonium) is under way.

Fig. I-7. Calculated Rates of Uranium Transfer for Batch Transfer System

Fig. I-8

Calculated Rates of Uranium Transfer
for Continuous Salt Transport Systems

Fig. I-9. Equipment for Testing Salt Transport Process. Experiments with up to 100-gram quantities of unirradiated plutonium can be conducted in this equipment, which is housed in a hood (not shown). The two resistance-heated reaction vessels are interconnected by a heated transfer line to permit movement of process solvents between vessels.

Fig. I-10. Calculated Rates of Plutonium Transport for Batch-transfer Systems. Calculations are based on the following:

- 99% completion of donor equilibrations
- 99% completion of acceptor equilibrations
- 90% salt transfer efficiency

In the current reference flowsheet (Figure I-1), the plutonium donor alloy is Cu-33 w/o Mg at 600°C. Since all of the plutonium is assumed to be in solution in the donor alloy prior to the transport step, no constant rate period (as observed in the uranium experiments) will be encountered, and the plutonium transport rate will be primarily dependent on the distribution coefficient and the salt/metal ratio in the donor system. This can be seen in Figure I-10 where theoretical plutonium recoveries for batch contacts are shown as functions of the number of cycles and the salt/metal weight ratio for the case of 90% salt transfer efficiency and 99% completion of the equilibration reactions. As indicated, plutonium recoveries exceeding 99.9% may be achieved in a few cycles for high salt/metal ratios. The percent recovery is independent of the amount of plutonium processed for all cases in which the solubility of plutonium in the donor alloy is not exceeded.

A series of engineering experiments is being made to determine the rates of transfer of various solutes (plutonium, uranium, copper, magnesium, zinc, and selected fission product elements) in the salt transport step. The purpose of these tests is to provide information which will make it possible to calculate mass transfer rates for various batch and continuous versions of the salt transport step. In an immiscible liquid metal-molten salt system, the mass transfer rate of a solute is a function of the geometry, mixing conditions, solute mass transfer coefficients, and difference in solute activities in the bulk salt and metal phases. In a plutonium transfer experiment, the mass transfer rate observed was 5 to 10 times greater than the rates observed for uranium during uranium transport experiments (for equivalent mixing conditions and geometries). The rapid plutonium transfer rate is attributed to the absence of a precipitate-dissolution resistance to the mass transfer.

II. VOLATILITY AND FLUIDIZATION PROCESSES

The reaction of fluorinating agents with nuclear reactor fuel materials in fluid-bed systems to produce volatile UF_6 and PuF_6 is the basis of fluid-bed fluoride volatility processing. Currently, major attention is being directed toward the demonstration of fluoride volatility processes for low-enrichment UO_2 - PuO_2 power reactor fuel clad in Zircaloy. The primary objective of this effort is to develop the technical data required for the design of an all-volatility commercial plant for the reprocessing of power reactor fuels. The reference process flowsheet (Figure II-1) under development is based on the use of bromine pentafluoride to selectively convert uranium to volatile UF_6 while plutonium is converted to solid PuF_4 . The process involves four principal steps.

(1) Zircaloy-clad fuel is immersed in a fluid bed of refractory alumina and then contacted with HCl gas at 350°C to remove the cladding as volatile ZrCl_4 which is subsequently converted to solid ZrO_2 by pyrohydrolysis with steam.

(2) Since the direct reaction of sintered, massive oxide fuel with BrF_5 does not proceed readily, the oxide fuel is pulverized to U_3O_8 - PuO_2 powder by reaction with oxygen at 450°C prior to fluorination.

(3) Uranium is recovered from the oxide fines as gaseous UF_6 by reaction of the fines with 5 to 15 v/o BrF_5 at 300°C (Fluorination I).

(4) Plutonium, which is converted to solid PuF_4 in the previous step, is recovered as PuF_6 by reaction of the PuF_4 with fluorine at 300 to 550°C (Fluorination II).

Fig. II-1. Interhalogen Flowsheet for Reprocessing of UO_2 Fuel Material Using Bromine Pentafluoride

The UF_6 produced in the BrF_5 fluorination step is collected in a condenser together with excess BrF_5 , bromine, and certain volatile fission product fluorides. The UF_6 is separated and recovered from the fission products and interhalogens by fractional distillation and sorption techniques. Plutonium hexafluoride is collected in a cold trap and then revaporized and transferred to a separate vessel for final purification.

Process development effort is divided into several projects. Studies are being carried out in a laboratory-scale 2-in. dia. fluid-bed reactor to establish optimum processing conditions for fluorinating sintered UO_2 - PuO_2 pellets containing simulated fission product oxides. Experiments are under way in an engineering-scale 3-in. dia. fluid-bed reactor to establish the effects of process variables on the fluorination of oxidized UO_2 with BrF_5 . The experimental program in the engineering-scale alpha facility is directed towards defining the behavior of PuF_6 in process equipment during the fluorination of PuF_4 with fluorine. Studies are also being made in a 1 1/2-in. dia. fluid-bed reactor to determine the distribution of fission products in the reactor system during the processing of highly irradiated UO_2 - PuO_2 fuel. To complete the process flowsheet, methods are being developed for preparing a highly purified plutonium product. Information on the separation chemistry of neptunium is also being obtained.

A. Recovery of Uranium and Plutonium from Power Reactor Fuels

1. Laboratory-scale Investigations of Uranium and Plutonium Fluorination

Experimental studies are being carried out in a 2-in. dia. fluid-bed reactor to demonstrate the oxidation and fluorination steps in the interhalogen flowsheet (Figure II-1) and to establish the fluorination conditions that would result in a minimum retention of uranium and plutonium in the fluid bed. Major emphasis in this program was placed on the development of the recycle-fluorination sequence for plutonium recovery. Experimental procedures were evaluated principally on the quantity of plutonium which remained in the alumina bed at the end of the fluorination step.

The fuel material used in these studies was cylindrical pellets prepared by blending UO_2 and PuO_2 powders with nonradioactive fission product oxides and sintering the mixture in hydrogen for 8 hr at 1700°C . The pellets simulated typical commercial nuclear fuel materials, and contained nominally 0.4 w/o plutonium, 86 w/o uranium, and 1 w/o fission products. For each experiment, 650 g of UO_2 - PuO_2 -fission product pellets were charged to the fluid-bed reactor to form a packed bed of pellets 2-in. deep. The fluid-bed material was 1100 g of -40+170 mesh, high-fired alumina. To simulate more closely the fission product distribution expected from irradiated fuel, CsF (0.92 g/kg of pellets) was added to the alumina bed material. Processing of the oxide fuel material involved three steps:

(1) oxidation of the pellets to a mixture of U_3O_8 and PuO_2 fines by reaction with 20 v/o oxygen in nitrogen for 4 hr at $450^\circ C$; (2) fluorination of U_3O_8 to UF_6 and PuO_2 to PuF_4 by reaction of the oxide fines with 10 v/o BrF_5 in nitrogen for 2 hr; and (3) fluorination of PuF_4 to PuF_6 using 90 v/o fluorine, under conditions of fluorine recycle, at temperatures of 300 to $550^\circ C$.

Effect of Temperature during BrF_5 Fluorination. A series of experiments was performed to determine the effect of temperature during

Fig. II-2. Plutonium Concentrations in Alumina Fluidized Beds Following Fluorination of Uranium with BrF_5

subsequent plutonium fluorination. Of the three temperatures evaluated, $300^\circ C$ appears to be the best temperature for fluorination of uranium with BrF_5 .

Analyses of the BrF_5 fluorination step in these experiments showed that the average UF_6 production rates ranged from 14 lb UF_6 /(hr)(sq ft) at $200^\circ C$ to 45 lb UF_6 /(hr)(sq ft) at $400^\circ C$; the peak production rate at $400^\circ C$ was 140 lb UF_6 /(hr)(sq ft). Utilization of BrF_5 , based on the total fluorine available, varied from 8% at $200^\circ C$ to 30-40% at 300 and $400^\circ C$. Rate constants for the reaction of U_3O_8 with BrF_5 were calculated from the rate of change in uranium concentration in the alumina beds at 200, 300, and $400^\circ C$. The values were in excellent agreement with the values obtained in boat-reactor experiments (ANL-7175, pp. 54-59) and thermobalance studies (ANL-7225).

fluorination with BrF_5 on the extent of plutonium removal during subsequent fluorination with fluorine. In these experiments, uranium fluorination was carried out at temperatures of 200, 300, and $400^\circ C$. The course of plutonium removal from the alumina bed by recycle fluorination with 90 v/o fluorine is shown in Figure II-2. In the test in which the BrF_5 fluorination step was conducted at $200^\circ C$, the recycle-fluorination scheme was initiated at $200^\circ C$. It was observed in this case that the rate of fluorination of plutonium to PuF_6 in the temperature range 200 to $300^\circ C$ was very low. On the basis of the relative rates of plutonium removal and the final plutonium concentrations in the alumina beds as shown by the curves in Figure II-2, it appears that the temperature at which uranium is fluorinated with BrF_5 does affect

Behavior of Neptunium. The recovery of neptunium during fluoride volatility processing of spent fuel may be a significant economic factor in the design of a commercial process. Therefore the reaction of neptunium during fluorination with BrF_5 and with fluorine is of particular interest.

Fig. II-3. Concentrations of Uranium, Plutonium, and Neptunium in Fluidized Alumina Bed during Fluorination with BrF_5 Followed by Fluorine

contained 0.002 w/o neptunium, corresponding to the removal during both fluorination steps of 95% of the neptunium charged to the system. These results indicate that neptunium can be volatilized by fluoride volatility techniques and that the product appears in both the UF_6 and PuF_6 streams.

In one experiment, 0.46 g neptunium as NpO_2 was added to the alumina bed. This quantity of neptunium was added to provide alumina bed samples that contained neptunium in amounts above its limits of analytical detection. In addition to neptunium, the alumina bed for this experiment contained both cesium fluoride and rubidium fluoride in proportion to the UO_2 - PuO_2 -fission product charge. The change in concentration of uranium, plutonium, and neptunium in the alumina bed during both fluorination steps is shown in Figure II-3. The addition of RbF and CsF to the alumina bed did not affect the fluorination of uranium and plutonium. The final bed contained 0.003 w/o uranium and 0.005 w/o plutonium, indicating a removal of more than 99.9% of the uranium and 98% of the plutonium from the bed. The concentration of neptunium in the fluid bed increased during the first hour of fluorination with BrF_5 , owing to the rapid depletion of U_3O_8 by reaction to form UF_6 . At the end of the BrF_5 step, 0.2 g of neptunium remained in the bed, indicating that approximately one-half of the neptunium had volatilized. The final alumina bed after recycle-fluorination with fluorine

Effect of Reuse of Alumina Bed on Uranium and Plutonium

Retention. A series of three experiments were performed to evaluate the reuse of the alumina bed for the processing of several successive batches of oxide fuel as a means for reducing plutonium losses in the waste solids. The procedure employed in these experiments involved the following steps: (1) charging of the oxide fuel pellets, (2) oxidation of the pellets to U_3O_8

and PuO_2 fines for 4 hr at 450°C with 20 v/o oxygen in nitrogen, and (3) fluorination with 10 v/o BrF_5 in nitrogen for 2 hr at 300°C to form volatile UF_6 and nonvolatile PuF_4 . Three processing cycles were performed, and the nonvolatile PuF_4 was allowed to accumulate in the alumina bed. Fluorination of the plutonium to volatile PuF_6 was accomplished after the third cycle using 90 v/o fluorine. The fluorination step was carried out as follows: 10 hr at 300°C , 5 hr while the temperature of the fluid-bed reactor was increased from 300 to 550°C , and 3 hr at 550°C .

The concentrations of uranium and plutonium in the final alumina bed were 0.003 w/o and 0.009 w/o, respectively. These values correspond to a removal of 99.9% of the uranium and 99% of the plutonium charged to the reactor in the three experiments. The amount of plutonium remaining on the alumina after three uses of the same bed was less than two-thirds of the amount which would have remained if three separate beds had been used for the processing of three separate charges of fuel. This processing concept offers an additional advantage in that the time required for the recycle-fluorination step is significantly reduced compared with the time required to fluorinate separately successive batches of fuel.

2. Engineering-scale Alpha Facility Operations

Development work on the fluid-bed fluoride volatility process for the recovery of uranium and plutonium from spent uranium dioxide fuels is being carried out in the engineering-scale alpha facility. The facility comprises two alpha boxes for the containment of plutonium, one containing process equipment and the other containing equipment for scrubbing and filtration of ventilation air and process exhaust gases. The process equipment includes a fluid-bed fluorinator for fluorinating mixed oxide fuel to UF_6 and PuF_6 , a converter reactor for converting PuF_6 to PuF_4 by thermal decomposition, and a system of condensers and chemical traps for collecting hexafluoride products.

Demonstration tests in the engineering-scale facility have included (1) the fluorination of 0.5 w/o PuO_2 - UO_2 -fission product pellets using the two-zone oxidation-fluorination scheme (see ANL-7175, p. 71), (2) the separation of plutonium from UF_6 - PuF_6 mixtures by the thermal decomposition of PuF_6 to solid PuF_4 , (3) establishing the feasibility of transferring PuF_6 quantitatively from one process vessel to another, and (4) the fluorination of 100-g quantities of PuF_4 to simulate the plutonium recovery step of the interhalogen flowsheet.

Two-zone Oxidation-Fluorination Studies. A series of three experiments were performed to evaluate the two-zone oxidation-fluorination process for the recovery of uranium and plutonium from oxide fuel. These experiments were conducted prior to the adoption of the current flowsheet which involves BrF_5 fluorination of uranium. The results are, nevertheless,

of interest to the current program. In each experiment 8.8 kg of $\text{UO}_2\text{-PuO}_2$ -fission product pellets were fluorinated in a fluid bed of alumina. The same alumina bed material was reused in each experiment. The operating procedure, in general, involved two-zone fluorination for 8 hr at 400 to 450°C with 13 to 23 v/o oxygen and 6 to 10 v/o fluorine, followed by recycle fluorination with 90 v/o fluorine at 450 to 550°C for an additional 12 to 20 hr. Results of chemical analyses of the alumina bed material indicated that, after the bed had been used for fluorination of three charges of oxide fuel, over 99.9% of the uranium and 97% of the plutonium had been removed from the bed. These values are considered acceptable recoveries. (Slightly higher plutonium recovery might be achieved with additional use of the bed material.)

It was observed in these experiments that, although PuF_6 exhibits a tendency to decompose to solid PuF_4 which deposits on process vessels and lines, the decomposed plutonium can be readily recovered by contact with fluorine at elevated temperatures. Upon completion of the series of three fluorination experiments, the plutonium that had accumulated within the

process equipment was recovered by exposure of the equipment components to 90 v/o fluorine at 300 to 350°C for periods up to 57 hr. (The long exposure periods employed in these initial experiments are not considered to be standard since recent experiments have shown that satisfactory plutonium recovery can be achieved in periods as short as 8 hr.) The PuF_6 formed in this cleanup operation was collected in beds of NaF pellets. As an aid in observing the course of plutonium movement through the process equipment, portable neutron counters were employed to detect the presence of plutonium. These counters consist of a battery-operated meter with a boron trifluoride gas probe which detects neutrons derived from (α -n)-type reactions (see Figure II-4). The probe is shielded by a cadmium sheet and a paraffin

Fig. II-4. Portable Neutron Probe Being Used to Detect Plutonium in Process Equipment inside an Alpha Enclosure

moderator. Reasonably accurate quantitative estimates of plutonium contents have been made by employing a scaler counter in conjunction with the probe. Depending upon background and geometry, the counter can detect as little as 0.1 to 1 g plutonium within equipment in the engineering-scale facility. The portable neutron probe provided a reliable means for indicating the complete removal of plutonium from the process equipment.

Chemical analyses of interim and product streams have provided preliminary information on the behavior of molybdenum (present in the oxide fuel at fission product concentration) during the fluorination steps. The bulk of the molybdenum was volatilized during the fluorination and collected with the mixed hexafluorides (UF_6 and PuF_6) in the condenser. Very little molybdenum was found in the fluid bed after fluorination. It was observed in experiments to demonstrate the separation of plutonium from UF_6 - PuF_6 mixtures by thermal decomposition of PuF_6 to PuF_4 at 300°C , that the molybdenum passed unaffected through the thermal-decomposition reactor and appeared in the UF_6 product. Approximately 20% of the molybdenum remained as a high-boiling material in the mixed hexafluoride condenser and was not fed to the thermal-decomposition reactor. This molybdenum was recovered during the cleanup fluorination with fluorine at 300°C . This finding suggests two possible modes of behavior: (1) a fraction of the volatile molybdenum was reduced to a nonvolatile form in the condenser and this material was then refluorinated to a volatile compound by fluorine at high temperatures, or (2) a high-boiling compound, perhaps an oxyfluoride or MoF_5 , was formed during the fluorination step and was volatilized only when the condenser was heated to 300°C during the cleanup fluorination. The presence of such compounds, capable of reducing PuF_6 , could account for much of the decomposition of PuF_6 .

Studies on the Thermal Decomposition of PuF_6 . Three experiments were made to examine the feasibility of separating plutonium from UF_6 - PuF_6 mixtures by thermal decomposition of PuF_6 in a fluid-bed reactor. In this process, a mixture of UF_6 - PuF_6 is passed through a fluidized bed at 300°C and the plutonium deposits on the surface of the particles as PuF_4 . These experiments were performed using a 2-kg bed of alumina as a stand-in for a conceptual bed of PuF_4 . The same alumina bed was used in the three experiments. In each experiment, approximately 10 kg of a PuF_6 - UF_6 mixture (up to 0.4 w/o plutonium) diluted to 40 v/o hexafluoride with nitrogen, was processed in 8 hr.

The results of these experiments indicated that the decomposition process is very efficient as evidenced by the low plutonium content of the UF_6 off-gas stream. Based on analyses of process streams during the third experiment, a plutonium separation of about 99.9% was achieved. The final alumina bed contained 1.46 w/o plutonium and only 0.19 w/o uranium, indicating satisfactory separation of uranium from plutonium. It was observed

that the deposition of PuF_4 occurred preferentially on the surface of the bed particles, rather than in the gas phase, producing a solid product that was easy to transport. Thus, the feasibility of this separation technique has been satisfactorily demonstrated.

Plutonium Hexafluoride Transfer Experiments. Inherent in the development of volatility processes for reactor fuel materials is demonstrating reliably the ability to transfer hexafluorides, particularly PuF_6 , from one process vessel to another. Several tests were performed to evaluate techniques for performing such transfers. In one test, 160 g of UF_6 was vacuum transferred from a supply vessel to a large cold trap (~1 cu ft) maintained at -52°C . The UF_6 was then transferred to a small nickel receiver (800 ml) using nitrogen as a carrier gas. In this operation, the cold trap was heated to 75°C and the UF_6 was swept from the trap by the nitrogen gas stream. The receiver vessel was maintained at temperatures between -38 and -57°C . A small NaF trap was used to collect any UF_6 which passed through the receiver vessel. Approximately 123 g UF_6 was collected in the receiver and 35.2 g in the NaF trap; collectively, these numbers represent a UF_6 material balance of about 99% in the two transfer operations.

The transfer of PuF_6 was demonstrated in the same equipment under the same operating conditions. During the vacuum transfer step, 89.4 g of PuF_6 was transferred to the cold trap. In the second transfer, 74.0 g PuF_6 was collected in the receiver vessel and 13.4 g PuF_6 was collected in the NaF trap. The PuF_6 material balance, taking into account the alpha decomposition of PuF_6 during an 8-hr period at a rate of 2% per day, was 98.4% for the transfer experiment, which is considered to be highly satisfactory.

Fluorination of Plutonium Tetrafluoride. Several experiments have been performed to simulate the Fluorination-II step of the interhalogen flowsheet (Figure II-1). In each experiment, approximately 135 g of PuF_4 in a bed of alumina (6,700 g) was fluorinated with 80 to 90 v/o fluorine at 200 to 550°C . In two tests, 40 g CsF (simulating fission product cesium) were added to the bed. Analyses of bed samples taken periodically throughout the runs indicated that the rate of plutonium removal by fluorination was less in runs in which CsF was present than in runs in which CsF was absent. The concentration of plutonium in the alumina beds after fluorination was also greater when CsF was present (~0.10 w/o) than when CsF was absent (~0.005 w/o).

In order to simulate more closely the plutonium fluorination step, a subsequent experiment was performed using a feed material generated in experiments that had been carried out in the laboratory-scale fluid-bed facility. This material represented the fluid bed after the uranium had been recovered by fluorination of oxidized UO_2 - PuO_2 -fission product

pellets with BrF_5 . The charge to the alpha facility fluorinator consisted of 6,400 g of the mixture which contained 25.7 g plutonium and 3 g CsF . This material was contacted with 80 v/o fluorine for 9.7 hr while the bed temperature was slowly increased from 300 to 550°C, and for 5.2 hr at 550°C. The final bed after fluorination contained 0.013 w/o plutonium which represents the removal of 98% of the plutonium. An additional clean-up fluorination step for 10 hr at 550°C did not result in the fluorination of additional plutonium. This high plutonium removal suggests that the effect of CsF on plutonium retention may be less marked in the presence of other fission products.

A BrF_5 feed and disposal system is being installed in the alpha facility. After the installation work is completed, demonstration tests will be performed with UO_2 - PuO_2 -fission product pellet fuel to evaluate the various processing steps (except decladding) of the interhalogen flowsheet.

3. Bench-scale Fluid-bed Studies with Irradiated Fuels

A program demonstrating the fluid-bed volatility process with irradiated fuel materials is in progress. Experiments are being conducted in a 1 1/2-in. dia. fluid-bed reactor installed in the Senior Cave Facility of the Chemical Engineering Division. Present work is directed to the determination of the distribution of the actinides and fission products in each of the process streams (except decladding) for the interhalogen process. The fuel charge used was highly irradiated UO_2 pellets and the bed material was alumina.

A series of three runs has been completed using a processing scheme consisting of oxidation of UO_2 to U_3O_8 at 400 to 450°C; uranium volatilization with BrF_5 at ~300°C, and plutonium volatilization with fluorine at 300 to 560°C. The first of these runs was made using a nonirradiated charge of UO_2 to establish experimental procedures and to determine the levels of activity in the various samples which result from processing in equipment contaminated with radioactive material. The other two runs were made with irradiated UO_2 charges.

The apparatus and procedures employed in these tests were similar to those used in the processing of irradiated uranium alloy fuels (see ANL-7175, pp. 89-97). Prior to the start of these tests the equipment was modified slightly by the installation of a sintered nickel filter in a separate chamber above the fluid-bed reactor. This filter replaced the packed-bed filter previously used.

The feed material for each run using irradiated fuel was 108 g of declad UO_2 irradiated to 40,000 Mwd/metric ton. The oxide fuel had cooled approximately one year prior to processing. The process conditions and average fission product distributions following each process step are shown in Figure II-5.

*Sintered nickel, 10 micron pore, grade G, Pall Trinity Micro Corp.

**Membrane filter, 0.4 micron pore, Metrice VF-6 (fluorinated vinyl), Gelman Corp.

† The stack gas passed through an AEC high efficiency filter and a charcoal filter before it was sampled and discharged to the environment.

†† The atmospheric concentrations at ground level were calculated from the stack gas analysis allowing a dilution factor of 10 from stack to ground level. The RCG value represents the percent of the recommended limiting concentration of the radioisotope as proposed in Radioactive Concentration Guide (see Ref. 2 in text).

** The uranium traps consisted of two beds in series each containing ~1.3 kg soda lime followed by a bed containing 0.85 kg activated alumina.

*** Run BRF-1 only.

Fig. II-5. Processing of Irradiated UO₂ Charges Using an O₂-BrF₅-F₂ Process Scheme. Average Values for Runs BRF-1 and -2.

The Oxidation Step. Only a small amount of activity volatilized during the conversion of the UO₂ to U₃O₈. The principal volatile activity was krypton-85; about 17% of the total krypton activity was released during this step. It should be noted that the irradiated charges had been de-clad prior to processing and that the krypton released upon cladding removal is not known. Other volatile species detected after oxidation were trace¹ amounts of cesium, niobium, and ruthenium. Analysis of the stack gas

¹A trace is considered to be any amount detected yet less than 1 x 10⁻⁴% of that present in the charge.

showed that, in addition to the krypton, ruthenium-106 was present at a concentration that was about 0.6% of the recommended limiting concentration.²

The Uranium Volatilization Step. During the uranium volatilization by reaction with BrF_5 , the principal activities which also volatilized and collected with the uranium in the soda lime and activated alumina traps were 61% of the ruthenium, 76% of the molybdenum, and trace amounts of cerium, cesium, zirconium, and niobium. Also, the remainder of the krypton (83%) volatilized during the uranium fluorination step. In run BRF-1, 0.025% of the plutonium in the oxide fuel accompanied the uranium and collected in the soda lime trap.

In addition to krypton, small amounts of ^{106}Ru and $^{125\text{m}}\text{Te}$ were detected in the stack gas.

The Plutonium Volatilization Step. The volatilization of plutonium from the reactor was accomplished by the use of fluorine at temperatures from 300 to 560°C. About 0.8% of the gross beta and gamma was volatilized during this step. The major gamma active isotopes found with the plutonium in the NaF trap were ruthenium and niobium. Small amounts of cesium, cerium, and zirconium (less than 0.1%) collected in the activated alumina trap downstream of the NaF trap. The process off-gas contaminants were found to be mainly ruthenium and tellurium. About 3% of the recommended limiting value² for ^{106}Ru and a small amount of $^{125\text{m}}\text{Te}$ were found in the stack effluent.

Reactor Bed Residues. The average values (percentage of charged material) for the retention of actinides and fission products in the final alumina beds were 0.20% uranium, 2.0% plutonium, 34.4% gross gamma, 35.6% gross beta, 57% cerium, 54% strontium, 39% cesium, 52% zirconium, 1.5% niobium, and <1.7% molybdenum.

A comparison of the results for the inactive run and the two runs with irradiated charges indicated that the gamma activity of the samples obtained after processing with a nonirradiated charge is very small as compared with that obtained after processing an active charge, and therefore the contribution of activity from residual deposits within the equipment can be neglected.

This experimental program has been useful in defining problems associated with the processing of irradiated nuclear fuels. In particular, these experiments have identified the fission products that appear in the uranium and plutonium products. This information has prompted the development of methods for the separation of these specific fission product impurities from the uranium and plutonium.

²Radioactivity Concentration Guide, AEC Manual, Chapter 0524, Standards for Radiation Protection, (approved Aug. 12, 1963). Copy can be obtained from AEC Headquarters, Division of Operational Safety, Washington, D.C.

B. Supporting Investigations

1. Chemistry of Neptunium Fluorides

Neptunium-237 is a valuable constituent of spent power reactor fuels since it can be transmuted to plutonium-238, which has potential use as an isotopic power source. Therefore, it is necessary to consider means for recovering neptunium in the fluoride volatility processing of reactor fuels. An experimental program is under way to study the chemistry of neptunium fluorides with specific emphasis on defining the behavior of neptunium in the various processing steps and establishing methods for the separation and recovery of neptunium.

In the course of this program, the kinetics of the reactions of NpF_4 with BrF_5 and with BrF_3 have been measured. These experiments involved passing gaseous mixtures of BrF_5 or BrF_3 diluted with nitrogen over a sample of powdered NpF_4 in a nickel boat and measuring the weight loss of the sample. Reaction rate data obtained at 300, 325, and 350°C for the NpF_4 - BrF_5 reaction were found to conform to the diminishing-sphere rate law: $(1 - F)^{1/3} = 1 - kt$, where k is the rate constant, F is the fraction of solid reacted, and t is the reaction time. At 400°C, the rate data did not conform to the diminishing-sphere model. An activation energy of 26 kcal/mole was calculated for the NpF_4 - BrF_5 reaction. In comparison, the activation energy for the UF_4 - BrF_5 reaction is 16.9 kcal/mole, and the activation energy of the NpF_4 - F_2 reaction is 20 kcal/mole.

The rate constant for the reaction of NpF_4 with BrF_3 (6 to 13 v/o in nitrogen) at 350°C was determined to be 0.0051 min^{-1} . At the same temperature, the rate constant for the reaction of NpF_4 with BrF_5 (33 v/o in nitrogen) was significantly less, 0.0013 min^{-1} . A similar behavior was observed previously³ in the fluorination of UF_4 with BrF_5 and with BrF_3 ; in this case the rate constant for the UF_4 - BrF_3 reaction was about a factor of five greater than for the UF_4 - BrF_5 reaction.

Infrared spectrophotometric analyses of the gaseous reaction products indicated that volatile NpF_6 was produced in the reaction between NpF_4 and BrF_5 at 300 to 500°C. Chemical analyses of solid residues remaining after partial conversion of NpF_4 to NpF_6 with BrF_5 showed no evidence of formation of neptunium fluorides intermediate between NpF_4 and NpF_6 .

A brief study of the fluorination of NpO_2 with fluorine and with BrF_5 was performed in order to establish the mechanism of the reaction and to compare the mechanism with those observed in the fluorination of UO_2 and PuO_2 . The fluorination of UO_2 by either fluorine or BrF_5 proceeds through the formation of UO_2F_2 as an intermediate

³Chemical Engineering Division Semiannual Report January-June 1966, ANL-7225.

compound.^{4,5} In contrast, the fluorination of PuO_2 proceeds through the formation of PuF_4 .⁶ In this study, powdered NpO_2 was exposed to pure fluorine at 310°C and to 33 v/o BrF_5 in nitrogen at 350°C . In both experiments, the major portion of the solid residue was converted to NpF_4 . X-ray diffraction analysis indicated that the only solid phases present were NpF_4 and NpO_2 . Thus, in this respect, the mechanism of the fluorination of NpO_2 is similar to that of PuO_2 . Also, it appears that a secondary reaction of NpF_6 with NpO_2 , analogous to that exhibited by UO_2 ,⁵ is not significant in the fluorination of NpO_2 .

In the course of the studies on the reaction of NpF_4 with BrF_5 , it was observed that when the condensed reaction products were warmed from -78°C to $+30^\circ\text{C}$ a nonvolatile solid was produced in the condenser. Further experiments indicated that NpF_6 reacts readily with bromine at 30°C to form solid NpF_4 . Infrared spectrophotometric analyses showed that the bromine is fluorinated to BrF_3 , but not to BrF_5 , even in the presence of excess NpF_6 . Thus the reaction appears to proceed according to the equation

Since UF_6 does not react with bromine, this reaction affords a means for separating uranium from neptunium. An experimental program is under way to define the conditions whereby complete reduction of neptunium (VI) to (IV) can be achieved.

2. Basic Studies of Fluidized-bed Behavior Related to Process Operations

The effects of walls on the characteristics of particle movement within a fluidized bed are important to the understanding and control of fluidized-bed reactors. For most reactors, heat is either introduced or removed through the vessel walls. Reactor walls also affect the characteristics of gas and particle mixing within fluid-bed reactors. Therefore, knowledge of particle behavior at the walls of a reactor is of practical importance to the design of fluid-bed systems.

Currently, experimental studies are being conducted to determine the effect of column width on fluidized particle movement in a two-dimensional column (see Figure II-6). The results of the current experimental studies have been compared with a theoretical treatment based on a cylinder rising through an ideal fluid between parallel walls.

⁴Chemical Engineering Division Summary Report July, August, September 1958, ANL-5924, pp. 28-33, 1959.

⁵Chemical Engineering Division Semiannual Report July-December 1966, ANL-7325, 1967, in preparation.

⁶M. J. Steindler, D. V. Steidl, and R. K. Steunenberg, Nucl. Sci. Eng., 6, 333 (1959).

Fig. II-6. Experimental Two-dimensional Column Showing Gas Bubble Collapsing at Surface of Fluidized Bed

This theoretical analysis suggests that the motion of fluidized particles around a rising bubble can be described by the hypothetical motion of an ideal fluid. The stream function for the flow of an ideal fluid around a cylinder of approximately circular cross section located mid-way between parallel walls has been found to be:⁷

$$\psi = U \left[y - a \tan \frac{\pi a}{2d} \left(\frac{\sin \frac{\pi y}{d}}{\cosh \frac{\pi x}{d} - \cos \frac{\pi y}{d}} \right) \right] \quad (1)$$

where ψ = stream function

U = velocity of stream

a = bubble radius

d = one-half the distance between the walls.

An objective of this work was to apply this mathematical expression for describing the flow around a cylinder to the case in which wall effects become significant. The movement of the fluidized particles is predicted by integrating, along a constant streamline, the difference between the velocity of the particle and the stream velocity at infinity as the bubble rises from minus infinity to plus infinity.

$$X = \int_{-\infty}^{\infty} \left(\frac{2\psi}{2y} - U \right) dt$$

where X = distance of particle movement in the X direction

t = time.

The integration was performed numerically using a high speed digital computer.

A comparison of the trajectories of actual fluidized particles with the theoretical prediction was made by photographic observations of

⁷R. Collins, Chem. Eng. Sci., 20, 747 (1965).

Fig. II-7. Comparison of Theoretical with Experimental Particle Drift Profiles

a fluidized bed in a two-dimensional column. Glass beads with black tracer particles constituted the bed material.

A set of data obtained with 0.27-mm diameter glass beads as the fluidized particles in a 7.3-cm wide column are plotted in Figure II-7, along with the data predicted by the numerical integration. The initial position of the particles is shown by the solid horizontal line. The theoretical drift profile (left side of the figure) of the particles, in relation to their original positions along the horizontal line, can be compared with the observed drift profile (right side of the figure). The drift for three different bubble sizes, resulting in a/d ratios of 0.41, 0.46, and 0.66, are shown.

The data indicate increased particle movement with increased bubble size. The largest observed bubbles had the greatest effect on the particles near the wall, and there was no movement of the particles at the wall for the smallest bubble. This

is in contrast to the theoretical prediction, based on an ideal fluid, that the influence of the bubble would extend to the particles at the wall.

It was also concluded from other tests that:

1. Particle movement is primarily in the vertical direction with negligible horizontal movement.
2. The extent of influence by the bubble on particle movement decreases with an increase in particle size.
3. Theory implies that only the a/d ratio would influence the extent of particle motion relative to the bubble; experimental results indicate that both the a/d ratio and the absolute bubble size are significant parameters.

Models proposed to predict coefficients of heat transfer from a gas-fluidized bed to the reactor wall generally require a knowledge of

the residence time of fluidized particles at the wall. During the current work, attention has been directed toward improvement of these models and toward experimental verification of the predicted coefficients.

An experimental apparatus has been erected and successfully operated to measure both heat transfer rates and residence times at the same section of the fluid-bed column wall. Data obtained with this apparatus were very reproducible.

Preliminary data for residence times and heat transfer coefficients have been obtained for 1/8-in. dia. acetate spheres fluidized in air. The data indicated that heat transfer rates increased as the particle residence time was decreased:

Air Velocity Based on Empty Column, ft/sec	Heat Transfer Coefficient, Btu/(hr)(sq ft)(°F)	Mean Residence Time, sec
3.53	18.4	9.2
4.05	24.6	2.4

The mean error in the heat transfer data was about 2%.

This study is being extended to include small-particle systems. In particular, two systems of ~30 mesh and ~45 mesh black glass beads and white glass beads are being investigated. These particle sizes are more typical of material usually used in fluid-bed systems.

3. Environmental Contamination Control⁸

Implicit in the development of fluoride volatility processing techniques for power reactor fuels is the need to provide methods for the treatment of process gas streams containing fission product fluorides (such as tellurium fluorides) and reagents such as fluorine gas. An experimental program has been established to investigate the chemistry of tellurium fluorides and to develop techniques for the disposal of gaseous fluorinating agents.

Studies of the reactions of volatile tellurium fluorides were primarily directed toward determining the conditions whereby tellurium is fixed on solid materials and to investigate the kinetics of the reaction. In these studies, TeF₆ was contacted with various solids, and the effectiveness of the solid as a suitable material for the removal of TeF₆ from

⁸Complete details of this program are presented in Chemical Engineering Division Semiannual Report July-December 1966, ANL-7325, 1967, in preparation.

a process gas stream was evaluated in terms of the rate of TeF_6 sorption, the capacity of the solid for TeF_6 , and the retention of TeF_6 on the solid under vacuum. The results of these studies indicated that activated alumina, Linde type 13X Molecular Sieve, BPL activated charcoal, magnesium fluoride, and copper turnings are promising reagents for the removal of TeF_6 from gas streams.

Experiments performed in a 2-in. dia. fluid-bed reactor have demonstrated that a fluid bed of activated alumina is an effective agent for removing fluorine from process gas streams. It was observed that the reaction between fluorine and activated alumina can be characterized by an initial period during which the fluorine concentration in the off-gas from the fluid-bed reactor remains at a constant value, less than 50 ppm, and by a breakthrough period in which the fluorine concentration increases rapidly to greater than 50 ppm. Results of demonstration tests indicated that (1) increasing the bed temperature from 300 to 400°C, increasing the bed depth-to-diameter ratio from 3 to 6, and decreasing the alumina particle size from 24-48 mesh to 48-100 mesh were all effective in increasing the capacity of activated alumina for fluorine disposal; (2) changing the fluidizing gas velocity (1.25 to 1.65 times the minimum fluidizing velocity) and changing the fluorine concentration in the inlet gas stream (from 5 to 75 v/o in nitrogen) had no effect on the capacity of the bed. In the course of this work fluorine capacities up to 85% of the theoretical capacity were achieved. Of other solid reagents tested, soda ash also appears promising as an agent for fluorine disposal.

III. MATERIALS CHEMISTRY AND THERMODYNAMICS

A. High Temperature Materials Development

1. Thermodynamics of Urania¹

Under the general program of collecting basic data on the vaporization and chemical stability of potential nuclear reactor fuels, the projected experiments² on high-temperature thermodynamic properties of urania have been completed. The majority of the results were presented in the preceding report,³ although not in their final form. Final processing of the data was delayed to await the outcome of experiments carried out to assess possible errors from such sources as temperature measurements and contamination by the container. At present, it appears that the corrections required are negligible. Also discussed in that report was the initiation of a study⁴ of the congruently vaporizing composition of urania as a function of temperature. This study has been completed. The results, presented in Figure III-1, show that the composition of congruently vaporizing urania is hypostoichiometric between 2026 and 2377°C, the oxygen deficiency increasing with temperature.

Because of the accumulation of interrelated data, the refinement of earlier data, and the addition of the results of new measurements, it seems appropriate at this time to examine the self-consistency of our present information. Accordingly, a simplified treatment of the data is given below which illustrates the approach to be pursued later when a comprehensive thermodynamic description of urania at high temperatures is attempted. The results used in this treatment consist of the following items which appear in Figures IV-1, -2, -3, -4, and -5 of the preceding report³ and Figure III-1 of this report, respectively.

- (a) The uranium-urania phase diagram at elevated temperatures. Of special pertinence here is the delineation of the hypostoichiometric urania phase boundary.
- (b) The total vapor pressure over the uranium-urania two-phase system. The total pressures of uranium-bearing species for the two-phase system, as measured by the Knudsen effusion technique, apply to urania at its hypostoichiometric phase boundary.

¹The term urania will be used in Section IIIA to denote a solid phase of fluorite structure with composition unspecified; the terms hyperstoichiometric and hypostoichiometric refer to the oxygen in UO₂.

²ANL-6875, pp. 116-123.

³ANL-7175, pp. 119-126.

⁴The experimental method was discussed in ref. 3. Simply put, the congruent compositions were determined by analysis of the residue left in a tungsten effusion cell after vaporizing, in an ultrahigh vacuum, about half of a 2- to 3-gram sample of urania. The urania initially had either an excess or a deficit of oxygen relative to the final composition.

- (c) The partial vapor pressures over the uranium-urania two-phase system. The partial pressures, P_U , P_{UO} , and P_{UO_2} , were determined by combining the results of mass spectrometric measurements of ratios with the total pressure results of item (b).
- (d) The total pressure of uranium-bearing species as a function of urania composition. These results were obtained by the technique of transpiration in a buffering carrier gas ($H_2O + H_2$), thereby controlling the urania composition.
- (e) The monatomic oxygen partial pressure as a function of urania composition. These results were obtained by calculation from the compositions (H_2O/H_2) of the exiting carrier gases of the transpiration experiments of item (d).
- (f) The congruently vaporizing composition of urania as a function of temperature. (See ref. 4.)

Except for established high temperature data on the equilibrium $O_2(g) \rightleftharpoons 2 O(g)$, only the results cited in items (a) through (f) are used in the treatment so that the calculations remain independent of thermochemical data in the literature.

Fig. III-1
Composition of Congruently Vaporizing
Urania vs. Temperature. (Numbers at
data points indicate run numbers)

The illustrative treatment makes use of only a portion of the data, namely, that at a selected temperature, 2185°K. This temperature is chosen mainly because it is low enough that congruent vaporization takes place at very nearly the stoichiometric composition, thereby simplifying

Fig. III-2. Total and Partial Vapor Pressure Curves Calculated for Urania at 2185°K. (▲, measured total pressure of uranium-bearing species; ■, measured P_U , P_{UO} , P_{UO_2} at hypostoichiometric phase boundary; ●, measured P_{O_2} .)

to yield the satisfactory fit to the circled points seen in the figure.⁶ Next, the appropriate integration of this curve, in conjunction with the Gibbs-Duhem equation, was carried out successively to yield the partial pressure curves for U, UO, and UO₂. For this purpose, the square points in the

the calculations. Otherwise the data at this temperature seem typical. The partial pressures of the species⁵ vaporizing from urania are designated as follows: P_U , P_{UO} , P_{UO_2} , P_{UO_3} , P_O , and P_{O_2} . The composition variable for the solid urania phase is designated z , the deviation from stoichiometry indicated in the formula UO_{2+z} . (Most of the data were obtained with hypostoichiometric urania and, consequently, for negative values of z .) The composition variable for the gas phase is designated ν , the deviation of the average composition indicated in the hypothetical formula $UO_{2+\nu}$.

Figure III-2 shows the vapor pressure curves derived for urania at 2185°K as well as the experimental data employed in the derivations. The computational method follows.

An empirical equation for P_O was developed

⁵These species were identified mass spectrometrically in this work, and have been noted as well in previous literature.

⁶The scatter of the points near the composition O/U = 2.00 is due to the extreme sensitivity of all the partial pressures, except P_{UO_2} , to urania composition in the region near $z = 0$.

figure, which are from items (a) and (c) above, were used as integration limits. The curve for diatomic oxygen was calculated from the P_O curve and the known equilibrium relations between diatomic and monatomic oxygen. Thus, the only partial pressure curve remaining to be determined was that for the UO_3 species.

The UO_3 species was, as has been noted, observed mass spectrometrically, but it was believed that the relative concentrations were highly uncertain.⁷ It is, however, possible to determine a value for P_{UO_3} at the congruent composition, which may then be used as the limit in the integration procedure. This value may be obtained as follows.

The composition (in O/U atom ratio units) of the species effusing from a cell at any moment is given by

$$\frac{O}{U} = \frac{R_{UO} + 2 R_{UO_2} + 3 R_{UO_3} + 2 R_{O_2} + R_O}{R_U + R_{UO} + R_{UO_2} + R_{UO_3}} \quad (1)$$

where R , the rate of effusion, is proportional to $\sqrt{P/\text{molecular weight}}$. For the condition of congruent effusion, the composition of the solid and vapor phases must be equal, by definition. Thus, the composition variables z and ν , previously designated for the solid and vapor phases, are also equal, i.e., $z = \nu = O/U - 2$. The composition of the congruently effusing vapor can therefore be expressed by

$$\nu = \frac{-0.519 P_U - 0.251 P_{UO} + 1.414 P_{O_2} + P_O + 0.237 P_{UO_3}}{0.259 P_U + 0.251 P_{UO} + 0.243 P_{UO_2} + 0.237 P_{UO_3}} \quad (2)$$

For 2185°K, the value $\nu = \sim -0.001$ is obtained from item (f) above (i.e., from Fig. III-1). Substitution in Eq. 2 of this value and of the derived partial pressure values leads to the result that P_{UO_3} is (within +5%) equal to P_{UO} at the congruently vaporizing composition. On the basis of this limit, the curve given in Figure III-2 for the UO_3 species was calculated.

The total pressure curve in Figure III-2 was obtained by summing the partial pressure curves.⁸ Comparison of this curve with the directly determined total pressures (triangular points) shows satisfactory agreement, the latter values generally being larger and within a factor of two. The derived curve has an extremum (minimum) as required for a phase exhibiting congruent vaporization.

⁷In this work, $UO_3(g)$ was generally a minor species, and there was also evidence of fragmentation.

⁸The curve shown is actually the sum $P_U + P_{UO} + P_{UO_2} + P_{UO_3}$; the contributions of P_O and P_{O_2} are negligible for this composition range and temperature.

A few other comparisons are worth noting. (1) The P_O value at the hypostoichiometric phase boundary of Figure III-2 is larger by a factor of ~ 2.5 than that calculated from existing thermochemical data.⁹ The present P_O value is considered more reliable. (2) The curve for the UO_2 species shows the required maximum¹⁰ at the stoichiometric composition. (3) The factor-of-two discrepancy between the derived and measured total pressures is by no means large for investigations at such high temperatures. Yet the same factor results from a similar comparison with directly determined total pressures from the effusion study of Ackermann, Gilles, and Thorn.¹¹ Thus it is possible that the derived values of either P_{UO_2} or $(P_{UO} + P_{UO_3})$ should be higher. A decision between these alternatives is not possible at the present time. However, it is certain from the shape of the congruent composition curve in Figure III-1 that the relative importance of the UO_3 species must increase with temperature. The increasing contribution of P_{UO_3} probably accounts for the upward deviation of Ackermann, Gilles, and Thorn's high-temperature effusion data from their extrapolated low-temperature data. (It also follows from the temperature dependence of the congruently vaporizing composition, that the partial molar enthalpy of vaporization for the UO_3 species from stoichiometric urania is appreciably greater than for the UO species.)

The general approach to the intended comprehensive analysis is apparent from the above treatment. However, some additional considerations are involved. As mentioned earlier, a single mathematical equation for the monatomic oxygen species leads to equations for each of the other species when a value is known for an integration limit. The illustration above was for a single temperature. Including temperature as a variable in addition to the variable of urania composition would be of importance for two reasons. First, simultaneous fitting of the total data (of all kinds and for all temperatures) could be performed to yield a minimization of errors. Second, such an equation would yield optimized expressions of temperature dependencies and, consequently, of partial molar entropies and enthalpies of vaporization for all the species.

Finally, the most important contribution of the present, thorough study of urania, in the long run, is likely to be to the defect theory of non-stoichiometry. Application of quantum-statistical mechanics to detailed models of solid urania would permit the selection of a "best" model, i.e., the one giving the best agreement with the thermodynamic observations. An atomistic model would take into account the energies, charges, and relative positions of atoms, vacancies, interstitials, etc.

⁹R. J. Ackermann, E. G. Rauh, and M. S. Chandrasekharaiah, "A Thermodynamic Study of the Urania-Uranium System," ANL-7048, July 1965, p. 30.

¹⁰A thermodynamic proof given previously in ANL-7020, p. 155, shows that a maximum in P_{UO_2} must occur at $z \approx \pm 10^{-10}$.

¹¹R. J. Ackermann, P. W. Gilles, and R. J. Thorn, J. Chem. Phys. 25, 1089 (1956).

2. Refractory Plutonium-bearing Fuel Materials

A program has been initiated to collect basic data on the vaporization and chemical stability of plutonium-bearing materials, the purpose being to assist in the growth of fast-reactor fuel technology. A survey and evaluation of the literature has been undertaken for the urania-plutonia and uranium carbide-plutonium carbide systems. Studies generally analogous to those carried out for the urania system, under discussion above, of the equilibria between vapor and condensed phases are projected. We have completed an extensive redesign of our experimental facilities to meet safety requirements for working with plutonium-bearing materials. The new designs make it possible to convert most of the apparatus on hand without having to make new acquisitions, but with some compromise as to optimization. It is estimated that all conversions will be completed within the next year. Initial experimentation will be concerned with the U-Pu-O system and directed toward determination of: (1) phase boundaries of $(\text{U,Pu})\text{O}_{2\pm x}$, by thermal analysis and other techniques; (2) oxygen partial pressures and total vapor pressures of phase-boundary compositions, by transpiration techniques; (3) equilibria among the gaseous species Pu, PuO, PuO₂, and O, by mass spectrometric techniques; and (4) congruently vaporizing compositions of plutonia, by effusion techniques. Generally, the projected measurements will be carried out at temperatures in excess of 1500°C, and thus yield data for a temperature range not being investigated elsewhere.

B. Chemistry of Fast Reactor Fuels

The program on the chemistry of fast reactor fuels was initiated in July, 1966. The main objective of this program is to determine the chemical behavior of fast reactor fuels during irradiation in order to form a basis for the development of new fuels with increased burnup capabilities. Studies will be coordinated with those of other groups at Argonne on the metallurgical and safety aspects of the fast reactor program.

1. Fuel-evaluation Facilities

Thus far, a major effort has gone into the selection of instruments and facilities to execute the program. The instruments include a spark source mass spectrometer, a solid-state radiation analyzer system, a shielded metallograph, and a shielded electron probe microanalyzer. Detailed designs have been completed for a cave-instrument complex. Work on extensive modifications of one of the cells in the Chemistry Division cave facilities was begun in the latter part of January, 1967.

The working facilities must be designed to handle microsampling of radioactive samples (both alpha and beta-gamma) of the levels associated with fuel of about 20 a/o burnup, approximately 100 days cooled. The facilities must also be capable of maintaining the surfaces of reactive samples

(such as plutonium and uranium carbides) free from contamination by reactive components in the atmosphere. For this reason the cave complex is being provided with a helium atmosphere and a recirculation-purification unit. During the transfer of analytical samples between the cave and instrument complex sample integrity must also be maintained; a pneumatic tube system is being considered as a means of accomplishing this.

2. Program Development

The initial phase of program development has been the evaluation of various analytical tools that will be required to meet the program's objectives. The analysis of fuel microstructure is expected to contribute significantly to the understanding of the changes that take place throughout the fuel and cladding during irradiation. Therefore, considerable emphasis is being placed on techniques of microsampling and direct microanalysis.

a. Electron Microprobe Studies

The electron probe microanalyzer accomplishes microsampling and analysis directly. An electron beam is focused on an area as small as 1μ in dia.; the composition of this area is determined by the analysis of the characteristic X-rays emitted.

Initial electron probe experiments with irradiated material were conducted to determine the limitations of the unshielded probe in analyzing irradiated specimens. A sample of UO_2 fuel irradiated to 1.0 a/o burnup and cooled for 1 year was chosen for the tests. The sample was specially mounted for insertion into the unshielded probe; the sample volume was kept to a practical minimum (0.05 in. in dia. by 0.007 in. thick). The radiation had a negligible effect on the instrument detectors and was not a hazard to the instrument operators. Increased radiation levels will be evaluated; it is expected that an increase by a factor of ten or more can be tolerated. A limited, but significant amount of work undoubtedly can be accomplished on the unshielded probe in this manner.

Electron probe analysis of the irradiated UO_2 specimen showed the presence of inclusions that contained large amounts of iron, and lesser amounts of nickel and chromium, a composition that is indicative of stainless steel.¹² The distribution of these elements in a selected area can be seen in Figure III-3, at a magnification of 800X. An optical image of the area is shown in Figure III-3a; Figures III-3b through III-3f are scanning images obtained with the electron probe microanalyzer. The brightness in the specimen current image (III-3b) is inversely proportional to the mean

¹²The presence of stainless steel inclusions is not unusual; such inclusions have been found in many unirradiated UO_2 samples.

a. Optical

b. Specimen Current Image

c. Iron $K\alpha$ X-ray Image d. Nickel $K\alpha$ X-ray Image e. Chromium $K\alpha$ X-ray Image f. Uranium $M\beta$ X-ray Image

Fig. III-3. Electron Probe Images of Stainless Steel
Inclusions in Irradiated UO_2 . (800X)

atomic number of the elements present, i.e., UO_2 appears dark gray, stainless steel appears light gray, and voids appear as white areas. The relative brightnesses in the X-ray images for iron (III-3c), nickel (III-3d), chromium (III-3e), and uranium (III-3f) are directly proportional to concentration.

No fission products were found in any of the inclusions examined. Particular emphasis was placed on attempts to detect the elements molybdenum, ruthenium, barium, zirconium, cerium, and lanthanum, which were found in inclusions in irradiated UO_2 by Bradbury et al.^{13,14}

An attachment for detection of low energy X-rays has recently been installed on the Division's electron probe. The soft X-rays are analyzed by dispersion with a lead stearate crystal. This system is capable of working down to the K-emission-wavelength range of nitrogen, carbon, and boron. Our interest in this capability is in its application to the analysis of uranium and plutonium ceramic fuels, particularly the oxides and carbides.

The major difficulty in the analysis of uranium carbide X-ray emission spectra is that the proximity of the uranium $\text{N}_{\text{VI}}\text{-O}_{\text{IV}}$ line at $43.6 \text{ \AA}$ to the carbon $\text{K}\alpha$ line at $44.7 \text{ \AA}$ does not allow quantitative analysis of each component. However, preliminary investigations suggest the possibility that the stoichiometry of various uranium carbides can be identified by monitoring the shape and peak wavelengths of the combined carbon $\text{K}\alpha$ and uranium $\text{N}_{\text{VI}}\text{-O}_{\text{IV}}$ emission band rather than by monitoring the X-ray intensity at a particular wavelength.

In these preliminary studies, the source of uranium carbides was the product of the reaction of molten uranium with graphite at 1770°C . Examination of various areas of the sample showed the presence of several uranium-carbon phases. Their descriptions and tentative identifications are as follows: (1) shiny, lustrous phase (UC_2), (2) porous black phase (UC), (3) brown dendrites (U_2C_3), and (4) blue-gray phase (mixed carbides).

Combined carbon $\text{K}\alpha$ and uranium $\text{N}_{\text{VI}}\text{-O}_{\text{IV}}$ emission bands of the four phases are presented in Figure III-4; emission spectra of metallic uranium and graphite are also shown for comparison. It can be seen from the figure that each uranium-carbon phase has an emission band of distinctive shape. The inhomogeneity of the mixed carbide phase was demonstrated by obtaining spectra at various locations within the phase; the shapes of the bands (one of which is shown in Fig. III-4) corresponded to various combinations of the other spectra.

¹³B. T. Bradbury, J. T. Demant, P. M. Martin, and D. M. Poole, "Electron Probe Microanalysis of Irradiated UO_2 ," AERE-R-4845 (1965).

¹⁴B. T. Bradbury, J. T. Demant, and P. M. Martin, "Solid Fission Products in Irradiated Uranium Dioxide," AERE-R-5149 (1966).

Fig. III-4. Carbon $K\alpha$ and Uranium $NvI-IV$ X-ray Emission Bands from Uranium, Graphite and Various Uranium-Carbon Compounds

We will try to establish the shapes of the carbon K -emission bands for the pure U-C phases and graphite as accurately as possible. The resolution and sensitivity of the microprobe probably can not be substantially increased but even a small increased resolution will make an appreciable improvement in the microphase analysis. The examples shown with uranium are the most difficult and complex because of the uranium interference. The plutonium carbides will not have this added complication.

b. Laser Pulse Vaporization

Laser pulse vaporization is being investigated as a microsampling technique. A small ruby laser coupled to an optical microscope has been tested. A precise sampling location can be made with a microscope, and a single laser pulse can be shot through the same optical system to vaporize holes 4 to 15 μ in dia. and 3 to 10 μ deep. (For reference, a hemispherical sample of UO_2 10 μ in dia. weighs $\sim 5 \times 10^{-9}$ g.) The vaporized material can be collected on a mounting material suitable for the analysis to be performed. Laser microsampling is expected to be a useful technique for preparing samples for mass spectrometry and for solid-state alpha and gamma-ray spectrometry.

C. Preparation of Reactor Materials

The preparation of ceramic fuels is being studied to develop processes which economically fit into appropriate fuel cycles, and to make well-defined fuel compounds for further experimental studies, particularly irradiation studies. At the present time, processes are being developed for the preparation of uranium and uranium-plutonium monocarbide fuels.

The fluidized-bed technique appears to be especially attractive for preparation of carbide fuels (see ANL-7175, p. 126); it affords efficient gas-solids contacting, and the product is a powder which can be fabricated into fuel pellets or densified for vibratory compaction into fuel elements. Two fluidized-bed processes are being developed for preparing monocarbides: (1) carburization of hydrided metal or alloy at 750 to 850°C and 1-10 atm pressure with methane-hydrogen gas mixtures, and (2) conversion of oxides at 1600 to 1800°C either by reaction with admixed carbon or with

a fluidizing gas containing methane. The former problem, currently requiring the larger effort, is discussed below. The latter, which is described in ANL-7225 is still in the equipment preparation stage and will not be discussed further.

1. Demonstration of Fluidized-bed Process for Preparation of (U,Pu)C

A series of twelve runs has been conducted in a 1 5/8-in. ID reactor to demonstrate the preparation of high purity (U, 15 w/o Pu)C by the fluidized-bed technique. In each run, 300 g of U-Pu alloy (3/8-in. dia. rods) was hydrided at 250°C to form a powder; this in turn was fluidized and reacted, usually at 800°C and 2-4 atm pressure, with methane-hydrogen gas mixtures to form the monocarbide. The run conditions and product analyses are shown in Table III-1.

TABLE III-1. Preparation of (U, 15 w/o Pu)C in a Fluidized-bed Reactor
(300-g scale, 3/8-in. dia. alloy rods hydrided at 250°C prior to carburizing)

Run No.	Carburizing Conditions					Product Analysis (w/o)				X-ray Analysis ^c	
	Temperature (°C)	Pressure (atm)	CH ₄ Conc. ^a (v/o)	Carburizing Time (hr)	Final H ₂ Treatment (hr)	Carbon	Oxygen	Nitrogen	Equivalent Carbon ^b	Major	Minor
1	750	4	10 ^d	6	0	4.11	0.04	- ^f	4.16	MC	βMH ₃
2	750	4	10 ^d	12	0	4.96	0.016 0.084 ^e	- ^f	4.99	MC	none
3	550-750	4	10	11.6	0	4.89	0.049	- ^f	4.95	MC	none
4	750	4	10 ^d	11.8	0	4.92	0.077 0.12 ^e	- ^f	5.00	MC	M ₂ C ₃
5	800	4	10	10.3	2	4.78	0.073 0.35 ^e	- ^f	4.85	MC	none
6	800	1.33 4 }	10	10.5	2	4.89	0.18	- ^f	5.05	MC	M ₂ C ₃
7	800	4	10	6.8	1.5	4.80	0.058	- ^f	4.86	MC	none
8	800	2	8	6.8	0.5	4.92	0.057	- ^f	4.98	MC	none
9	800	4	- ^g	11.4	2.5	4.76	0.02	0.008	4.79	MC	none
10	800	2	8	7.9	5.5	4.83	0.086	0.013	4.90	MC	none
11	800	2	8	7.0	0.6	4.64	0.12	0.016	4.74	MC	none
12	800	2	8	14.3	6.0	4.70	0.036	0.017	4.74	MC	none

^aBalance hydrogen.

^bOxygen and nitrogen are soluble in (U,Pu)C and replace carbon in the lattice; therefore, the equivalent carbon concentration in weight percent, $C_{eq} = w/o\ C + (12/16)\ w/o\ O + (12/14)\ w/o\ N$.

^cM = (U, 15 w/o Pu).

^dNear the end of the run, CH₄ concentration was decreased to 2.5 v/o.

^eThe higher values were assumed to be due to sample contamination. These higher values were not used in the equivalent carbon calculation.

^fSpurious results; a value of 0.02 was assumed for calculating the equivalent carbon concentration.

^gVariable as follows: 0 to 0.8 hr, 1.0 v/o; 0.8 to 3.8 hr, 2.6 v/o; 3.8 to 6.5 hr, 5 v/o; 6.5 hr to end of carburizing, 10.0 v/o.

In these runs, the control of the carbon content and purity of the product were emphasized. Uranium-plutonium monocarbide that is stoichiometric or slightly hyperstoichiometric with respect to carbon is

the preferred carbide fuel for fast reactors. The methods for controlling the carbon content of the product in this series of runs were: (1) adjusting the methane concentration in the methane-hydrogen fluidizing gas to prevent formation of free carbon; (2) stopping the reaction after the appropriate extent of carburization had been reached; and (3) treating with hydrogen at the end of the carburization period to remove excess carbon.

Fig. III-5. Effects of Process Variables on the Preparation of (U,Pu)C in a Fluidized Bed

The methane concentrations of the inlet and outlet gas streams were determined by infrared analysis. The rate of carburization was determined from the difference between the inlet and outlet methane concentrations and from the gas flow rate. It was thus possible to plot the extent of carbiding versus time, and to determine the effects of various changes in the reaction conditions on the rate of carbiding. These effects are illustrated in the data from runs 6, 7, and 11 in Figure III-5.

From the twelve experiments, it was concluded that the operating conditions of pressure, temperature, and methane concentration should be chosen such that free carbon would not form, since formation of free carbon inhibits carbiding. This inhibiting effect is demonstrated in the initial portion of run 6 (Figure III-5) in which free carbon was deposited during operation at low pressure. The subsequent increase in the pressure caused the removal of the free carbon with a resultant

increase in the reaction rate. However, even under conditions that did not produce free carbon, the rate of carbiding decreased when a carbon content of about 4.2 w/o was reached (stoichiometric monocarbide contains 4.8 w/o carbon). When this occurred, the rate could be increased by treating the bed with pure hydrogen either at lower temperatures (below 400°C) to cause rehydriding (run 7 of Figure III-5), or at the carbiding temperature to remove a higher carbide (sesquicarbide) reaction layer (run 11 of Figure III-5).

The low impurity levels obtained in these runs (Table III-1) indicate that the reactant gases, methane and hydrogen, introduce very small amounts of impurities, a conclusion that is in agreement with calculations based on the flow rates and the impurity contents of the gases.

The carbon contents of the last six runs, in which a final hydrogen treatment was employed, ranged from 4.70 to 4.92 w/o. It is anticipated that this range will be narrowed even further when process conditions are optimized.

Sieve analyses of the carbide products showed an average particle size of about 40 to 60 μ . This relatively fine material is suitable for fabrication into pellets by pressing and sintering, with no intermediate processing. Preliminary work on pressing and sintering of one batch of this material has shown that densities in excess of 90% of theoretical can easily be obtained (see ANL-7267, p. 59 and ANL-7279, p. 27).

An analysis of the data on rates of reaction indicated that it is possible to prepare 100 kg of (U,Pu)C by this process in a period of 10 to 12 hr if the carbiding is carried out at a pressure of 10 atm and a reactor of suitable size (8 in. in dia.) is employed. This rate of production is sufficient to resynthesize fuel from three 1000 MW(e) nuclear power reactors.

Equipment design and operational concepts that would be applicable to a large-scale, remotely operated fluidized-bed process are being tested in the preparation of UC on a scale of 1 to 2 kg per batch. The fluidized-bed reactor for this work is being operated under the following conditions: 10 atm pressure, recirculation of the fluidizing gas, automatic methane concentration control, and pneumatic discharge of the product to an external receiver. Further details on this work are given in ANL-7225.

In summary, the fluidized-bed method appears to be well suited both for preparation of high-purity (U,Pu)C for irradiation testing and for a remotely operated process for resynthesis of carbide fuels from feed material obtained by pyrochemical reprocessing.

2. Thermobalance Experiments

Thermobalance experiments were continued to determine equilibrium conditions and to obtain data on the kinetics of the reaction of hydrocarbon gases with uranium-plutonium alloys. These experiments will assist in determining the proper carburization conditions for the fluidized-bed production of uranium-plutonium monocarbide. In recent experiments uranium-20 w/o plutonium alloy samples were reacted with methane-hydrogen gas mixtures to determine the equilibrium methane concentration for the reaction

The equipment and procedure were described previously (ANL-7175, p. 128). Briefly, the procedure consists of reacting about 3 g of metal with hydrogen at about 250°C in the thermobalance to yield finely divided

hydride, and then reacting the hydride at 650 to 810°C with a hydrogen-hydrocarbon mixture. The carburizing gas flow is begun as soon as hydriding is complete in order to prevent sintering as the temperature is raised. The change in weight of the sample is recorded as a function of time.

From data of earlier experiments (ANL-7175, p. 128), the equilibrium methane concentration for the above reaction was determined to be <1 v/o at 750°C and 1 atm pressure. In those experiments the reaction rate was very rapid; formation of the monocarbide was completed in two or three hours in some instances. After installation of a gas purification system to decrease oxygen contamination, the equilibrium methane concentration was found to be much lower than that observed previously and the reaction rate was lower, 24 hr being required to form the monocarbide. In a recent experiment at 750°C, 1 atm pressure, and a methane concentration of 0.25 v/o, the weight of the carbide product continued to increase at a rate of 0.11 mg/hr after the theoretical weight gain for stoichiometric monocarbide was achieved. The weight increase beyond the stoichiometric value was due to the formation of the sesquicarbide. When the methane flow was terminated (i.e., the gas was pure hydrogen), the weight gradually decreased, indicating decomposition of the sesquicarbide to the monocarbide.

Evaluation of this experiment indicates that the equilibrium methane concentration for the system $(U, 20 \text{ w/o Pu})C$, $(U, 20 \text{ w/o Pu})_2C_3$, CH_4 , and H_2 is less than 0.25 v/o CH_4 at 750°C and 1 atm pressure. This would yield a free energy change more negative than -7 kcal/mole of $(U, 20 \text{ w/o Pu})_2C_3$ at 750°C for the reaction:

The higher reaction rates which were found in the earlier experiments with impure gases were probably the result of imperfections in the lattice structure due to the presence of interstitial oxygen and nitrogen.

D. Calorimetry

The Calorimetric Laboratory is determining the thermodynamic properties of substances of interest in high temperature chemistry and nuclear technology. Two basic types of data are being obtained: standard enthalpies of formation at 25°C ($\Delta H_f^\circ_{298}$) and high temperature enthalpies relative to 25°C ($H_T^\circ - H_{298}^\circ$).

Fluorine reaction calorimetry has been developed to obtain the enthalpies of formation of substances not amenable to more conventional types of calorimetry (oxygen combustion, solution, etc.). Fluorine has been used as an oxidant both in bomb and flow calorimeters.

Two high temperature enthalpy calorimetric systems of the drop type have been designed and constructed. One employs a resistance-heated furnace for use up to a maximum of 1500°C; the other employs an electron-bombardment-heated furnace for use up to 2500°C. Both systems employ receivers which are aneroid, copper-block calorimeters. An adiabatic calorimeter has also been constructed to serve as a receiver. It may also be used for direct measurements of heat capacity from room temperature to several hundred degrees C.

1. Standard Enthalpies of Formation

The standard enthalpies of formation which have been measured during this report period are summarized in Table III-2. The table also lists the various kinds of samples employed and indicates whether the ΔH_f° values were directly or indirectly determined. While the values for all the substances studied were of intrinsic scientific interest, it may be useful to record some of the technological reasons for these specific studies. Tungsten hexafluoride is widely used for the deposition of thin, protective tungsten coatings on objects. The thermodynamics of the reaction of WF_6 with hydrogen in the vapor-plating process are of interest. Uranium monosulfide and monophosphide are potential nuclear fuels. Thorium tetrafluoride has been an intermediate in thorium metal production and a suggested breeder blanket material. Carbon tetrafluoride is an end product of the fluorination of all organics and of inorganic carbides. As such, it is necessary to establish its enthalpy of formation with the same kind of accuracy as required

TABLE III-2. Standard Enthalpies of Formation

Compound	$-\Delta H_f^\circ$ ^a (kcal mol ⁻¹)	Sample Arrangement
$WF_6(g)$	411.5 ± 0.4	Suspended W foil
UP(c)	81	UP powder in Ni crucible
US(c)	73	Sintered US pellet in Ni crucible
$ThF_4(c)$	505.2	Stacked Th foils; ThF_4 bomb liner
$CF_4(g)$	222.7	Graphite flakes in Ni crucible
$PF_3(g)$	228.8	PF_3 and F_2 gases interact on opening valve
$ErF_3(c)$	406	Er granules on ErF_3 disk
$HoF_3(c)$	406.5	Ho granules on HoF_3 disk
$LaF_3(c)$	415	La foil on LaF_3 disk

^aData given without uncertainties are unpublished and should be considered preliminary.

of carbon dioxide for oxygen bomb calorimetry. Phosphorus trifluoride has the unusual property of acting as a defluorinating agent (e.g., reacting with UF_6 to produce UF_4 and PF_5), and may find many uses as an auxiliary calorimetric reactant. Finally, the enthalpies of formation of erbium, holmium, and lanthanum trifluorides were required to complete a study of the variation of crystal lattice energy with lattice parameter in the rare earth trifluorides.

Although all the determinations involve oxidation with fluorine gas, four different techniques were employed. A single-chambered bomb was used to determine ΔH_f° values for ErF_3 , HoF_3 , LaF_3 , and ThF_4 . For WF_6 , UP, and PF_3 , a two-chambered reaction vessel¹⁵ for spontaneously combustible materials was used. (The reaction of F_2 with PF_3 is the first all-gas reaction that we have used to determine enthalpy-of-formation data.) For CF_4 , a sturdier two-chambered reaction vessel (see Figure III-6) was constructed and used because of the need to contain fluorine at higher pressures. For US, the fluorine flow calorimeter (see Figure III-7) was used.

Fig. III-6. Calorimetric Apparatus for Determination of Enthalpy of Formation of CF_4 . The graphite sample and fluorine are kept separate within a high-pressure two-compartment bomb (A) until the combustion is carried out within the calorimeter (B). Temperature rise of the calorimeter is measured semiautomatically by electronic equipment consisting of a programmer (C), an electronic timer (D), and a thermometer (E) from which leads to the quartz-crystal sensors can be seen. The printer (F) provides simultaneous print-out of time-temperature data.

¹⁵R. L. Nuttall, S. Wise, and W. N. Hubbard, *Rev. Sci. Instr.* **32**, 1402 (1961).

Fig. III-7. Flow Calorimetric System. The calorimeter (A) and its surrounding constant-temperature water bath (B) are shown in the lowered position. The sample is contained in the reaction vessel (C) which is attached by tubing to the calorimeter lid (D) and the water-bath lid (E). Flowmeters (F) measure the flow rates of gases entering the reaction vessel. The exiting gases pass through an analytical train, part of which, the weighable U-tubes (G), can be seen.

The completion and operation of the higher pressure two-chambered reaction vessel and of the fluorine flow reaction system considerably extends the number of reactions that can be studied.

The preceding report (ANL-7175, p. 141) indicated that thermochemical data for plutonium compounds were very sparse, and stated that because of the great need for additional data in this field, this laboratory was planning to explore various experimental methods for their accumulation. Since then the equipment for such a program has been acquired. A rotating-bomb calorimeter, gas-charging and -discharging manifold, balances, and other auxiliary equipment have been assembled within a glovebox in the Division's alpha radiation facility. The manifold is connected to a

vacuum system and to pressure tanks which supply fluorine, chlorine, oxygen, and argon. The entire system and the proposed operating procedures have undergone an extensive safety review, and exploratory combustions of plutonium in chlorine and fluorine have been made.

Fig. III-8. Electron-beam-heated Calorimetric System. The sample is suspended at the end of a tungsten rod in the furnace (A). Surrounding the sample is a rotating tantalum cylinder which is heated by a pair of opposed electron guns (B) and which, in turn, radiantly heats the sample. Sample temperature is measured by an automatic optical pyrometer (C) via an optical viewing port and prism located below the furnace. At the appropriate time, the drop mechanism (D) plunges the sample into a copper-block calorimeter located below the optical viewing port. Temperature rise of the copper block is measured by platinum resistance or quartz-crystal thermometry.

density, allowed faster heating of the calorimeter, and, hence, more nearly simulated the time-temperature characteristics of a drop. A constant-temperature water bath, a temperature controller, and a circulating pump maintain the calorimeter jacket temperature constant to within $\pm 0.002^\circ\text{C}$.

A solution calorimeter is being designed to function as part of the rotating-bomb calorimeter in the glovebox. This calorimeter, when finally completed and tested, will further increase the number of possible reactions which can be employed to obtain thermochemical properties of plutonium compounds.

2. High Temperature Enthalpies

A highlight of the past year was the completion of the 2500°C , electron-beam-heated, calorimetric system for measurement of high temperature enthalpies (see Figure III-8). Copper-block calorimeter II, with its associated optical viewing port and water-cooled shutter, has been assembled. Provision was made for measuring the temperature of the block with either a capsule-type, platinum resistance thermometer or a quartz-crystal thermometer. The design of the electrical heater around the receiver well was changed to provide more surface area. This resulted in a lower power

Electrical calibration of the calorimeter has been carried out with both thermometers. The quartz thermometer provided as precise results as the platinum resistance thermometer. It has the advantage that reading and recording of data are considerably simplified by automatic print-out. Check-out runs on tungsten slugs have been made at random temperatures up to 2000°K. Because of the small heat capacity of the furnace section and the speed of the electrical calibration runs, the entire system seems to be readily adaptable to making multiple runs each day.

E. Chemistry of Liquid Metals

1. Thermodynamic Properties of Liquid Binary Alkali Metal Solutions

The alkali metals are simple metals for which the nearly-free-electron model and similar approximations are reasonably valid. Accordingly, the electronic structures and properties of their binary alloys should be more amenable to theoretical calculation than those of non-alkali metal alloys. Many such calculations have been done, e.g., Christman^{16,17} has recently calculated the thermodynamic properties of all the binaries which form among sodium, potassium, rubidium, and cesium. Comparisons of any of these calculations with measurements are hampered by the unavailability of experimental values for the excess entropy of mixing of the alloys. The purpose of the present study, therefore, was to obtain reliable values for the excess Gibbs energies of selected binary alkali metal alloys and to combine these with reliable values¹⁸ for the enthalpies of mixing to obtain entropies of mixing. The requisite data are being obtained by determination of the activities of one or both components in selected alloys.

The method is that of vapor-phase absorption spectrophotometry. Resonance radiation characteristic of an alkali metal is beamed through the vapor over the pure alkali metal or its alloys. The absorption is a measure of the partial pressure of monomeric alkali metal in the vapor. Comparison of the absorption by the alloy (p_i) to that by the pure metal (p_i^0) yields the activity ($a_i = p_i/p_i^0$) of that metal in the alloy. Activities were determined in this way for sodium and potassium in Na-K alloys, rubidium in Rb-Cs alloys, and sodium in Na-Rb alloys.

a. Na-K Alloys

Data for the Na-K system, the first in the series to be studied, were reported previously.¹⁹ Strong evidence for ordering was found;

¹⁶J. R. Christman and H. B. Huntington, Phys. Rev. 139A, 83 (1965).

¹⁷J. R. Christman, private communication.

¹⁸T. Yokokawa and O. J. Kleppa, J. Chem. Phys. 40, 46 (1964).

¹⁹ANL-7175, p. 151.

the partial molar excess entropy of sodium in dilute solution in potassium was surprisingly large and negative (-1.6 eu). This loss of entropy was interpreted in terms of sodium-sodium pairing. Stabilization of the pair was attributed to the fact that the volume of two sodium atoms is nearly equal to that of one potassium atom. From this model and simple thermodynamic arguments, it follows that the activity of sodium in very dilute solutions may not obey Henry's Law; instead, to the extent that in these solutions sodium is dimeric rather than monomeric, its activity should vary as the square root of the sodium atom fraction. To test these deductions and thereby the validity of the model, the concentration dependence of sodium activity in the range between 0.1 and 0.01 atom fraction Na will be measured. It should be noted that if future activity measurements support the pairing model, the existence of a molecule in a liquid alloy will have been demonstrated.

b. Rb-Cs Alloys

Rubidium-cesium alloys, unlike all other binary alkali metal alloys, form exothermally.¹⁸ Because thermodynamic data for systems with negative as well as positive enthalpies of mixing are desirable for testing theory, the Rb-Cs system was studied.

Absorption measurements were made with the 7800 Å rubidium line. Over the short temperature span of the measurements (42 to 47°C), no variation of activity outside of experimental uncertainty was observed. The measured activities were adjusted to 111°C, the temperature of available enthalpy-of-mixing data, by means of the equation

$$\frac{\partial \ln a_{\text{Rb}}}{\partial T} = - \frac{\bar{L}_{\text{Rb}}}{RT^2}$$

in which $\bar{L}_{\text{Rb}}$, the partial molar enthalpy of mixing of rubidium, was calculated from the data of Yokokawa and Kleppa.¹⁸ Table III-3 gives for each

TABLE III-3. Thermodynamic Activities and Excess Thermodynamic Functions of Rb in Rb-Cs Alloys at 111°C

a/o Rb	a_{Rb}	γ_{Rb}	$\bar{G}_{\text{Rb}}^{\text{xs}}$ (cal/g-atom)	$\bar{L}_{\text{Rb}}^{\text{a}}$ (cal/g-atom)	$\bar{S}_{\text{Rb}}^{\text{xs}}$ (eu)
20.3	0.199 ± 0.006	0.98 ± 0.03	-16 ± 23	-75.6 ± 3.0	-0.16 ± 0.06
35.5	0.362 ± 0.010	1.02 ± 0.03	15 ± 23	-49.5 ± 2.0	-0.17 ± 0.06
51.9	0.534 ± 0.016	1.03 ± 0.03	23 ± 23	-27.5 ± 1.1	-0.13 ± 0.06

^aCalculated from data of ref. 18.

of three Rb-Cs alloys, the thermodynamic properties found for rubidium, namely, the activity (a_{Rb}), the activity coefficient (γ_{Rb}), the partial molar excess Gibbs energy ($\bar{G}_{\text{Rb}}^{\text{xs}}$), the partial molar enthalpy of mixing, and the partial molar excess entropy ($\bar{S}_{\text{Rb}}^{\text{xs}}$).

The two most significant results of this investigation are that (1) γ_{Rb} does not differ from unity by more than its uncertainty, and (2) $\bar{S}_{\text{Rb}}^{\text{xs}}$ is small and approximately constant at -0.15 ± 0.06 eu. Because γ_{Rb} is so close to unity, the Gibbs-Duhem relationship requires that γ_{Cs} also be near unity. Hence, if enough data were available to compute ΔG^{xs} , the excess Gibbs energy of mixing, there is little doubt that its value would be small. The Rb-Cs system is probably as close to ideal as any liquid metal solution known.

Since the deviation of γ_{Rb} and γ_{Cs} from unity at other compositions is not likely to be larger than the experimental uncertainty, continuation of this study was not considered worthwhile. Consequently, measurements on the Rb-Cs system were discontinued.

Fig. III-9. Variation of Sodium Activity with Composition in Na-Rb Solutions at 143°C

c. Na-Rb Alloys

To determine whether or not order exists in liquid sodium binaries other than Na-K, the sodium-rubidium system is being studied.

Preliminary data on the variation of sodium activity with composition over the range 23 to 70 a/o Na at 143°C are shown in Figure III-9. It is evident that sodium and rubidium form solutions which exhibit significant positive departures from ideality. The departures are

more positive than those in the Na-K system.²⁰ This result is consistent with expectations based on measured enthalpies of mixing.¹⁸

To complete the study of the composition dependence of the sodium activity, additional measurements will be made on alloys more dilute in sodium than 23 a/o.

²⁰ ANL-6925, p. 95; ANL-7055, p. 81.

2. Solubility of Argon in Liquid Sodium

The solubility of the rare gases in liquid alkali metals is being measured. Interest in these solutions arises from two general considerations. (1) The rare gases dissolve as neutral atoms;^{21,22,23} hence the attractive interaction responsible for solution is believed to arise principally through polarization of the rare gas atoms by the ions of the metal. (2) The electronic structures of the alkali metals are better understood than those of other metals; hence the use of the alkali metals as solvents simplifies the evaluation of the repulsive interaction factor.

Solubility data for the argon-sodium and krypton-sodium systems were reported previously.²⁴ Subsequent reevaluation of the procedure used with argon revealed that not all of the argon dissolved in the sodium had been recovered for analysis. Consequently, a new series of argon solubility experiments was carried out. The present argon solubilities are about 2.5 times larger than those measured earlier.

The pressure (P) dependence of the solubility (x) at 480°C is shown in Figure III-10. The data may be represented by the Henry's Law equation $x = K_H P$. The mean value of the Henry's Law constant (K_H) calculated by the method of least squares is $5.49 \pm 0.47 \times 10^{-9} \text{ atm}^{-1}$ (95% confidence level).

Fig. III-10. Solubility of Argon in Liquid Sodium at 480°C vs. Pressure (Henry's Law)

The dependence of the Henry's Law constant on temperature is shown in Figure III-11. These results may be represented by the equation

$$\log K_H = -2.130 - 4542 T^{-1} \quad (330 \text{ to } 530^\circ\text{C}) \quad (1)$$

which reproduces the data with an uncertainty of 18% at the 95% confidence level. From equation 1, the enthalpy of solution of argon in liquid sodium is $20.8 \pm 2.0 \text{ kcal/mole}$.

The solubility and enthalpy of solution of argon in liquid sodium have been calculated according to models proposed by McMillan,²⁵ Johnson and Shuttleworth,²¹

²¹G. W. Johnson and R. Shuttleworth, *Phil. Mag.* **4**, 957 (1959).

²²G. W. Johnson, *Phil. Mag.* **6**, 943 (1961).

²³H. S. Slotnick, R. E. Cleary, and S. M. Kapelner, TID-21583 (1965).

²⁴ANL-6875, p. 48.

²⁵W. G. McMillan, BNL-353 (T-63) (1955).

Fig. III-11. Henry's Law Constant vs. Temperature in the Argon-Sodium System (330-530°C)

and Pierotti.²⁶ The first two models yielded solubilities which were several magnitudes larger than the measured values, whereas the hard-sphere model of Pierotti yielded solubilities comparable with the measured values. Furthermore, although the enthalpy of solution calculated by either of the first two models was considerably smaller than the observed, the enthalpy of solution calculated by the hard-sphere model of Pierotti was of the right magnitude. Further study of the solubility of gases in liquid alkali metals is expected to yield data which will permit further refinement of the hard-sphere model.

3. Nature of Carbon in Sodium

It has been established that various metals may be significantly carburized or decarburized when in contact with liquid sodium. This phenomenon presents a potentially serious objection to the use of sodium in nuclear reactors because very

small changes in carbon content may produce undesirable changes in the mechanical properties of structural materials, such as steel. Various proposals have been set forth regarding the mechanism of carbon transport in the presence of liquid sodium, but none has been generally accepted. We have proceeded on the assumption that a better understanding of carbon transport might commence from a better understanding of the nature of carbon species in sodium.

Experience has shown that the nature of the carbon-bearing species, as well as their amounts, varies with the prior history of the sample. Accordingly, all characterization experiments were performed on one large source of United States Industrial Co. reactor-grade sodium which, typically, contained a total of 32 ± 5 ppm of carbon. On the basis of information²⁷ obtained from aqueous dissolution, filtration, mass spectrometric, and optical spectroscopic experiments, this carbon was shown to be distributed as follows: ~ 6 ppm as Na_2CO_3 , either in solution or as particles fine enough to pass through a 5μ -porosity stainless steel filter; ~ 1 ppm as CH_4 , NaCH_3 , or metal carbide; less than 1 ppm as NaCN , $\text{Na}_6(\text{CO})_6$, or Na_2C_2 ; and at least 14 and possibly as much as 25 ppm elemental carbon, most (but not all) of which is removable by a 5μ filter.

²⁶R. A. Pierotti, J. Phys. Chem. **67**, 1840 (1963).

²⁷ANL-7175, pp. 143-146.

The existence of micron-sized, carbon-bearing particles in sodium made it apparent that the true solubility of carbon could be determined only if it were possible to differentiate between carbon which dissolves and carbon which pre-exists in sodium as nonfilterable carbonaceous material. Because early solubility experiments by Gratton²⁸ seemed inadequate to make this distinction, the solubility of elemental carbon in sodium was measured using amorphous carbon labeled with ^{14}C . The use of this tracer not only allowed the required discrimination, but also increased the sensitivity of the measurements manyfold. Concentrations of ^{14}C -labeled carbon as low as 5 parts in 10^9 parts of sodium could be detected.

The radioactive carbon (specific activity 2.4×10^6 dpm/mg) was added to 300 g of liquid sodium in the form of a pellet (135 mg). The total carbon content of the sodium charge (32 ± 5 ppm) was determined by a lengthy series of analyses. Samples of sodium filtered through stainless steel (5μ porosity) were withdrawn periodically over four months from a stirred and settled melt at various temperatures up to 450°C . The average total carbon content of the samples was 9.8 ± 3.2 ppm. No trend with time or temperature was apparent; thus, two thirds of the total carbon in this particular batch of sodium was ascertained to be particulate material which did not pass through a 5μ filter. The remaining third of the carbon was either dissolved or of smaller particle size than 5μ , but it could not have been in equilibrium with solid carbon because none of the samples contained any significant amount of radiocarbon. It thus appears that the true solubility of elemental carbon in liquid sodium is less than 0.005 ppm up to 450°C .

As noted above, a wealth of experimental evidence has been accumulated which strongly indicates that carbon-bearing materials, varying in size and nature, are dispersed in reactor-grade sodium. Approximate calculations showed that unless the density difference between the suspended particles and liquid sodium were very small, segregation of the suspended material should be possible by centrifugation at achievable speeds. Experiments to test the feasibility of centrifugal segregation of carbon were performed. However, it was decided to use a Na-44 w/o K alloy (m.p. 19°C) as an expedient substitute for sodium because of the temporary unavailability of a high-speed centrifuge capable of operation at temperatures above the melting point of sodium.

The alloy, which contained 52 ± 9 ppm total carbon, was sealed in stainless steel centrifuge tubes. The tubes were then centrifuged either (1) at 17,000 rpm ($\sim 35,000$ g) for 40 minutes and then incrementally slowed to a stop during the next 20 minutes, or (2) at 40,000 rpm ($\sim 130,000$ g) for $3\frac{3}{4}$ hours. In the latter experiment, the centrifuge was cooled to 0°C during

²⁸J. C. Gratton, KAPL-1807, June 30, 1957.

the last 1 1/2 hours in order to freeze the alloy while it was still spinning. To prevent remixing, the tubes were cooled by immersion in liquid nitrogen and then transferred to a glovebox where they were opened and warmed slowly to room temperature. Samples withdrawn from the top of the liquid by pipette were analyzed for carbon. After centrifugation at either speed, the top layers contained 26 ± 3 ppm of carbon. Statistical analysis of the results based on eight samples indicated that there was a significant (95% confidence level) segregation of suspended, carbon-bearing material; the direction was that expected for a solid which is denser than the supporting liquid. The segregation attained was probably not the maximum achievable; some redistribution of small particles by convection and vibration was likely during melting and sampling. Nevertheless, the results are sufficiently encouraging to warrant further investigation of size distribution of particles in liquid sodium by means of a heated, high-speed centrifuge.

Segregation of carbon has also been observed in other experiments. For example, when reactor-grade liquid sodium was drawn up into clean quartz or stainless steel tubes (10-mm ID) and allowed to freeze, the sodium adjacent to the tube walls was found to contain significantly greater (>3 X) concentrations of carbon than the central cores. The connection between this segregation and the size distribution of the particulate matter is being examined further.

IV. REACTOR SAFETY

The program on reactor safety is concentrated in two areas of research: (1) studies relating to thermal (water-cooled) reactors, and (2) studies relating to fast (sodium-cooled) reactors.

A. Thermal Reactor Safety Studies

In water-cooled reactors, coolant failure or a severe nuclear excursion could cause the reactor core metals to melt and disperse rapidly in the water. Chemical reactions between the metals and water could result in the release of energy approaching or exceeding the energy released by the fission process during a nuclear excursion. The dispersion of molten materials in the water coolant can also cause an explosive energy release as demonstrated in the destructive tests of SPERT 1 (Special Power Excursion Reactor Test) and BORAX-1 (Boiling Reactor Experiment). Studies of these chemical reactions and physical interactions¹ are being carried out so that realistic estimates can be made of the rates and extents of reactions and interactions occurring during hypothetical reactor accidents. Both nuclear excursion and loss-of-coolant accident simulation experiments are under investigation. In addition, calculational studies are being made in which the experimental results are correlated and methods of accident analysis are developed.

1. Nuclear Excursion Accident Simulations in TREAT

One general method of studying metal-water reactions involves nuclear heating of typical reactor fuel materials submerged in water. A series of eighteen photographic experiments was carried out in the Transient Reactor Test (TREAT) facility to obtain additional information on the in-pile behavior of aluminum-clad fuel materials. In these experiments, high-speed color motion pictures were taken of small samples of aluminum-clad fuel submerged in 30°C water during their exposure to transient bursts of neutrons in TREAT. Two types of fuel samples, SPERT 1-D and HFIR (High Flux Isotopes Reactor), were used in these experiments. The two fuel types showed qualitatively similar behavior in the extents of metal-water reaction observed. In each case, no significant reaction was noted until a threshold fission energy input was reached; from this point on, the extent of reaction increased fairly rapidly with increasing energy input. The sequence of events during the nuclear transient is illustrated for a sample of SPERT fuel

¹For the purposes of this report, the studies of the physical interactions (pressure pulse and transient heat transfer) accompanying the dispersal of molten materials in water coolant are discussed together with similar work being done in sodium coolant under Fast Reactor Safety Studies. This is because of the similar nature of the experimental and theoretical work involved in both.

Sample Heating,
Water Boiling

Sample Melting

Sample Melted,
 H_2 Bubbles Evolve

Initiation of Vapor-
phase Reaction

Vapor-phase
Reaction

Sample Fragmenting

Fragments Reacting

Fig. IV-1. Selected Frames of High-Speed Motion Picture of SPERT Fuel Undergoing a Nuclear Transient in TREAT

in Figure IV-1 in which selected frames of the high-speed film are shown. Detailed results are reported in ANL-7225.

As a result of these photographic studies, plus the earlier non-photographic TREAT studies (see ANL-7175, p. 171), the following qualitative description of the aluminum-water reaction in the TREAT experiments now seems evident.

- 1) Below temperatures of 1750°C, the reaction of aluminum is characterized by the formation of a protective oxide and the evolution of hydrogen bubbles. The samples rapidly quench after the nuclear burst and only limited reaction occurs.
- 2) At 1750°C, an ignition (owing to the onset of vapor phase burning) occurs in which self-heating raises the sample temperature several hundred degrees (to >2000°C).
- 3) In subcooled water (30°C), violence due to agitation of the water causes fragmentation of the sample. The extent of reaction depends on the violence and time of quenching of individual particles.
- 4) In heated water, no fragmentations have been noted even though ignition and very extensive reactions do occur at the higher energies.

Experiments were also continued in TREAT to investigate the safety problems associated with the behavior of metal-clad, UO_2 -core fuel rods. Recent experiments were performed to extend to higher fission energy inputs the correlations previously obtained with single pins. In addition, high-speed motion pictures have been taken to characterize the response of the fuel pins to destructive neutron bursts in TREAT. A comparison of the pressure-time records from all of the experiments performed with single UO_2 -core pins clad with Zircaloy-2 indicates that with a nuclear energy input of less than 400 cal/g UO_2 , the pressure rise rate is modest, being of the order of 100 psi/sec. For meltdowns with energy inputs of 500 cal/g UO_2 or more, the rise rate is invariably a few thousand psi/sec, increasing progressively with energy input. Between 400 and 500 cal/g, either behavior can occur. The final equilibrium pressure is the sum of the partial pressures of the hydrogen evolved, the water vapor, and helium² at the temperature of the test capsule. The results of several photographic experiments at input energies below 400 cal/g UO_2 indicated that both stainless steel and Zircaloy-2 cladding are very effective in containing molten UO_2 in an environment of subcooled water.

Experiments in TREAT using a scale-up autoclave (see ANL-7020, p. 186) were also continued. Two experiments were performed with bundles

²Test capsules are precharged with 15 psia helium.

of four Zircaloy-2-clad, vibrationally compacted (vibra-packed) UO_2 -core fuel rods submerged in 30°C water.

In one of these experiments, each rod was fabricated with 1500 psia helium internal gas pressure to simulate the pressure of fission product gases. The helium in the rods of the other bundle was at a pressure of 15 psia. The primary purpose of these two experiments was to compare the meltdown behavior in water of simulated fuel elements with and without a high internal gas pressure. The experiments also permitted a comparison of the behavior of vibra-packed UO_2 fuel with that of sintered UO_2 fuel used in previous experiments. Both bundles were subjected to approximately the same fission energy input (~ 470 cal/g UO_2). The extents of metal-water reaction and the average particle sizes of the fragmented fuels were nearly identical for the two bundles (see ANL-7225 for details). The cladding temperature records, however, indicated major differences in the two runs. For the rods with an internal helium pressure of 1500 psia, only about 30% of the total nuclear energy had been released when failure was indicated by the temperature record; apparently the high-pressure gas ruptured the cladding at a low temperature. For the rods with 15 psia internal helium pressure, approximately 85% of the total energy had gone into the rods when failure was indicated, apparently as a result of melting of the Zircaloy cladding. The peak pressures generated in these experiments with vibra-packed UO_2 were ~ 2.5 times as great as in similar experiments performed with sintered UO_2 -core fuel rods. The maximum pressure rise rates were ~ 100 times greater than in previous experiments with sintered fuels. Additional photographic-type experiments are being carried out with vibra-packed UO_2 fuel to characterize further its behavior during meltdown.

2. Loss-of-coolant Accident Simulation Experiments

A high-pressure furnace (see ANL-6875, p. 135) has been used for experiments designed to simulate the environment of the fuel of a water-cooled power reactor following a loss-of-coolant accident. Previous studies (ANL-7175, p. 164) of the reaction of single Zircaloy-2-clad and type 304 stainless steel-clad, UO_2 -core simulated fuel elements (8-in. long rods) with high temperature steam have been extended to include bundles of four such rods. The extent of reaction per rod of a 4-rod bundle with type 304 stainless steel cladding was approximately the same as that of single rods reacted under identical conditions. The extent of reaction per rod of a 4-rod bundle with Zircaloy-2 cladding was about twice that observed in single-rod experiments under identical conditions. The increased extent of reaction is attributed to self-heating, which was not observed in the runs with single rods.

Four experiments were also performed in the high-pressure furnace in an attempt to simulate the loss-of-coolant accident under conditions of limited steam flow rate. The Zircaloy-2-clad, UO_2 -core fuel rods,

oxidized under limited steam conditions, showed the development of a zone of concentrated reaction about $1/3$ of the way down from the top of the fuel rod. This was believed to be caused by a combination of a vertical temperature gradient (hotter at the top), which promoted reaction at the upper end of the rod, and the limited steam availability, which promoted reaction toward the lower end of the rod (steam flow direction upward).

An experiment was performed by induction heating of a single Zircaloy-2-clad, UO_2 -core fuel rod in an attempt to observe some of the features of the meltdown and collapse of the fuel rod. Although preliminary in nature, the experiment indicated that there was no tendency for the molten Zircaloy to drop from the fuel rod. The residue from the experiment indicated that there was some interaction between the molten Zircaloy and the UO_2 .

A series of three in-pile experiments in TREAT were completed which were also designed to simulate the meltdown phase of the loss-of-coolant accident. In each experiment a cluster of three Zircaloy-2-clad, UO_2 -core fuel rods was located above a pool of water and subjected to a "flat-top" transient in TREAT, in which fission heating remained reasonably constant over periods of 12, 32, and 50 sec, respectively, for the three experiments. Meltdown occurred in each experiment, and the total metal-water reaction for the three experiments varied from 30 to 44%. Encouraging results of the experiments were the absence of large quantities of very fine particles and the absence of "spike" pressure rises. Together these observations indicated that no steam explosions or very violent boiling occurred as the molten fuel material entered the water pool.

3. Calculation of the Extent of Metal-Water Reaction and Core Heating during a Loss-of-coolant Accident (CHEMLOC Program)

Analysis of the effect of the reaction of steam with fuel cladding metal in a loss-of-coolant accident in a water-cooled reactor has continued. The loss-of-coolant accident resulting from a break in a primary-system water pipe has been taken to be the "maximum credible accident" for most of the power reactors built to date. With such an accident, the decay energy in the core is sufficient to cause the fuel cladding to be heated within a few minutes to temperatures at which metal-steam reaction can occur.

In previous analyses using the proposed LOFT (Loss of Fluid Test) reactor as a model, calculations were made for 25-mil thick Zircaloy-clad and 15-mil thick stainless steel-clad, UO_2 -core fuel (see ANL-7020, p. 190 and ANL-7175, p. 173). In these analyses, the core was divided into 156 equal-volume segments, each of which was assigned to one of 10 groups according to its decay heating rate. The effects of heat transfer in the core by conduction, radiation, and convection, and the effects of unequal steam distribution to the various segments due to hydrogen formation were neglected in the analyses.

A recently developed Fortran computer program (designated CHEMLOC-I), which describes the core heating and chemical reaction up to the time of fuel melting, takes into consideration the effects of evaluating the temperatures of the gas, cladding, and fuel separately; the effects of transfer of heat by axial conduction in the cladding and fuel, by radial conduction between cladding and fuel, by radial radiation from cladding to cladding, and by convection between the cladding and the flowing gas; and the effects of changing hydrogen concentration in the steam.

For the analysis, the core is divided into a number of radial zones, each having the same number of fuel rods. The center zone is a cylinder while the remaining zones are annuli. The decay heating varies axially within each zone as well as radially from zone to zone. Steam enters the bottom of the core at a rate which may be constant or may vary with time.

As the steam flows upward through the core, the concentration of hydrogen increases due to chemical reaction of the steam with the cladding; thus, the cladding in the lower sections of the core tends to be contacted by gas having a higher steam concentration. Since, on reaction with the cladding, one mole of water vapor forms one mole of hydrogen, the molar flow rate of gas does not vary with vertical (axial) core position.

A heat and mass balance is made on an elemental section of a fuel rod together with the associated gas flow area (for details, see ANL-7267, p. 78). The heat generation and heat transfer terms are expressed in terms of (1) dimensions of core, fuel, cladding, and fuel rod; (2) densities, specific heats, thermal conductivities, diffusivities, and other physical properties of the fuel, cladding, steam, and hydrogen as functions of temperature; (3) chemical reaction rate constants; (4) reactor power and its variation over the core, and decay in fission product heating; (5) radiation emissivity; and (6) initial temperatures.

In the computer program, provisions are made to include other oxidizable surfaces, such as cans around subassemblies, and to include the heat capacity effects of materials, such as control rods, in addition to the fuel, fuel cladding, and cans.

The LOFT core was used as a model for the initial CHEMLOC-I calculations. The LOFT core consists of 3328 UO_2 fuel rods each 0.39 in. in dia. by 3 ft long with 0.025-in. thick Zircaloy-2 cladding. The rods are spaced on a square lattice with 0.58 in. between centers. The core was divided into 13 radial zones for purposes of the CHEMLOC calculations.

Computer calculations were made both for an initial core temperature of 285°C and for an initial core temperature distribution corresponding to the equilibrium temperature at operating power. Calculations

Percent Hydrogen in Steam
Leaving Top of Core

a

Temperature Profile Map (Approx.
10% of core at or above 2800°C)

d

Initial Core Temperature 285°C; Steam Flowrate 1000 lb/hr

b

e

Initial Core Temperature--That Corresponding to Operating Power; Steam Flowrate 1000 lb/hr

c

f

Initial Core Temperature--That Corresponding to Operating Power;
Steam Flowrate Initially 3600 lb/hr (Decreasing exponentially)

Fig. IV-2. Typical Data Excerpts from CHEMLOC-I Computations for a Loss-of-coolant Incident

were made for constant steam flow rates of 100, 1000, 5000, 7500, and 10,000 lb/hr and for a variable steam flow rate starting at 3600 lb/hr and decreasing exponentially with time.

Figure IV-2 (a, b, and c) shows typical computed results for the concentration of hydrogen in the gas leaving the top of the core from the various zones as a function of time. The data are for initial core temperatures and steam flow rates as indicated. (The crossing of the lines at zone 9 is caused by the increase in enrichment at zone 9.) When the core is initially at a temperature corresponding to operating power, the core is sufficiently hot for considerable steam-zirconium reaction to take place immediately (complete steam utilization in zones 1, 2, and 3, for example). The cladding is assumed to have an initial oxide film corresponding to 10^{-4} cm of metal; this causes an initial rapid oxidation since the chemical reaction rate is inversely proportional to the oxide thickness. As the oxide film increases, the oxidation rate decreases and then increases as the temperature increases.

Figure IV-2 (d, e, and f) shows temperature profile maps of the core for the conditions of Figure IV-2 (a, b, and c, respectively). Contour lines are shown for 1852°C (m.p. of zirconium) and 2800°C (m.p. of UO_2) at the time when approximately 10% of the core volume is at or above 2800°C .

Figure IV-3 shows the percent of cladding reacted as a function of time for various initial core temperatures and steam flow rates.

Fig. IV-3. LOFT Cladding Reacted as a Function of Time for Various Temperature and Steam Conditions. (CHEMLOC-I Calculations).

The computer calculations indicate that for an initial core temperature of 285°C, core heatup is prevented when the steam flow rate is 7500 lb/hr or greater. Fuel melting begins at times from 100 sec to over 1000 sec in every other case calculated. The CHEMLOC-I computer program has recently been extended to include assumptions regarding the mechanism by which the reactor core melts down (CHEMLOC-II). The extended program will provide a means of predicting the course of the accident through the period of core meltdown.

B. Fast Reactor Safety Studies

In sodium-cooled systems (fast reactors), coolant failure or a severe nuclear excursion could cause melting and rapid dispersion of reactor materials in the sodium. To assess these and other potential problem areas, the following studies relating to the safety of fast reactors are being carried out: (1) transient heat transfer associated with the dispersal of fuel and cladding materials into liquid sodium, (2) fuel migration and segregation in mixed uranium-plutonium compounds, (3) reaction of sodium with air, (4) high temperature physical properties of fast reactor materials, and (5) in-pile meltdown of typical fast reactor fuel materials.

1. Transient Heat Transfer Studies

Experimental studies of the transient heat transfer from small hot particles moving through liquid coolant are continuing. Knowledge of the rate and quantity of energy transfer that occurs between the fuel particles and the coolant is necessary in order to analyze the consequences of a reactor incident in which hot fuel materials may be dispersed into a liquid coolant (water or sodium). This study was initiated because neither theoretical nor experimental information was available to allow calculation of the heat transfer that occurs in such a situation.

Experimental studies of the heat transfer between small metal spheres and water or sodium have been carried out by the swinging-arm method, in which the heated sphere is either pulled or pushed through a tank of the appropriate coolant. Preliminary experiments with a gravity-powered swinging arm utilizing a 1/4-in. dia. nickel sphere passing through water were presented in ANL-7225. In recent experiments, motor-driven swinging arms have been developed for experiments in both water and in sodium. The sodium experiments are detailed below.

a. Studies in Sodium

The basic apparatus for the studies in liquid sodium consists of a motorized swinging arm with a 1/2-in. dia. tantalum sphere attached to the end of the arm (see Figure IV-4). (Tantalum was selected as the sphere material because of its high melting point and the ease with which it can be machined.) A W-5% Re/W-26% Re thermocouple is welded

into the sphere at a point just under the leading surface. The sphere is supported by a tantalum support tube attached to the shaft of a printed-circuit d-c motor. The sphere is heated inductively by the 3-turn coil shown in the figure. The angular velocity of the sphere assembly is measured with a photocell timing unit at the rear of the motor. The sodium is contained in a stainless steel tank which is located directly below the sphere assembly as shown in Figure IV-4. The entire assembly is housed in an argon-atmosphere glovebox.

Fig. IV-4. Sodium Heat Transfer Apparatus

In an experiment, the heated sphere is moved from the furnace through the sodium at a preset velocity, backward to a holding position at low velocity, and again into the furnace position.

Sodium temperatures of 300 and 450°C and sphere velocities of 6.0 and 10.0 ft/sec have been used in experiments. Initial sphere temperatures ranged up to 1980°C.

The data collected for each experiment consist of a temperature-versus-time measurement at the radial position corresponding to the location of the thermocouple junction. A typical temperature-time trace is shown in Figure IV-5. From this measurement for each experimental run, a series of values of the instantaneous sphere surface

temperature and heat flux are calculated using the method of Stolz.³ Results for a sphere velocity of 10.0 ft/sec and a sodium temperature of 300°C are given in Figure IV-6. Heat transfer rates up to 2700 cal/(cm²)(sec) were calculated from the data. Experimental results can be correlated by the following empirical expression

$$q/A = C(T_W - T_B)^{0.88}, \quad (1)$$

where

q/A = heat flux, cal/(cm²)(sec)

T_W = surface temperature of sphere, °C

T_B = sodium bulk temperature, °C

$C = 3.76 \text{ cal}/(\text{cm}^2)(\text{sec})(^\circ\text{C})^{0.88}$ for velocity = 10 ft/sec, $T_B = 300^\circ\text{C}$

$C = 2.82 \text{ cal}/(\text{cm}^2)(\text{sec})(^\circ\text{C})^{0.88}$ for velocity = 6 ft/sec, $T_B = 300^\circ\text{C}$

$C = 2.96 \text{ cal}/(\text{cm}^2)(\text{sec})(^\circ\text{C})^{0.88}$ for velocity = 10 ft/sec, $T_B = 450^\circ\text{C}$

Fig. IV-5. Temperature-Time Trace for 1/2-in. Tantalum Sphere Moving through Sodium

Fig. IV-6. Heat Flux vs. Surface Temperature for 1/2-in. Diameter Sphere Moving through Liquid Sodium ($U_\infty = 10.0 \text{ ft/sec}$, $T_{Na} = 300^\circ\text{C}$)

A check on the method of calculating instantaneous heat flux was employed in which the total heat loss from the sphere during the period of immersion in the sodium was calculated. The total heat loss computed from a summation of instantaneous values was compared with the total heat loss from the sphere determined from the difference in sphere temperature just before immersion and that after emergence from the sodium. A correction was included for the small heat loss rate to the argon environment after emergence of the sphere. Values of total heat loss computed by the two methods generally agreed within 10%.

³G. Stolz, Jr., "Numerical Solutions to an Inverse Problem of Heat Conduction for Simple Shapes," Trans. ASME, Series C, 82, 20 (1960).

Although theoretical studies of film boiling as related to heat transfer are being made, a simplified theory based upon potential flow has been used to study the experimental results. The assumption has been made that there is a vapor film surrounding the hot sphere which is thin in comparison with the radius of the sphere. Liquid velocity at the liquid-vapor interface was assumed to be unaffected by vapor drag and was therefore described by the laws of potential flow. It was also assumed that the sphere has a uniform surface temperature. (This assumption may be removed in a more refined treatment.) It was shown that thermal radiation could be neglected.

The development of the equations was based on an energy balance on a small element of vapor adjacent to the sphere surface. It was found that the heat used to form vapor in this element was negligible in comparison to the heat transferred from the element of vapor into the bulk sodium. The development of the equation describing the heat transferred from the liquid-vapor interface into the bulk sodium followed the general treatment outlined by Sideman.⁴ The resulting equation is

$$q/A = 1.13 \left[\frac{U_{\infty} \rho_{\ell} (C_p)_{\ell} k_{\ell}}{D} \right]^{1/2} (T_{\ell} - T_B) \quad (2)$$

where

U_{∞} = sphere velocity

ρ_{ℓ} = sodium density (liquid),

$(C_p)_{\ell}$ = sodium specific heat (liquid),

k_{ℓ} = sodium thermal conductivity (liquid),

D = sphere diameter,

T_{ℓ} = sodium interface temperature, and

T_B = sodium bulk temperature.

Calculations of heat fluxes based upon equation (2) are compared with experimental results in Figure IV-6. If it is assumed that the sodium boils at the saturation temperature, 883°C, at 1 atm pressure, without superheating, then $T_{\ell} = T_{\text{sat}}$ and the straight line in Figure IV-6 is obtained. It is apparent from Figure IV-6 that the experimental data show an increasing heat flux with increasing surface temperature. If it is assumed that the liquid-vapor interface temperature, T_{ℓ} , is the sphere surface temperature, T_w , i.e., complete superheating occurs, then the upper curve in Figure IV-6 is obtained. A good fit to the data is obtained

⁴S. Sideman, "The Equivalence of Potential Flow and Penetration Theory," Ind. Eng. Chem. 58(2), 55 (1966).

by using a constant fraction of the value calculated from equation (2) while substituting $T_\ell = T_w$ as follows

$$q/A = K \left[\frac{U_\infty \rho_\ell (C_p)_\ell k_\ell}{D} \right]^{1/2} (T_w - T_B) \quad (3)$$

The heat fluxes calculated by using a value of 0.675 for K are represented by the lower curve in Figure IV-6.

The thickness of the vapor film required to transfer these large quantities of heat is extremely small. For example, the thickness of the vapor film at the 90-degree position on a 1/2-in. dia. sphere at 1911°C moving at 10.0 ft/sec was calculated to be 7.6×10^{-6} in. Although the sphere surfaces were relatively smooth, it is believed that the magnitude of the roughness of the surface greatly exceeded this value. It is possible that protuberances on the sphere surface could extend through the vapor film into the liquid sodium. This would cause the film to become unstable and possibly to collapse completely. This collapse would bring liquid sodium into contact with the sphere's surface which is at a high temperature. The sodium would then tend to assume the sphere surface temperature and could become highly superheated.

The agreement between experimental data and the theory that was developed by assuming superheating of liquid sodium indicates that this theory is adequate to describe the actual physical phenomenon. The physically unrealistic vapor film thicknesses that were calculated also tend to support the theory of superheating.

The results of this study indicate that large quantities of energy can be transferred from extremely hot spherical particles to highly subcooled liquid sodium without vapor formation.

b. Conclusions

Studies of energy transfer from very hot spheres to sodium and to water have shown the great importance of superheating. Recent experimental results indicate that water can remain in the liquid form in contact with a moving sphere at temperatures of the order of 300-400°C before transition to film boiling occurs. In sodium, there was no evidence for the development of film boiling even at the highest temperatures studied (~1800°C). These findings make it clear that future attempts to understand the overall process of explosive vapor generation must take the superheating phenomenon into account. Future studies will be aimed at determining the conditions required for vapor formation at lower sphere velocities.

2. Other Fast Reactor Safety Studies

Other studies undertaken during the past year are briefly described below.

Calculation of the effects of plutonium migration under a thermal gradient for initially homogeneous $\text{PuO}_2\text{-UO}_2$ fuels indicates that, while significant alteration of the Doppler shutdown capability is not likely in the cases considered, changes in the local composition because of the migration could lower the melting point of such regions. These regions might then be at a temperature near their melting point in certain reactor situations. Preliminary experiments to test the thermal gradient furnace for extended use are in progress (see ANL-7225). Pellets of $\text{UO}_2\text{-CeO}_2$ have been heated continuously for periods up to 500 hr. In the gradient obtained, approximately $1000^\circ\text{C}/\text{cm}$, pore migration toward the hotter end of the pellets was observed; columnar grain growth also occurred in this area.

The experimental study of the transient pressure and the aerosol produced by the liquid sodium-air reaction in simulated spray-type accidents is continuing. As part of this study, calculations have been carried out (see ANL-7225) for equilibrium conditions in sodium-air and sodium-air-water mixtures using a computer program designed to minimize free energy. An apparatus has been constructed in which a pneumatically operated piston will spray sodium through suitable orifices into a reactor chamber of known volume. Pressure generation rates, peak pressures and temperatures, and the nature and post-reaction behavior of the reaction products will be studied as functions of the initial conditions. Preliminary tests of the apparatus using water as the driven fluid have been made.

Studies have continued of the high temperature physical properties of materials that are important in the field of reactor safety. Experiments to measure the specific heat of molten UO_2 are progressing. The initial work has consisted of tests of the suitability of tungsten as an encapsulation material at temperatures above the melting point of UO_2 . Tests have been carried out using a wide variety of sources of tungsten and in no case was gross attack of the container observed (see ANL-7225). One crucible made from wrought tungsten tubing and filled with UO_2 was heated to about 3350°C for two minutes. A metallic precipitate (identified as tungsten by metallographic examination and electron microprobe analysis) was observed in the oxide (see Figure IV-7). The area shown contains a much higher than average tungsten concentration. Chemical analysis showed the O:U ratio to be unchanged from the initial $\text{UO}_{2.00}$ and revealed the presence of only 1.1 w/o tungsten in the residue. This and other experiments have shown the suitability of tungsten as a container material for UO_2 . Design and construction of an appropriate calorimeter system is also proceeding.

Fig. IV-7. Section of Tungsten Capsule Containing UO_2 after Heating to 3350°C for 1-2 min

Preparations have been initiated for a forthcoming series of energetic fuel meltdown tests in a sodium environment in TREAT. Design and construction of the in-pile assembly has been completed. Nine stainless steel-clad rods, 5 of which are fueled with 10%-enriched UO_2 pellets and 4 of which are unfueled, are located in an environment of liquid sodium. A piston which is coupled to a linear motion transducer is located directly above the liquid level. The liquid sodium is coupled directly to a pressure transducer. Records from the linear motion transducer and the pressure transducer are expected to yield the detailed course of the development of the pressure pulse resulting from fuel destruction.

V. ENERGY CONVERSION

Investigations of thermally regenerative galvanic cells and the chemical systems upon which they are based have continued. Thermally regenerative galvanic cells operate on a closed cycle, regenerating the reactants for the cell by thermal decomposition of the products from the cell, consuming heat from a nuclear reactor (or some other source) in the process. The reactants from the regenerator are returned to the cell, where they are again combined electrochemically to generate electrical energy. This process, which absorbs heat at a high temperature, and rejects heat at a lower temperature, has an efficiency which is Carnot-cycle limited. The proper design and operation of these systems depends on a thorough knowledge of the thermodynamics of the binary metal systems involved.

A. The Thermodynamics and Performance Characteristics of the Sodium-Bismuth Bimetallic Cell System

The thermodynamic study of the sodium-bismuth system, oriented to the needs of the regenerative galvanic cell program, has had two broad experimental aspects. These were the measurement of cell emf's and the determination of liquid-vapor equilibrium parameters.

Electromotive force measurements (see ANL-7225) were performed on cells of the type

The cell emf's were measured as a function of cathode composition (pure bismuth to 60 a/o sodium in bismuth) and cell temperature (550 to 1050°K). Under these conditions, the cathode consisted of either a single-phase liquid alloy or a saturated solution of NaBi or Na₃Bi in liquid bismuth.

Liquid-vapor equilibria were studied by means of transpiration experiments on sodium-rich systems at 1173°K and by total vapor pressure measurements as a function of temperature for a series of compositions ranging from pure sodium to 33.2 a/o sodium in bismuth. The total vapor pressure measurements were made by the quasistatic (Rodebush-Dixon) technique¹ and by the boiling point method.

An analysis of the results in terms of a thermodynamic model (quasi-ideal solution) was performed using the liquid-vapor equilibrium data for the temperature 1173°K. Since the emf measurements did not cover the entire composition range, they were not used in the overall interpretative

¹W. H. Rodebush and A. L. Dixon, Phys. Rev. 26, 851 (1925).

study. However, where feasible, the two sets of experimental data were compared. The quasi-ideal solution model was found to be capable of correlating the activity coefficients that were calculated from the liquid-vapor

Fig. V-1. Sodium-Bismuth System: Log of Activity Coefficients as a Function of Composition. The solid lines were calculated from the quasi-ideal solution treatment of the liquid-vapor equilibrium data and are based on the equilibrium constants $K_1(\text{NaBi}) = 3 \times 10^2$ and $K_2(\text{Na}_3\text{Bi}) = 2 \times 10^5$. Experimentally determined points for sodium (and corresponding points for bismuth derived from the sodium data by a graphical Gibbs-Duhem integration) at the temperature 1173°K are shown by $\bigcirc$. The broken lines were obtained from emf measurements at 700 and 950°K .

equilibria. In the application of this model, it was assumed that the compounds Na_3Bi and NaBi persist in the melt, and that the compound species behave ideally. Mathematical expressions were derived which interrelate the equilibrium constants for the formation of the compounds (K_1 for NaBi and K_2 for Na_3Bi), the activity coefficients of the components, and the system composition. The experimental data provided a starting point for the estimation of the equilibrium constants, and a computer aided in the refinement of the values of these constants to give the final fit which is shown in Figure V-1. The curves calculated from the quasi-ideal model are shown as solid lines. The data for sodium from the liquid-vapor equilibrium data are shown as points, as are the values for bismuth which were calculated from the experimental data for sodium by means of a graphical Gibbs-Duhem integration. Although the agreement between points and curves is good, the success of this treatment does not, of course, prove that the postulated molecules exist as such in the liquid metal. This question of the persistence of intermetallic compounds in liquid metals is still unsettled and requires additional clarification.

In the treatment of the emf data, it was found necessary to add a correction to the experimental cell potential-temperature-composition data to compensate for what appears to be a "mixed" ionic and electronic conductivity in the solid NaCl electrolyte. Mixed conductivity may be caused by the solubility of sodium metal in the solid NaCl . The dissolved sodium atom ionizes and the sodium ion is held in a cation vacancy in the crystal while the electron forms an F-center by becoming trapped in an anion vacancy. The electrons which are thermally excited from the F-centers into conduction bands cause the electrolyte to become electronically conducting.

The cell-potential correction, which ranged from 4 mv at 673°K to 36 mv at 973°K, was calculated by a comparison of the literature data²⁻⁴ for a cell containing a cathode alloy of 40 a/o sodium in lead to data gathered using a similar cell operated with a solid NaCl electrolyte.

A least-squares treatment was used to calculate an equation for the activity coefficients of sodium and bismuth from the corrected emf data. The calculated activity coefficients are shown in Figure V-1 as the two dashed curves. The emf of the sodium-bismuth cell as a function of cathode composition, calculated using the equation, is shown in Figure V-2. Cell temperatures of 700, 950, and 1050°K were arbitrarily chosen for the calculations. For comparison with these results, emf's were calculated for equivalent cells at 1173°K using the activity data obtained from the liquid-vapor measurements. The curve representing the vapor pressure results also appears in Figure V-2.

Fig. V-2. Calculated Emf's of the Cell: $\text{Na}(\ell)/\text{Na}^+\text{Electrolyte}/\text{Na in Bi}(\ell)$ as a Function of Cathode Composition. Dashed curves from emf data; solid curve from liquid-vapor equilibrium data.

By applying the Gibbs-Duhem relationship to the emf data, standard free energies of formation of solid NaBi and Na_3Bi were also calculated. These results are shown in Figure V-3 as a function of temperature.

²K. Hauffe and A. L. Vierk, Z. Elektrochem. **53**, 151 (1949).

³M. F. Lantratov, Russ. J. Inorg. Chem. **4**, 927 (1959).

⁴B. Porter and M. Feinleib, J. Electrochem. Soc. **103**, 300 (1956).

Fig. V-3

Standard Free Energy of Formation of Solid NaBi and Na₃Bi as a Function of Temperature (calculated from emf data)

Results from emf and vapor pressure measurements indicated that the sodium-bismuth system may be a suitable one for use in a thermally regenerative bimetallic cell because of the reasonably high cell emf's and the low vapor pressure of bismuth over the sodium-bismuth melt. The construction of a sodium-bismuth cell for test purposes was therefore justified. The characteristics of this cell are discussed below.

The high current density and low overvoltage characteristics of the sodium-bismuth cell, making it attractive as a secondary (or rechargeable) cell, were recognized early in the program (see ANL-7020, p. 215). Its long life was established by a successful 17-month test run (see ANL-7175, p. 201), using the 3-in. ID stainless steel cell shown in Figure V-4. Whether maximum current density had been achieved in the first tests (100-200 ma/cm²) was doubtful; therefore, the cell was modified by improving the anode current collector to the present configuration, a stainless steel spiral. An effort was also made to minimize the thickness of the molten-salt electrolyte (31.6 m/o NaCl, 53.2 m/o NaI, and 15.2 m/o NaF), in order to minimize the cell resistance. The electrolyte thickness was reduced from 1 in. to 5/32 in.

Fig. V-4
Sodium-Bismuth Cell

The cell voltage-current characteristics were determined at various temperatures from the melting point of the electrolyte (535°C) to 615°C ; typical curves are presented in Figure V-5. These points were determined for an interfacial sodium concentration of approximately 20 a/o in the cathode alloy. The curves are essentially linear except in the high-current regions; this indicates that no significant activation or concentration over-voltages exist at the electrodes. The internal cell resistance calculated from the slope of these curves is approximately 0.0136 ohm. This may be compared with a value 0.003 ohm calculated for the electrolyte resistance utilizing an estimated specific resistance of 0.34 ohm-cm. The difference between the two resistance values indicates that some improvement can be made in current collection.

Fig. V-5
Voltage-Current Characteristics of Sodium-Bismuth Cell

The cell was charged and discharged electrically at currents up to 50 amp (about 1.1 amp/cm^2) at temperatures 535°C to 615°C . Charging was usually initiated from the completely discharged state and was conducted at a constant current. The charge was terminated before the resistance-free cell voltage exceeded the decomposition voltage of the

electrolyte (~ 2.2 volts at normal cell temperature). At this point, the cell open-circuit voltage usually exceeded 1.2 volts, thereby indicating that the cathode-electrolyte interfacial sodium concentration was nearly zero. After a high current density charge, such as 1.1 amp/cm^2 , the bulk concentration of sodium was still considerably higher than that of the interface. Allowing the cell to stand on open circuit for a short time or reducing the charge rate made it possible to continue the charge to completion.

Discharging was usually initiated from the fully charged state, which was indicated by an open-circuit voltage of 1 volt or higher. In the heavy discharge region, i.e., above 0.88 amp/cm^2 , the interfacial concentration of sodium in the cathode alloy reached the concentration of solid alloy formation while the bulk sodium concentration was still considerably lower. The charge-discharge performance of the cell at high current densities should be improved by renewing the cathode interface, for example, by convective stirring of the bulk cathode alloy.

The charge-discharge operations were repeated over 50 times at various temperature levels with no signs of cell deterioration. The high current densities that were expected (on the basis of electrode reversibility observed during emf measurements) were obtained in this engineering device; values considerably in excess of the 1.1 amp/cm^2 already obtained seem achievable by reducing the internal resistance of the cell and by enhancing the rate of transfer of sodium in the cathode alloy.

B. Studies of Sodium Transfer in Bimetallic Cells

In bimetallic cells with sodium anodes and fused salt electrolytes, an undesirable mass transfer of sodium from anode to cathode occurs through the electrolyte, even on open circuit. This mass transfer is caused partly by diffusion and convection of metallic sodium dissolved in the electrolyte, and partly by the internal short-circuiting effect due to the electronic conductivity imparted to the electrolyte by the dissolved metallic sodium. In order to learn more about this self-discharge process, the corresponding rates of mass transfer of sodium in a small sodium-bismuth cell were observed at a constant current density of 250 ma/cm^2 (total current 0.896 amp), after initial thermal equilibration periods on open circuit, for electrolyte depths of 0.5 and 1.6 cm. The electrolyte consisted of the eutectic composition of NaI-NaCl-NaF. For each electrolyte depth, the initial cathode composition was varied while the cell temperature remained constant (569°C).

The results from the cell with an electrolyte depth of 0.5 cm indicated that the self-discharge rate is not dependent on the composition of the cathode in the range 0 to 27 a/o sodium in bismuth. The average coulombic efficiency was $78 \pm 2\%$; this loss of efficiency corresponds to a mass

transfer rate of $0.061 \pm 0.006 \text{ g}/(\text{hr})(\text{cm}^2)$ for an equilibration time of 30 min. The average specific conductivity of the electrolyte was $1.66 \pm 0.7 \text{ mho}/\text{cm}$.

For the cell in which the electrolyte depth was increased to 1.6 cm, the cathode composition again did not appear to affect the sodium transfer rate. However, variation of the equilibration time (6 to 45 min) apparently did affect the transfer rate, probably because of the greater thermal convection in the cells with the greater electrolyte depth. The average coulombic efficiency was $83 \pm 3\%$ and the average mass transfer rate was $0.043 \pm 0.009 \text{ g}/(\text{hr})(\text{cm}^2)$. The average specific conductivity of the electrolyte was $2.0 \pm 0.4 \text{ mho}/\text{cm}$.

These data indicate that the sodium transfer rate decreases with increasing electrolyte depth, as might be expected. However, the voltage loss in the electrolyte (the loss due to Joule heating) also increases with electrolyte thickness; therefore, a compromise must be sought to minimize the combined losses in a practical cell.

C. Engineering Materials Corrosion Studies

Potential construction materials for thermally regenerative galvanic cell systems are being evaluated with respect to corrosion by the liquid metals of interest. Static corrosion test results at temperatures up to 1000°C have been reported previously (ANL-7225). Dynamic corrosion tests have also been conducted, using thermal convection loops fabricated of selected test materials. A summary of the previous results was presented in ANL-7225. These results indicated that neither stainless steel nor carbon steel is suitable for use in a sodium-bismuth cell system at temperatures above 800°C with a temperature difference of more than 250°C between the cell and the regenerator. Recently, special efforts have been made to fabricate corrosion loops from some refractory metals. Loops made of molybdenum-30 w/o tungsten and tantalum have been tested. A Mo-30 w/o W alloy loop containing bismuth operated for 2488 hr at hot- and cold-leg temperatures of 1050 and 700°C , respectively; a tantalum loop containing 30 a/o lithium in tin operated for 110 hr before a heater failed. Both loops showed little or no corrosion. The results to date on both of these materials, although limited, are very encouraging. An adequate choice of refractory metals is available for use in the regenerator section and of certain ferrous alloys for use in the cell section.

D. Design, Construction, and Performance of a Raman Spectrophotometer for Use in the Investigation of Molten Salts

A better understanding of the behavior of molten salts may be gained from the identification of species and molecular associations (for example, complex ions, neutral molecules, pseudo-lattice structures) in these

systems. Raman spectra evidence is particularly suitable for providing such information. Unfortunately, commercially obtainable Raman spectrophotometers are not readily adaptable for use with high-temperature, corrosive molten salt samples. Therefore, a versatile, highly sensitive Raman spectrophotometer has been designed and constructed.

The source of excitation light is a Spectra Physics Model 125 continuous He-Ne gas laser with a nominal power output of 50 mW at 6328 Å. The sample containers are mounted on an optical bench which consists of a modified 6-ft lathe bed. The strength and rigidity of the lathe bed allows the experimenter flexibility in the use of special sample containers and furnaces. The Raman light scattered by the sample is analyzed in an f/6.8 Spex Model 1400 scanning double monochromator equipped with a pair of 103-mm-square, 1200 lines/mm gratings blazed for 7500 Å.

The double monochromator is, in effect, two monochromators operated in series. This series operation greatly reduces stray light and grating ghost intensities, and permits the study of weak Raman lines in the presence of high-intensity, directly reflected exciting light. The light passing through the double monochromator is detected with a specially selected R136 photomultiplier tube.⁵ The signal from the photomultiplier is amplified either by means of a d-c amplifier or, after chopping the laser beam with a conventional rotating sector disc, by means of a lock-in a-c amplifier. The a-c detection method eliminates most of the problems caused by black body radiation from molten salt samples. The amplified signal is fed to a strip chart recorder.

The LiH-LiCl system was chosen for initial Raman investigations because of the possibility of the formation of polynuclear ions in this system. However, the physical and chemical nature of the LiH-LiCl system poses several difficulties: (1) the molten LiH-LiCl mixtures react with all known window materials, (2) a hydrogen atmosphere is required to reduce dissociation of the LiH, (3) the sample must be maintained at temperatures of 500 to 800°C, and (4) the ionic bonding of any polymeric species present would probably result in low specific Raman intensities. These difficulties impose certain requirements on the apparatus; not only must the apparatus be capable of handling molten LiH-LiCl, but it also must have a sensitivity comparable to or greater than the sensitivity attainable with conventional samples.

The design and operation of a 45° mirror cell for use with corrosive molten-salt samples is illustrated in Figure V-6. A metal sample cell is used to contain the melt. A slot in the lid of the sample cell permits the entrance of the laser light and the exit of the Raman light. A metal

⁵ Manufactured by the Hamamatsu Television Co., Ltd.

45° mirror (4 in Figure V-6) immersed in the melt causes the laser beam to pass horizontally down the length of the melt. A large 45° mirror outside of the furnace allows the Raman light originating from the horizontal "rod" of illuminated sample to be focused on the vertical entrance slit of the spectrometer. The sample cell (1) is surrounded by a nickel block (6) containing a small wedge-shaped hole to provide for the necessary passage of light (8). The nickel block is enclosed in a quartz tube (7), thereby providing for a controlled atmosphere around the sample. Passage of a stream of purified hydrogen, in the direction indicated by the arrows, tends to prevent corrosive vapors of the sample from reaching the quartz jacket. The entire sample region is surrounded by a tube furnace which can be operated at temperatures up to 1000°C.

Fig. V-6. Sample Cell and Its Peripheral Apparatus

The effectiveness of the 45° mirror cell has been tested at 250°C with a molten $\text{NaNO}_3\text{-KNO}_3$ eutectic mixture. An example of the spectrum attainable with the molten nitrate sample is given in Figure V-7. In spite of the use of a high scanning speed ($325\text{ cm}^{-1}/\text{min}$) and a short time constant (1 sec), the line at $\sim 1650\text{ cm}^{-1}$ is clearly visible above the background noise. Janz and James⁶ using a conventional Hg arc excitation with Hg arcs surrounding a transparent quartz sample cell, were able to detect the 1650 cm^{-1} line photographically but were unable to observe this line when using photoelectric detection, even with their favorable sample geometry. One may, therefore, conclude that the Raman apparatus developed in this laboratory will allow the investigation of molten salts with at least the same sensitivity as can be achieved elsewhere with samples of more favorable geometry.

⁶G. J. Janz and D. W. James, J. Chem. Phys. 35, 739 (1961).

Fig. V-7. Raman Spectrum of Molten $\text{NaNO}_3\text{-KNO}_3$
Eutectic Mixture at 250°C

In the preliminary investigations of molten LiH-LiCl mixtures, samples have been maintained at 500°C for many hours with no appreciable discoloration of the quartz envelope or of the 45° mirror immersed in the melt. The results are not yet complete enough to be included here.

VI. NUCLEAR CONSTANTS

A. Neutron Capture Cross Sections

Neutron capture cross sections of reactor, structural, and control materials are needed in calculations of the breeding gain of fast reactors. These data are also useful for testing and improving theories of nuclear reactions, so that unknown neutron cross sections can be predicted from theoretical considerations.

Measurements of neutron capture cross sections are being made as a function of neutron energy between about 5 keV and 3 MeV (see ANL-7175, p. 212). The experimental technique is the activation method, in which a sample is irradiated in a monoenergetic neutron beam and the radioactive capture product is measured by counting it in a beta counter or a gamma-ray spectrometer. Monoenergetic neutrons are produced by bombarding lithium or tritium targets with protons from the Van de Graaff accelerator, and neutron intensity is measured with a fission chamber.

In Figures VI-1 to VI-8, the experimental results for 8 isotopes are plotted, along with the data of other investigators¹⁻¹⁰ when available.

Fig. VI-1. Capture Cross Section of ^{41}K

Fig. VI-2. Capture Cross Section of ^{55}Mn

- ¹R. Booth, W. P. Ball, and M. H. MacGregor, Phys. Rev. **112**, 226 (1958).
- ²D. J. Hughes, R. C. Garth, and J. S. Levin, Phys. Rev. **91**, 1423 (1953).
- ³Yu. Ya. Stavitsky and V. A. Tolstikov, Atomnaya Energiya **10**, 508 (1961).
- ⁴A. E. Johnsrud, M. G. Silbert, and H. H. Barschall, Phys. Rev. **116**, 927 (1959).
- ⁵R. L. Macklin, N. H. Lazar, and W. S. Lyon, Phys. Rev. **107**, 504 (1957).
- ⁶S. P. Kapchigashev and Yu. P. Popov, Atomnaya Energiya **15**, 120 (1963).
- ⁷I. Vervier, Nucl. Phys. **9**, 569 (1959).
- ⁸V. A. Konks, Yu. P. Popov, and F. L. Shapiro, Zhur. Eksp. Teor. Fiz. **46**, 80 (1964).
- ⁹R. L. Macklin, J. H. Gibbons, and T. Inada, Phys. Rev. **129**, 2695 (1963).
- ¹⁰J. H. Gibbons, R. L. Macklin, P. D. Miller, and J. H. Neiler, Phys. Rev. **122**, 182 (1961).

Fig. VI-3. Capture Cross Section of ^{85}Rb Fig. VI-4. Capture Cross Section of ^{98}Mo Fig. VI-5. Capture Cross Section of ^{141}Pr Fig. VI-6. Capture Cross Section of ^{175}Lu for Production of 3.7-hour State of ^{176}Lu Fig. VI-7. Capture Cross Section of ^{176}Yb Fig. VI-8. Capture Cross Section of ^{237}Np

The data are also compared with calculations using the statistical model of the compound nucleus, which gives the energy averages of resonant compound nuclear cross sections. The curves were calculated using the model in the form given by Moldauer¹¹⁻¹³ in which the average compound nuclear cross section for capture of neutrons of energy, E , is given by

$$\sigma_{\text{cap}} = \pi^2 \lambda^2 \sum_{J\pi} \frac{2J+1}{2I_0+1} \langle \Gamma_0^{J\pi} \rangle \rho_{J\pi} \frac{\langle \Gamma_{\text{cap}}^{J\pi} \rangle}{\langle \Gamma^{J\pi} \rangle} S^{J\pi} \quad (1)$$

where λ is the rationalized deBroglie wavelength of the neutron; I_0 is the spin of the ground state of the target nucleus; $\langle \Gamma^{J\pi} \rangle$ is the average total width of compound states with spin J , parity π , and density $\rho_{J\pi}$, at excitation energy $U + E$, where U is the neutron separation energy in the compound nucleus; $\langle \Gamma_0^{J\pi} \rangle$ is the average partial width for emission of elastic neutrons; and $S^{J\pi}$ is the width fluctuation correction factor.¹²⁻¹⁴

The calculations also take into account the variation of radiation width and level density with excitation energy and spin of the compound nucleus, and the variation of neutron widths from level to level (Porter-Thomas distribution).¹⁵ The Weisskopf¹⁶ formula for electric dipole radiation is used for the energy variation of radiation width. The level density, ρ (the reciprocal of the level spacing, D), is taken to have the form

$$\rho_{J\pi}(U+E) = K \left[e^{-J^2/2\sigma^2} - e^{-(J+1)^2/2\sigma^2} \right] e^{2\sqrt{a(U+E)}} \quad (2)$$

where σ is the spin-dependence parameter and a is related to the sum of neutron and proton single particle spacings, δ , by $a = \pi^2/6\delta$.

The computations were performed with the Nearrex¹¹ computer code for compound nuclear cross sections, combined with the Abacus-2 code¹⁷ for optical model transmission coefficients.

All of the fittings of theoretical curves to experimental points were made using the optical model parameters given in Table VI-1. In Table VI-2 are listed the values of the statistical parameters used for each nuclide. The values of a and σ were taken from the papers of Gilbert and

¹¹A. A. Moldauer, C. A. Engelbrecht, and G. J. Duffy, "Nearrex, A Computer Code for Nuclear Reaction Calculations," ANL-6978 (1964).

¹²P. A. Moldauer, Rev. Mod. Phys. **36**, 1079 (1964).

¹³P. A. Moldauer, Phys. Rev. **135**, B642 (1964).

¹⁴A. M. Lane and J. E. Lynn, Proc. Phys. Soc. (London) **A70**, 557 (1957).

¹⁵C. E. Porter and R. G. Thomas, Phys. Rev. **104**, 483 (1956).

¹⁶J. M. Blatt and V. F. Weisskopf, Theoretical Nuclear Physics, Wiley, New York, 1952, p. 649.

¹⁷E. H. Auerbach, "Abacus-2," unpublished.

Cameron¹⁸ or from Benzi and Bortolani.¹⁹ Only one statistical parameter, the ratio of the radiation width to the observed level spacing, $\Gamma_\gamma/D_{\text{Obs}}$, was varied to obtain the fittings. As a first choice for the value of the ratio, experimental Γ_γ and D_{Obs} were taken from Hughes et al.²⁰ when available. When Γ_γ was not known experimentally, it was estimated from the systematics of its variation with nuclear mass. When D_{Obs} was not known experimentally, it was calculated from the formula of Gilbert and Cameron.¹⁸ First choice values of the ratio are given in parentheses in Table VI-2 when one or both of these terms was estimated as described above. It is seen by comparing the first choice values with the values used (the last two columns of Table VI-2), that even when the shape of the curve has been predicted correctly, one cannot always get a good absolute fit using the first choice values of $\Gamma_\gamma/D_{\text{Obs}}$ which are available either experimentally or by estimate.

TABLE VI-I. Optical Model Parameters

Real potential depth	46 MeV
Imaginary potential depth	14 MeV
Real well radius	$R = (1.16A^{1/3} + 0.5) \times 10^{-13} \text{ cm}$
Real spin-orbit potential depth	7 MeV
Real well diffuseness	$0.62 \times 10^{-13} \text{ cm}$
Imaginary well width	$0.5 \times 10^{-13} \text{ cm}$
Imaginary well radius	$(R + 0.5) \times 10^{-13} \text{ cm}$

TABLE VI-2. Statistical Parameters

Nuclide	U (MeV)	σ	$a \text{ (MeV)}^{-1}$	$\frac{\Gamma_\gamma}{D_{\text{Obs}}} \times 10^4$ (first choice) ^a	$\frac{\Gamma_\gamma}{D_{\text{Obs}}} \times 10^4$ (used)
⁴¹ K	7.53	2	5.56	(1.0)	3.3
⁵⁵ Mn	7.27	4	7.52	(2.5)	2.8
⁸⁵ Rb	8.82	4	11.0	(62)	30
⁹⁸ Mo (curve 1)	5.94	4	13	(1.2)	3.4
⁹⁸ Mo (curve 2)	5.94	4	4.1	38	3.4
¹⁴¹ Pr	5.85	4	18	7.8	7.0
¹⁷⁵ Lu	6.29	6	21	165	436
¹⁷⁶ Yb	5.56	4	22	(14)	8.5
²³⁷ Np	5.38	6	28.5	310	880

^aValues given in parentheses indicate that one or both terms of the ratio was estimated (see text).

¹⁸A. Gilbert and A. G. W. Cameron, "A Composite Nuclear Level Density Formula with Shell Corrections," Institute for Space Studies, NASA, New York.

¹⁹V. Benzi and M. V. Bortolani, Nuovo Cimento 38(1), 216 (1965).

²⁰D. J. Hughes, B. A. Magurno, and M. K. Brussel, "Neutron Cross Sections," BNL-325, 2nd Edition (1960).

The theoretical curves are accurately fitted to the experimental data for ^{41}K , ^{55}Mn , ^{85}Rb , ^{98}Mo , and ^{141}Pr , at least up to neutron energies at which the levels of the target nucleus are known. A large change in the parameter a for ^{98}Mo (shown as curve 2 in Figure VI-4), provides an improved fit at the higher energies. Although experimental data for ^{237}Np is limited, it is expected that agreement with the theoretical curve would be obtained at lower energies. The curves for ^{176}Yb and ^{175}Lu do not fit, probably because these are nonspherical nuclei, for which the transmission coefficients are not correctly calculated by the spherical optical model; no reasonable changes in the parameters provide good correlation.

VII. DETERMINATION OF BURNUP IN FAST REACTOR FUELS

The program for the development of methods for measuring burnup in fast reactor fuels is continuing. To achieve the program's objective it is necessary not only to develop accurate analytical methods of determining the concentration of fission products that can be used as burnup monitors, but also to establish accurate fast fission yield values for these fission products.

A. Methods for the Determination of Fission Products

During the past year, two methods of determining fission product concentration in irradiated fuels have been under investigation. The status of each of these methods is discussed below.

1. Determination of Total Rare Earths

A method of determining burnup that employs the rare earth group of fission products as the monitor is being developed. The advantages of this method and the general approach were presented previously (see ANL-7175, p. 223). As presently conceived, the method consists of the following steps: (1) a chemical separation from uranium by coprecipitation of the rare earths on calcium fluoride, (2) an ion-exchange separation of the rare earths from other interferences, including yttrium, and (3) a titration of the rare earths with ethylenediaminetetraacetic acid (EDTA).

Because the success of this approach for monitoring burnup depends quite heavily on the yttrium-rare earth ion-exchange separation, experiments were performed with yttrium-90 tracer to confirm the separation. It was found that 99% of the yttrium passed through the column under conditions in which the rare earths would be quantitatively retained. It was concluded that this degree of yttrium decontamination is completely adequate.

The separation from uranium, in which the rare earths are coprecipitated on calcium fluoride, has been successfully demonstrated. Less than 0.4% of the uranium originally present is coprecipitated on the calcium fluoride; the rare earth recovery is 100%.

The compatibility of the calcium fluoride separation with the ion-exchange and titration steps was demonstrated, using lanthanum as a stand-in for the rare earths. Six aliquots containing 500- μ g quantities of lanthanum were subjected to the entire procedure. The results showed a relative standard deviation of $\pm 0.9\%$ with no significant bias.

The entire procedure is now being checked with a mixture of rare earths whose composition closely approximates that which will be formed by the fission process in a fast reactor fuel.

2. Determination of Praseodymium-141

During the past year a method of determining burnup using praseodymium-141 (stable) as the monitor has been perfected. The praseodymium content of the fuel is determined by neutron activation; requisite accuracy is provided by the use of an internal flux monitor. The use of praseodymium as a burnup monitor and preliminary investigations of the feasibility of the method were discussed in ANL-7175, pp. 223-224.

The separation of praseodymium from uranium, plutonium, and the other fission products is effected by fluoride and hydroxide precipitations of the praseodymium, using lanthanum as a carrier, and by ion-exchange separations. The most critical step in the procedure is the separation of praseodymium from the other rare earths. This is done by absorbing the rare earths onto a cation exchange resin and chromatographically eluting them with a solution of α -hydroxyisobutyric acid. Since the recovery of praseodymium ranges from 60 to 80%, praseodymium-142 tracer is added in known quantity prior to the separation procedure for the determination of the yield.

Manganese-55 is used as the internal flux monitor in the assay of the praseodymium. (Sodium, originally proposed as the flux monitor, proved unsatisfactory because the separated praseodymium was contaminated with sodium from reagents.) A known amount of manganese-55 is added to the separated praseodymium and this solution, along with standards containing known amounts of both praseodymium and manganese, is irradiated in the reactor. The solutions are then assayed for manganese-56 (2.6 hours) and praseodymium-142 (19 hours) by gamma spectroscopy, and the praseodymium concentration is calculated.

Measurements of the praseodymium-141 content of EBR-I, Mark III fuel have been made with an accuracy of $\pm 2\%$. (No absolute fission yield value can be calculated because there is no independent way of ascertaining the number of fissions which took place in this fuel.)

B. Irradiation in EBR-II

An irradiation is being carried out in EBR-II to provide materials for establishing fission yield values of the desired accuracy ($\pm 1\%$). Samples of the fissile isotopes of interest will be irradiated until a significant fraction ($\sim 25\%$) of the atoms have fissioned. (This will require an irradiation of several years.) The number of fissions that have occurred can then be determined with an accuracy of $\pm 0.5\%$ from the initial weight and from pre- and post-irradiation mass spectrometric-isotope dilution analysis. In most instances, the number of fission product atoms can also be determined with an accuracy of $\pm 0.5\%$, using such analytical techniques as spectrophotometry, mass spectrometry, and compleximetric titration. Thus, it is expected

that most of the fission yields can be established with an accuracy of $\pm 1\%$. The general philosophy underlying this portion of the program was discussed in ANL-7175, p. 222.

During the past year, the encapsulation of materials was completed, and the irradiation assembly was charged to EBR-II in December 1966. The irradiation assembly is made up of 20 small nickel capsules in a special EBR-II irradiation tube. Each of the nickel capsules contains a known amount (100 mg or less) of an actinide of high and known isotopic purity.

Included in this irradiation are not only the principal fissile isotopes of interest to the burnup program, namely, uranium-233, uranium-235, and plutonium-239, but also the isotopes uranium-238, plutonium-240, and plutonium-241. In fast reactor fuels, the number of fissions of ^{238}U , ^{240}Pu , and ^{241}Pu , relative to the total number of fissions, will be significant. It is necessary, therefore, to establish fission yields for these isotopes also. If the fission yield of a particular burnup monitor varies significantly with the source of fissioning, it will be necessary to use a corrected yield value to calculate burnup.

Because the heavy element isotopic composition of nuclear fuels is of great importance to reactor design, operation, and fuel processing, a study of the nuclear transformations which have occurred as the result of such reactions as n,γ and $n,2n$ will also be made. This study will be made on each of the uranium and plutonium isotopes, as well as samples of ^{232}Th and ^{237}Np which have been included in the irradiation.

ADDENDUM

Publications

by

Chemical Engineering Division
Personnel

(From January 1, 1966 to April 30, 1967)

A. Open Literature Publications

L. Anastasia, P. Alfredson, and M. Steindler

Oxidation and Fluorination of Simulated UO_2 - PuO_2 Fuels in a Fluidized-Bed ReactorTrans. Amer. Nucl. Soc. 9(2), 416-417 (November 1966).

M. Baerns

Effect of Interparticle Adhesive Forces on Fluidization of Fine Particles

Ind. Eng. Chem. Fundamentals 5(4), 508-516 (November 1966).

L. Baker, Jr.

Nonisothermal Reaction of Uranium with Water by the Condenser Discharge Method

Nucl. Sci. Eng. 25(2), 116-130 (June 1966).

L. Baker, Jr.

Review of Metal-Water Reaction Studies for Reactor Safety Analyses

Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, R-22. Abstract.

L. Baker

Metal-Water Reactions

Nucl. Safety 8(1), 20-25 (Fall 1966).

L. Baker, Jr. and J. D. Bingle

The Kinetics of Oxidation of Uranium Between 300 and 625°C

J. Nucl. Mater. 20(2), 11-21 (1966).

L. Baker, Jr., J. G. Schnizlein, and J. D. Bingle

The Ignition of Uranium

J. Nucl. Mater. 20(2), 22-38 (1966).

J. J. Barghusen, M. J. Steindler, D. Ramaswami, and A. A. Jonke

The Use of Bromine Pentafluoride in the Reprocessing of Low-Enrichment Nuclear Reactor Fuels

Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, R-42. Abstract.

- J. E. Brugger, R. L. Nuttall, A. T. Hu, D. R. Fredrickson, R. Kleb, and W. N. Hubbard
A 1500°C Drop-Type Calorimetric System: A Survey of its Construction and Testing
Abstracts. 21st Annual Calorimetry Conference, Boulder, Colorado, June 22-24, 1966, p. 5. Abstract.
- J. A. Buckham and N. M. Levitz (ed.)
Fluidized-bed Technology
Chem. Eng. Prog. Symp. Ser., 62, No. 67 (1966).
- N. R. Chellev and R. K. Steunenberg
Extraction of Plutonium from Uranium-Plutonium Alloy by Uranium Trichloride
Nucl. Appl. 3(3), 142 (1967).
- N. R. Chellev, R. K. Steunenberg, and J. D. Schilb
Preparation of Mg^{24} from $Mg^{24}O$
Nucl. Instr. Methods 44(1), 149-150 (September 1966). Letter.
- I. G. Dillon, P. A. Nelson, and B. S. Swanson
High Temperature-High Pressure Cell for Measuring Densities of Metals by a Radiation Counting Technique
Rev. Sci. Instr. 37(5), 614-619 (May 1966).
- I. G. Dillon, P. A. Nelson, and B. S. Swanson
Measurement of Densities and Estimation of Critical Properties of the Alkali Metals
J. Chem. Phys. 44(11), 4229-4238 (June 1, 1966).
- T. W. Eckels and A. Smaardyk
Design of a Shielding Window for a Nuclear Reactor Containment Cell
Trans. Amer. Nucl. Soc., 9(2), 618 (November 1966)/Proc. 14th Conf. on Remote Systems Technology, Pittsburgh, October-November 1966. Am. Nucl. Soc., Hinsdale, Ill., 1966, pp. 107-114.
- R. K. Edwards and A. E. Martin
Phase Relations in the Uranium-Uranium Dioxide System at High Temperatures
Proc. IAEA Symp. on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids, Vienna, July 22-27, 1965. Intern. Atomic Energy Agency, Vienna, 1966, Vol. 2, pp. 423-430.
- H. M. Feder
Chemistry in Liquid-Metal Solvents*
39th Ann. Priestly Lectures. Penn. State Univ., University Park, Penn. 1965, Part 2, pp. 111-133.
- A. K. Fischer
Vapor Pressure of Bismuth
J. Chem. Phys. 45, 375-377 (July 1, 1966).

*Also listed in ANL-7175.

- A. K. Fischer
Quasistatic Vapor Pressure Measurements on Reactive Systems in
Inert Atmosphere Box
Rev. Sci. Instr. 37(1), 717-719 (June 1966).
- M. S. Foster and C. C. Liu
Free Energy of Formation of Li_2Te at 798°K by an Electromotive
Force Method
J. Phys. Chem. 70(3), 950-952 (March 1966). Note.
- M. S. Foster, C. E. Crouthamel, and S. E. Wood
Thermodynamics of Binary Alloys. II. The Lithium-Tin System
J. Phys. Chem. 70, 3042-3045 (October 1966).
- D. R. Fredrickson, R. L. Nuttall, R. Kleb, and W. N. Hubbard
Electron Beam Heated High Temperature Enthalpy Calorimeter
Abstracts. 21st Annual Calorimetry Conference, Boulder, Colorado,
June 22-24, 1966, p. 5. Abstract.
- J. D. Gabor
Axial Solids Mixing in Fluidized-Packed Beds
Chem. Eng. Prog. Symp. Ser., 62(67), 35-41 (1966).
- J. D. Gabor
Fluidized-Packed Beds
Chem. Eng. Prog. Symp. Ser. 62(62), 32-41 (1966).
- D. M. Gruen, R. L. McBeth, M. S. Foster, and C. E. Crouthamel
Absorption Spectra of Alkali Metal Tellurides and of Elemental
Tellurium in Molten Alkali Halides
J. Phys. Chem. 70(2), 472-477 (February 1966).
- L. J. Harrison and R. O. Ivins
A Photographic Study of the Transient Meltdown Behavior of Aluminum/
Uranium Fuel Plates in Water
Trans. Am. Nucl. Soc. 9(1), 305 (1966). Abstract.
- J. C. Hesson and L. C. Witte
Comment on "Film Boiling Heat Transfer Around a Sphere in Forced
Convection" by K. Kobayasi
J. Nucl. Sci. Tech. 3(10), 448-449 (October 1966). Note.
- W. F. Holcomb, D. M. Paige, and L. F. Coleman
Operating Experience with the EBR-II Fuel Cycle Facility Inert Atmo-
sphere Cell
Nucl. Appl. 2, 254-255 (June 1966).
- J. T. Holmes and A. A. Jonke
Fluidized Bed Disposal of Fluorine
Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York,
Sept. 11-16, 1966, R-45. Abstract.

- J. T. Holmes and D. Ramaswami
Control Valves Eliminated from Reactor Cooling System
Chem. Eng., 73(24), 154 (Nov. 21, 1966). Note.
- W. N. Hubbard
Thermochemistry
Encyclopedia Britannica, Vol. 21, pp. 1010-1015 (1967).
- R. O. Ivins, J. C. Hesson, and R. E. Wilson
Chemical Reactions Accompanying a Hypothetical Loss of Coolant in a Water-Cooled Power Reactor
Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, R-23. Abstract.
- R. O. Ivins, R. C. Liimatainen, and F. J. Testa
Reaction of Uranium with Water as Initiated by a Power Excursion in a Nuclear Reactor (TREAT)
Nucl. Sci. Eng. 25(2), 131-140 (June 1966).
- R. O. Ivins
The Effect of the Chemical Reaction between Steam and Cladding on the Analysis of a Power Reactor Accident
ANL Reviews 3(1), 93-101 (October 1966).
- R. L. Jarry and M. J. Steindler
The Reaction of Gaseous Bromine Pentafluoride with Uranium Compounds
Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, R-41. Abstract.
- C. E. Johnson, S. E. Wood, and C. E. Crouthamel
Studies of Lithium Hydride Systems. II. Solid-Liquid Equilibrium in the Sodium Chloride-Lithium Hydride System*
J. Chem. Phys. 44(3), 880-883 (Feb. 1, 1966).
- C. E. Johnson, S. E. Wood, and C. E. Crouthamel
Studies of Lithium Hydride Systems. III. Solid-Liquid Equilibrium in the Lithium Bromide-Lithium Hydride and Lithium Iodide-Lithium Hydride Systems*
J. Chem. Phys. 44(3), 884-889 (Feb. 1, 1966).
- C. Johnson, E. J. Hathaway, and C. E. Crouthamel
Lithium Hydride Systems. Solid-Liquid Phase Equilibria for the Ternary Lithium Hydride-Lithium Chloride-Lithium Fluoride System
J. Chem. Eng. Data 11(2), 372-374 (July 1966).
- C. E. Johnson, R. R. Heinrich, and C. E. Crouthamel
Thermodynamic Properties of Lithium Hydride by an Electromotive Force Method*
J. Phys. Chem. 70, 242-246 (January 1966).

*Also listed in ANL-7175.

- G. K. Johnson, H. M. Feder, and W. N. Hubbard
Fluorine Bomb Calorimetry. XV. The Enthalpy of Formation of Boron Trifluoride*
J. Phys. Chem. 70(1), 1-6 (January 1966).
- G. K. Johnson and W. N. Hubbard
The Enthalpies of Formation of Crystalline and Amorphous Boric Oxide by Fluorine Bomb Calorimetry
Abstracts. 21st Annual Calorimetry Conference, Boulder, Colorado, June 22-24, 1966, p. 21. Abstract.
- G. K. Johnson, E. Greenberg, J. L. Margrave, and W. N. Hubbard
Fluorine Bomb Calorimetry. Enthalpies of Formation of the Diborides of Zirconium and Hafnium
J. Chem. Eng. Data 12(1), 137-141 (January 1967).
- I. Johnson, K. E. Anderson, and R. A. Blomquist
Partial Constitutional Diagrams for the Cd-La, Cd-Ce, Cd-Pr, Cd-Nd, and Cd-Sm Systems
Am. Soc. Metals Trans. Quart. 59(2), 352-355 (June 1966). Note.
- I. Johnson, J. B. Knighton, and R. K. Steunenberg
Thermodynamics of Dilute Solutions of Plutonium in Liquid Magnesium
Trans. Met. Soc. AIME, 236, 1242-1246 (September 1966).
- G. Kesser, R. J. Meyer, and R. P. Larsen
Spectrophotometric Determination of Ruthenium with 1-Nitroso-2-naphthol*
Anal. Chem. 38(2), 221-224 (February 1966).
- R. W. Kessie
Plutonium and Uranium Hexafluoride Hydrolysis Kinetics
Ind. Eng. Chem. Process Design Develop. 6(1), 105-111 (January 1967).
- M. Kilpatrick and S. K. Lott
Reaction of Flowing Steam with Refractory Metals. II. Rhenium (850-1700°C)*
J. Electrochem. Soc. 113, 15-16 (January 1966).
- M. Kilpatrick and S. K. Lott
Reaction of Flowing Steam with Refractory Metals. III. Tungsten (1000-1700°C)*
J. Electrochem. Soc. 113, 17-18 (January 1966).
- J. Knighton, W. Knoch, and R. K. Steunenberg
New Pyrochemical Process for Fast Breeder Reactor Fuels.
I. Process Chemistry
Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, R-9. Abstract.

*Also listed in ANL-7175.

- L. B. Koppel, R. D. Patel, and J. T. Holmes
 Statistical Models for Surface Renewal in Heat and Mass Transfer:
 Part I. Dependence of Average Transport Coefficients on Age
 Distribution
 A.I.Ch.E. (Am. Inst. Chem. Engrs.) J., 12(5), 941-946 (September 1966).
- L. B. Koppel, R. D. Patel, and J. T. Holmes
 Statistical Models for Surface Renewal in Heat and Mass Transfer:
 Part II. Techniques for Measurement of Age Distribution at Transport
 Surfaces.
 A.I.Ch.E. (Am. Inst. Chem. Engrs.) J., 12(5), 947-955 (September 1966).
- S. Lawroski et al.
 Reactor Fuel Process. 8(4), (Fall 1965)*
 Reactor Fuel Process. 9(1), (Winter 1965-1966)
 Reactor Fuel Process. 9(2), (Spring 1966)
 Reactor Fuel Process. 9(3), (Summer 1966)
 Reactor Fuel Process. 9(4), (Fall 1966).
- L. Leibowitz and L. W. Mishler
 A Study of Aluminum-Water Reactions at High Temperature Using
 a Laser
 Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York,
 Sept. 11-16, 1966, R-24. Abstract.
- R. C. Liimatainen, M. D. Freshley, and F. J. Testa
 Transient Irradiations of Vibrationally Compacted UO_2 Fuel in TREAT
 Trans. Amer. Nucl. Soc. 9(2), 395-396 (November 1966).
- R. C. Liimatainen and F. J. Testa
 Thermal Reactor Safety Studies on UO_2 Core Fuel Pin Clusters:
 Transient Meltdowns
 Trans. Amer. Nucl. Soc. 9(2), 561-562 (November 1966).
- J. O. Ludlow, L. F. Coleman, P. A. Nelson, J. H. Schraidt, and M. A. Slawewski
 High-Purity Helium Atmosphere for Plutonium Research
 Trans. Amer. Nucl. Soc. 9(2), 614-615 (November 1966/Proc. 14th Conf.
 on Remote Systems Technology, Pittsburgh, October-November 1966).
 Am. Nucl. Soc., Hinsdale, Ill., 1966, pp. 66-72.
- W. E. Miller, G. J. Bernstein, D. C. Hampson, R. F. Malecha, and
 M. A. Slawewski
 Fusible Metal Seals in Process Equipment
 Trans. Amer. Nucl. Soc. 9(2), 626 (November 1966/Proc. 14th Conf. on
 Remote Systems Technology, Pittsburgh, October-November 1966).
 Am. Nucl. Soc., Hinsdale, Ill., 1966, pp. 213-218.
- P. A. G. O'Hare and W. N. Hubbard
 Fluorine Bomb Calorimetry. XVII. The Enthalpy of Formation of
 Tungsten Hexafluoride
 J. Phys. Chem. 70(10), 3353-3355 (October 1966). Note.

*Also listed in ANL-7175.

- P. A. G. O'Hare, J. L. Settle, and W. N. Hubbard
Fluorine Bomb Calorimetry. Part 14--Enthalpies of Formation of the Hexafluorides of Sulphur, Selenium, and Tellurium and Their Thermodynamic Properties to 1500°K
Trans. Faraday Soc. 62(519), Part 3, 558-565 (March 1966).
- P. A. G. O'Hare and H. M. Feder
Bond Dissociation Energies in Some Fluorides of the Phosphorus and Sulfur Subgroups
Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, V-163: Abstract.
- P. A. G. O'Hare and W. N. Hubbard
Fluorine Bomb Calorimetry. Part 18--Standard Enthalpy of Formation of Phosphorus Pentafluoride and Enthalpies of Transition Between Various Forms of Phosphorus. Thermodynamic Functions of Phosphorus Pentafluoride Between 0 and 1500°K
Trans. Faraday Soc. 62(526), Part 10, 2709-2715 (October 1966).
- E. J. Petkus, A. D. Tevebaugh, C. C. Payne, and J. P. Bartos
The Synthesis of Stoichiometric Uranium Monocarbide in a Fluidized Bed by the Uranium Metal-Hydrocarbon Gas Reaction
Chem. Eng. Prog. Symp. Ser. 62(67), 76 (1966).
- J. A. Plambeck, J. P. Elder, and H. A. Laitinen
Electrochemistry of the Lithium Hydride Cell
J. Electrochem. Soc. 113(3), 67C (1966). Abstract.
J. Electrochem. Soc. 113(9), 931 (1966).
- C. F. Reinke, L. E. Robinson, and R. O. Ivins
High Temperature Thermometry--Service and Related Experience
Proc. High Temperature Thermometry Seminar, Washington, February 24-25, 1965; USAEC Report WASH-1067 (March 1966), pp. 22.1-22.3.
- J. W. Reishus
Vapor Species Over Potassium Amalgams
J. Phys. Chem. 70, 3348-3349 (October 1966). Note.
- E. Rudzitis, E. H. Van Deventer, and W. N. Hubbard
Fluorine Bomb Calorimetry. Enthalpy of Formation of Nickel Difluoride
J. Chem. Eng. Data 12(1), 133-135 (January 1967).
- J. G. Schnizlein, L. Baker, Jr., and J. D. Bingle
The Ignition of Binary Alloys of Uranium
J. Nucl. Mater. 20(2), 39-47 (1966).
- J. G. Schnizlein and D. F. Fischer
The Kinetics of Oxidation of Plutonium Metal and a Plutonium-3.4 a/o Aluminum Alloy at Temperatures from 140° to 550°C
J. Electrochem. Soc. 114(1), 23-29 (January 1967).

- M. J. Steindler and T. J. Gerding
Absorption Spectrum of Neptunium Hexafluoride
Spectrochim. Acta 22, 1197-1200 (June 1966).
- D. L. Swift
The Thermal Conductivity of Spherical Metal Powders Including the Effect of an Oxide Coating
Int. J. Heat Mass Transfer 9(10), 1061-1074 (1966).
- H. G. Swope
Dose Distribution in the Argonne High Level Gamma Irradiation Facility
Atompraxis 12(8), 398-401 (August 1966).
- L. E. Trevorow, M. J. Steindler, and D. V. Steidl
Condensed Phase Equilibria in the System $\text{MoF}_6\text{-UF}_6$
Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, 0-47. Abstract.
- L. E. Trevorow, R. P. Wagner, and M. J. Steindler
Studies of the Properties of Plutonium Hexafluoride in the Development of a Volatility Method for Nuclear-Fuel Reprocessing
Trans. Am. Nucl. Soc. 9(1), 22-23 (June 1966). Abstract.
- E. Veleckis, R. V. Schablaske, I. Johnson, and H. M. Feder
Intermetallic Phases in the Systems of Zinc with Lanthanum, Cerium, Praseodymium, Neodymium, and Yttrium
Trans. Met. Soc. AIME 239, 58 (1967).
- W. J. Walsh, I. O. Winsch, R. D. Pierce, and L. Burris, Jr.
New Pyrochemical Process for Fast Breeder Reactor Fuels.
II. Uranium Transport Experiments
Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, R-10. Abstract.
- R. E. Wilson, C. Barnes, Jr., R. Koonz, and L. Baker, Jr.
Isothermal Reaction of Uranium with Steam Between 400 and 1600°C
Nucl. Sci. Eng. 25(2), 109-115 (June 1966).
- R. E. Wilson, L. Baker, Jr., and C. Barnes, Jr.
 UO_2 -Steam Reaction at 1500°C
Trans. Am. Nucl. Soc. 9(1), 24 (1966). Abstract.
- R. E. Wilson and C. Barnes, Jr.
Isothermal Studies on the Stainless Steel-Steam Reaction
Abstracts of Papers Presented at Am. Chem. Soc. Meeting, New York, Sept. 11-16, 1966, R-25. Abstract.
- S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard
Fluorine Bomb Calorimetry. XVI. The Enthalpy of Formation of Boron Nitride*
J. Phys. Chem. 70, 7-10 (January 1966).

*Also listed in ANL-7175.

- J. Wolkoff, D. A. Woodward, and A. J. Strecok
A Thermocouple for the Measurement of the Surface Temperature of a Liquid Metal
Chem. Eng. Sci. 21, 895-903 (October 1966).
- E. N. Ziegler and J. T. Holmes
Mass Transfer from Fixed Surfaces to Gas Fluidized Beds
Chem. Eng. Sci. 21, 117-122 (1966).
- B. Papers Accepted for Publication in the Open Literature
- L. Baker, Jr. and R. C. Liimatainen
Chemical Reactions
Accepted for publication as Chapter 17, Vol. 2 of The Technology of Nuclear Reactor Safety, MIT Press.
- F. A. Cafasso, V. M. Khanna, and H. M. Feder
Thermodynamic Properties and Ordering in Liquid NaK Alloys
Accepted for publication in Advan. Phys.
- C. Crouthamel and H. Recht (eds.)
Regenerative Galvanic Cells
Accepted for publication as an American Chemical Society monograph.
- A. K. Fischer
Phase Diagram Considerations for the Regenerative Bimetallic Cell
Accepted for publication as chapter in Regenerative Galvanic Cells, monograph, American Chemical Society.
- A. K. Fischer, S. A. Johnson, and S. E. Wood
Liquid-Vapor Phase Diagram and Thermodynamics of the Sodium-Bismuth System
Accepted for publication in J. Phys. Chem.
- M. S. Foster
Laboratory Studies of Intermetallic Cells
Accepted for publication as chapter in Regenerative Galvanic Cells, monograph, American Chemical Society.
- J. C. Hesson and H. Shimotake
Thermodynamics and Thermal Efficiencies of Thermally Regenerative Bimetallic and Hydride EMF Cells
Accepted for publication as chapter in Regenerative Galvanic Cells, monograph, American Chemical Society.
- R. L. Jarry and M. J. Steindler
The Reaction of Gaseous Bromine Pentafluoride with Uranium Compounds. I. The Kinetics of the Reactions with UF_4 and UO_2F_2
Accepted for publication in J. Inorg. Nucl. Chem.

- C. E. Johnson and R. R. Heinrich
Thermodynamics of LiH Regenerative Cell
Accepted for publication as chapter in Regenerative Galvanic Cells,
monograph, American Chemical Society.
- C. E. Johnson and M. S. Foster
Purification of Gases for Inert Atmosphere Enclosures
Accepted for publication in Nucl. Sci. & Eng.
- C. E. Johnson, S. E. Wood, and E. J. Cairns
Reply to Comments of Bredig (On Lithium Hydride-Alkali Halide
Systems)
Accepted for publication in J. Chem. Phys.
- R. W. Kessie
Removal of Plutonium Hexafluoride from Cell Exhaust Air by
Hydrolysis and Filtration
Accepted for publication in the 9th AEC Air Cleaning Conference,
TID report (USAEC).
- C. Luner, A. Cosgarea, Jr., and H. M. Feder
Solubility of Carbon in Sodium
Accepted for publication in International Atomic Energy Agency
Symposium on Alkali-Metal Coolants - Corrosion Studies and System
Operating Experience, IAEA, Vienna, Austria.
- H. Shimotake and J. C. Hesson
Corrosion by Fused Salts and Heavy Liquid Metals
Accepted for publication as chapter in Regenerative Galvanic Cells,
monograph, American Chemical Society.
- M. J. Steindler, N. M. Levitz, and A. A. Jonke
Development of Fluoride Volatility Methods for Reprocessing Reactor
Fuels
Accepted for publication in Proceedings of XXXVIth International Con-
gress on Industrial Chemistry, Brussels, Belgium, 10-21 September, 1966.
- A. D. Tevebaugh, L. Baker, and D. Swift
Explosive Heat Transfer at Liquid-Liquid Interfaces*
Accepted for publication in Symposium on Molecular Processes in
Chemical Engineering, University of Rochester (publisher).
- L. E. Trevorow, M. J. Steindler, D. V. Steidl, and J. T. Savage
The Melting-Point Diagram for the System Uranium Hexafluoride-
Plutonium Hexafluoride
Accepted for publication in Inorg. Chem. as a Note.
- L. E. Trevorow, M. J. Steindler, D. V. Steidl, and J. T. Savage
Condensed Phase Equilibria in the System Molybdenum Hexafluoride-
Uranium Hexafluoride
Accepted for publication in Advan. Chem. Ser.

*Also listed in ANL-7175.

- I. O. Winsch, M. L. Kyle, R. D. Pierce, and L. Burris, Jr.
Tungsten Crucibles in Pyrochemical Processing of Nuclear Fuels
Accepted for publication in Nucl. Appl.
- T. F. Young
Some Aspects of Equilibrium in Electrolytic Solutions
Accepted for publication in First Conference on the Biology of Hard
Tissue, Ann Budy, ed.; New York Academy of Science, New York (1967).
- C. ANL Reports
- L. J. Anastasia, J. D. Gabor, and W. J. Mecham
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 3. Fluid-bed Fluorination of Uranium Dioxide Fuel Pellets*
ANL-6898.
- I. G. Dillon, P. A. Nelson, and B. S. Swanson
Critical Temperatures and Densities of the Alkali Metals*
ANL-7025.
- T. W. Eckels and L. F. Coleman
Estimated Temperatures of EBR-II Fuel Cycle Facility Shielding Win-
dows at Gamma Radiation Level of 3.5×10^5 rad per hour
ANL-6853.
- T. W. Eckels and A. Smaardyk
Design, Performance, and Evaluation of Shielding Window for FARET
Containment Cell
ANL-7157.
- J. P. Elder
Electrode Kinetics*
ANL-7072.
- J. T. Holmes, H. Stethers, and J. J. Barghusen
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 8. Pilot-plant Development of a Process for Uranium Alloy Fuels*
ANL-6973.
- J. T. Holmes and D. Ramaswami
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 9. Computer Programs for Alloy-Fuel Process Calculations
ANL-6992.
- R. L. Jarry, A. V. Hariharan, J. Fischer, M. J. Steindler, J. J. Stockbar,
T. D. Baker, W. H. Gunther, and G. W. Redding
Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility
Processes. Part IX. The Fluid-Bed Fluorination of Plutonium-
Containing Simulated Oxidic Nuclear Fuel in a $1\frac{1}{2}$ -Inch-Diameter Reactor
ANL-7077.

*Also listed in ANL-7175.

- I. Johnson and I. G. Dillon
The Solubility of Metals in Liquid Zinc
ANL-7083.
- T. R. Johnson and N. K. Clark
Tables for the Calculation of Operating Parameters for Compound
Solvent-Extraction Columns
ANL-7165.
- T. R. Johnson, F. G. Teats, and R. D. Pierce
An Induction Probe for Measuring Liquid Levels in Liquid Metals
ANL-7153.
- R. W. Kessie and D. Ramaswami
Removal of Plutonium Hexafluoride from Cell Exhaust Air by Hydrolysis
and Filtration
ANL-7066.
- L. B. Koppel, P. G. Alfredson, L. J. Anastasia, I. E. Knudsen, and G. J. Vogel
A Generalized Computer Program for Flowsheet Calculation and Pro-
cess Data Reduction
ANL-7197.
- M. L. Kyle, J. D. Arntzen, and L. F. Coleman
Design and Operation of a Pilot-Plant Gettering System of Titanium-
Metal Sponge for Removal of Nitrogen from Argon
ANL-7128.
- M. Levenson, V. G. Trice, Jr., and W. J. Mecham
Comparative Cost Study of the Processing of Oxide, Carbide, and Metal
Fast-Breeder Reactor Fuels by Aqueous, Volatility, and Pyrochemical
Methods
ANL-7137.
- L. E. Link, J. E. Ayer, K. A. Hub, W. J. Mecham, V. G. Trice, J. T. Weills
A Large Metal-Fueled Fast Reactor Study. Part II. Core Design and
Fuel Cycle. Proc. Conf. on Safety, Fuels, and Core Design in Large
Fast Power Reactors, Argonne National Laboratory, October 11-14, 1965.
ANL-7120, pp. 94-103.
- L. E. Link, J. E. Ayer, D. K. Butler, K. A. Hub, W. B. Loewenstein,
W. J. Mecham, D. Meneghetti, D. H. Thompson, V. G. Trice, Jr., and
J. T. Weills
1000 MW(e) Metal-Fueled Fast Breeder Reactor
ANL-7001.
- D. Ramaswami, N. M. Levitz, and A. A. Jonke
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 2. Bench-scale Investigation of a Process for Aluminum-Uranium
Alloy and Stainless Steel-Cermet Fuels*
ANL-6830.

*Also listed in ANL-7175.

- D. V. Steidl, L. E. Trevorow, and M. J. Steindler
Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part XI. Vapor-Liquid Equilibria in the System Uranium Hexafluoride-Plutonium Hexafluoride
ANL-7186.
- D. L. Swift and L. Baker
Experimental Studies of the High-Temperature Interaction of Fuel and Cladding Materials with Liquid Sodium. Proc. Conf. on Safety, Fuels, and Core Design in Large Fast Power Reactors, Argonne National Laboratory, October 11-14, 1965.
ANL-7120, pp. 839-847.
- E. D. Traylor
The Mass Transfer of Single, Solid Uranium Spheres to Flowing Molten Cadmium in Laminar and Turbulent Flow
ANL-7091.
- L. E. Trevorow, M. J. Steindler, D. V. Steidl, and J. T. Savage
Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part XII. The Melting Point Diagram for the System Uranium Hexafluoride-Plutonium Hexafluoride
ANL-7234.
- L. E. Trevorow, M. J. Steindler, D. V. Steidl, and J. T. Savage
Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part XIII. Condensed Phase Equilibria in the System Molybdenum Hexafluoride-Uranium Hexafluoride
ANL-7240.
- D. R. Vissers and M. J. Steindler
Laboratory Investigations in Support of Fluid Bed Fluoride Volatility Processes. Part X. A Literature Survey on the Properties of Tellurium, Its Oxygen and Fluorine Compounds
ANL-7142.
- R. C. Vogel, M. Levenson, and F. R. Masten
Chemical Engineering Division Semiannual Report, January-June 1965*
ANL-7055.
- R. C. Vogel, M. Levenson, J. H. Schraidt, and J. Royal
Chemical Engineering Division Semiannual Report, July-December 1965
ANL-7125.
- R. C. Vogel, M. Levenson, J. H. Schraidt, and J. Royal
Chemical Engineering Division Research Highlights, May 1965-April 1966
ANL-7175.
- I. O. Winsch, K. R. Tobias, R. D. Pierce, and L. Burris, Jr.
Sampling of Liquid Metals*
ANL-7088.

*Also listed in ANL-7175.

D. Papers Presented at Scientific Meetings

L. Burris

Pyrochemical Processes for Nuclear Reactor Fuels*

Presented at the Seminar on Pyrochemical Processing, General Atomic, San Diego, Calif., Jan. 17, 1966.

E. Greenberg

Fluorine Bomb Calorimetry*

Two seminars presented at Morehouse College, Atlanta, Georgia, March 1 and 3, 1966.

W. N. Hubbard

Summary of Recent Thermochemical Studies at Argonne National Laboratory*

Presented at the Fourth Meeting of the Working Group on Thermochemistry, Chemical Propulsion Information Agency, Kennedy Space Center, Florida, March 16, 1966.

C. E. Johnson

Regenerative Galvanic Cells

Presented at Northern Michigan University, Marquette, Michigan, March 8, 1966.

C. E. Johnson

Chemical Problems Associated with Regenerative Galvanic Cells

Presented at Temple University, Philadelphia, Oct. 13, 1966.

C. E. Johnson and M. S. Foster

Purification of Gases for Inert Atmosphere Enclosures

Presented at 10th Conference on Analytical Chemistry in Nuclear Technology, Sept. 27-29, 1966, Gatlinburg, Tennessee.

I. Johnson

Processes for Fast Reactor Oxide and Carbide Breeder Fuels - Laboratory Development

Presented at EBR-II Information Meeting on Pyrochemical Processing, Idaho Falls, Idaho, Oct. 24, 1966.

T. R. Johnson, R. D. Pierce, and W. J. Walsh

Recent Developments in the Technology of Molten Metal-Molten Salt Extractions Presented at AIChE Regional Symposium, University of Toledo, April 15, 1966.

L. B. Koppel and J. T. Holmes

Advantages and Disadvantages of Factorial Experiments

Presented at a Chemical Technology Division Seminar, Oak Ridge National Laboratory, Oak Ridge, Jan. 10, 1967.

Presented at a Chemical Engineering Division Seminar, Argonne, Dec. 16, 1966.

*Also listed in ANL-7175.

- M. L. Kyle, R. D. Pierce, and L. Burris, Jr.
Containment Materials for Pyrochemical Processes
Presented at the 15th Annual AEC Corrosion Symposium at Oak Ridge,
May 24, 1966.
- M. Levenson
General Fuel Cycle Considerations for Advanced Systems*
Presented at Seminar on Pyrochemical Processing, General Atomic,
San Diego, Calif., Jan. 17, 1966.
- M. Levenson
Basic Factors Important to Fast Reactor Fuel Cycles.
Application of EBR-II Fuel Cycle Steps to Other Fast Reactor Fuel Cycles.
Processes for Fast Reactor Oxide and Carbide Breeder Fuels--
Economic Studies.
Presented at EBR-II Information Meeting on Pyrochemical Processing,
Idaho Falls, Idaho, Oct. 25-26, 1966.
- M. Levenson
Long Range Objectives of Fuel Cycles.*
Engineering Aspects of Nuclear Fuel Reprocessing--Aqueous, Fluoride
Volatility, and Pyrochemical Methods.*
Waste Disposal and its Relation to Reprocessing.*
Three papers presented at the Atom Forum, Utrecht, Netherlands,
March 11-15, 1966.
- M. Levenson
Chemical Engineering - Where and Why
Presented at ANS Meeting, Idaho Falls, Idaho, Feb. 22, 1966.
- N. Levitz
Fluidization and the Nuclear Fuel Cycle
Presented at College of Pharmacy, University of Illinois, Chicago, Ill.,
May 20, 1966.
- R. C. Liimatainen
Nuclear Reactor Safety: Studies on the Core Meltdown Problem
Presented at Purdue University, Nuclear Engineering Department,
Lafayette, Indiana, May 3, 1966.
- R. C. Liimatainen
Recent Experiments Pertinent to Nuclear Reactor Safeguards Analysis
Presented at Kansas State University, Nuclear Engineering Department,
Manhattan, Kansas, May 19, 1966.
- R. C. Liimatainen
Some Chemical Engineering Aspects of Nuclear Safety
Presented at The Tuskegee Institute of Technology, Tuskegee, Alabama,
May 26, 1966.

*Also listed in ANL-7175.

R. D. Pierce

Processes for Fast Reactor Oxide and Carbide Breeder Fuels -
Engineering Development

Presented at EBR-II Information Meeting on Pyrochemical Processing,
Idaho Falls, Idaho, Oct. 24, 1966.

H. Shimotake and J. C. Hesson

Corrosion of Refractory Metals by Liquid Bismuth, Tin, and Lead

Presented at 15th Annual AEC Corrosion Symposium, Oak Ridge,
May 23-25, 1966.

M. J. Steindler

The Actinide Fluorides

Presented at General Chemical Research Laboratory, Morristown,
New Jersey, Aug. 5, 1966.

R. K. Steunenbergh

1. Discussion of Pyrochemical Processes Development and its Appli-
cation to the EBR-II Fuel Cycle

2. Application of Pyrochemical Processes to other Reactor Fuels and
Miscellaneous Applications

Presented at EBR-II Information Meeting on Pyrochemical Processing,
Idaho Falls, Idaho, Oct. 24, 1966.

A. D. Tevebaugh

Regenerative Fuel Cells

Presented at Power Information Center, Philadelphia, March 30, 1966.

R. C. Vogel

Outline of Program and Scope of Pyrochemical Processes

Presented at EBR-II Information Meeting on Pyrochemical Processing,
Idaho Falls, Idaho, Oct. 24, 1966.

T. F. Young

Are There "Kinks" in Curves Showing the Temperature Variations of
the Properties of Liquid Water?

Presented to the Chemistry Division, Los Alamos Scientific Laboratory,
Los Alamos, New Mexico, July 21, 1966.

T. F. Young

Discontinuities in Temperature-Property Curves

Presented at an informal seminar, Chemistry Division, Oak Ridge
National Laboratory, Oak Ridge, Tennessee, June 14, 1966.

T. F. Young

Temperature Variations of the Properties of Liquid Water

Presented at a Symposium on Physical Chemistry of Water Desalination,
22nd Southwest Regional Meeting of the American Chemical Society,
Albuquerque, New Mexico, Nov. 30, 1966.