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Chemical Separations Processes
for Plutonium and Uranium

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ABSTRACT

The research and development program of Argonne's Chemical Engineering Division during 1968 comprised studies in the following areas: (1) development of two types of processes for the recovery and purification of fissile and fertile constituents of irradiated FBR fuels—a compact pyrochemical process (salt-transport process) in which uranium and plutonium are selectively transferred from one liquid metal solution to another by means of molten chloride salts and a fluid-bed fluoride volatility process in which uranium and plutonium hexafluorides are selectively volatilized to obtain separation and purification—(2) studies of the phase diagrams, thermodynamics, and physical properties of candidate FBR fuels at high temperatures, (3) studies of the chemical behavior of fuel constituents and fission products in irradiated mixed-oxide FBR fuels, (4) in-

vestigations of methods for detecting the location of a fuel failure in an operating fast reactor, (5) calorimetric studies of substances of interest in nuclear technology, (6) studies of the physico-chemical properties of liquid metals, with emphasis on those properties of liquid sodium that apply to its use as a reactor coolant, (7) development of methods for the preparation of ceramic FBR fuel materials, (8) studies of reactions that are important to the safe operation of nuclear reactors, (9) studies of electrochemical cells and systems for the conversion of thermal energy to electrical energy and for the storage of electrical energy, (10) determination of nuclear cross sections of FBR fuel, cladding, and structural materials, and (11) development of methods for determining the burnup of FBR fuels.

SUMMARY

Chemical Engineering Division Annual Report

I. Compact Pyrochemical Processes (pages 19 to 46)

Research and development work has continued on compact pyrochemical processes for the recovery of uranium and plutonium from fast breeder reactor fuels. Processes for ceramic fuels, i.e., oxides and carbides, are currently being investigated, but these processes are also applicable to metallic fuels. The separations of uranium, plutonium, and fission products in the processes being developed are based upon differences in the distribution of these elements between immiscible liquid metal and molten salt solvents.

The processes that are currently being developed incorporate salt-transport separations. These separations are based upon the selective transfer of solute plutonium

or uranium from one liquid metal solution (donor alloy) to another metal solution (acceptor alloy) by means of a molten chloride salt that circulates between the two metal solutions. The conceptual process flow-sheet that is being investigated employs salt-transport separations to isolate plutonium from uranium and the noble metal fission products. Processes that utilize salt-transport separations should be capable of achieving good fission product removals and high uranium and plutonium recoveries. The emphasis in the current investigations is being placed on the design of processing components and on the engineering development of pyrochemical processing concepts.

Chemical Investigations in Support of Pyrochemical Processes

Chemical studies in support of pyrochemical process development have included measurements of the distribution of neptunium between molten salts and liquid metal alloys; measurements of the solubilities of plutonium, chromium, and neptunium in liquid metal solutions; determinations of the liquidus composition-temperature relations for the $\text{MgCl}_2\text{-MgF}_2$ and $\text{CaCl}_2\text{-CaF}_2\text{-CaO}$ salt systems; and a determination of the activity of neptunium in liquid Cd-Np alloys.

Distribution measurements. The distribution coefficient ($D = \text{mol \% NpCl}_3 \text{ in salt/at. \% Np in alloy}$) of neptunium between a molten $\text{MgCl}_2\text{-30 mol \% NaCl-20 mol \% KCl}$ salt mixture and a liquid $\text{Mg-28 at. \% Zn}$ alloy varied from 0.01 at 425°C to 0.1 at 800°C. These values, when compared with those of plutonium (0.04 at 425°C to 0.1 at 800°C), indicate that a neptunium-plutonium separation based on this system might be achieved by multistage extraction at lower temperatures.

Solubility measurements. The solubility of plutonium in the liquid Zn-Mg alloys at 600°C was found to vary from about 0.1 at. % in pure zinc to 1.3 at. % in a Zn-43 at. % Mg alloy. At 750°C, the solubility varies from 1.3 at. % in pure zinc to 2.9 at. % in a Zn-26 at. % Mg alloy.

The solubility of chromium in liquid zinc varies from 0.56 at. % at 425°C to 2.3 at. % at 800°C.

The solubility of neptunium in liquid cadmium was measured as a function of temperature. These measurements combined with X-ray diffraction studies indicate that NpCd_{11} is the solid phase in equilibrium with the saturated liquid from the melting point of cadmium (~321°C) to 490°C. From 490°C, and up to at least 626°C, NpCd_6 is the equilibrium solid phase.

Molten salt systems. Studies were made of the liquidus composition-temperature relations in the CaCl_2 -rich region of the $\text{CaCl}_2\text{-CaF}_2\text{-CaO}$ system. A ternary eutectic exists at $\text{CaCl}_2\text{-17 mol \% CaF}_2\text{-4 mol \% CaO}$ and 625°C. Ternary peritectics were found at $\text{CaCl}_2\text{-23 mol \% CaF}_2\text{-10 mol \% CaO}$ and 660°C and at $\text{CaCl}_2\text{-23 mol \% CaF}_2\text{-13 mol \% CaO}$ and 670°C. A peritectic was found in the $\text{CaCl}_2\text{-CaO}$ binary system at 18.5 mol % CaO and 835°C. The incongruently melting compound is $\text{CaO} \cdot 2\text{CaCl}_2$.

The $\text{MgCl}_2\text{-MgF}_2$ system was found to have a single eutectic at 78 mol % MgCl_2 and 628°C.

Thermodynamic measurements. The temperature dependence of the standard free energy of formation of NpCd_{11} and NpCd_6 was derived from data from high-temperature galvanic cells. The temperature dependence may be represented by the equations

$$\text{NpCd}_{11}: \Delta G_f^\circ (\text{cal/mol}) = -44,700 + 43.3T(^{\circ}\text{K})$$

$$\text{NpCd}_6: \Delta G_f^\circ (\text{cal/mol}) = -28,400 + 21.7T(^{\circ}\text{K})$$

Engineering Studies of Salt Transport Separations

Flowsheet development. A conceptual flowsheet has been prepared for the pyrochemical processing of one ton per day of short-cooled fuel from a fast breeder reactor. Plutonium and uranium recoveries exceeding 99% and fission product decontamination factors greater than 10^6 are design objectives. The process steps include (1) dissolution of the stainless steel cladding in liquid zinc, (2) removal and collection of the volatile fission products in the head-end vessel, (3) efficient removal of rare earth and noble and refractory metal fission products from plutonium in a semicontinuous mixer-settler unit, (4) plutonium isolation by evaporation of the solvent metals, and (5) resynthesis of $(\text{U,Pu})\text{O}_2$ and UO_2 in a fluidized-bed converter. Plutonium and uranium accountability is provided by analyses of samples from liquid metal solutions that can be weighed accurately. Plutonium is separated from uranium early in the process, thereby allowing the alternative of delayed uranium decontamination in a large central plant, if desirable.

Feed preparation. Two experiments were performed to study the removal of stainless steel cladding from oxide fuels and subsequent reduction of the oxide. In each experiment, the stainless steel was dissolved from a simulated fuel assembly in molten zinc at 800°C. The bulk of the zinc-stainless steel solution was removed through a transfer line, and the balance of the zinc was removed by vacuum distillation. The fuel (UO_2 pellets and fines) that remained was reduced with a Mg-42 at. % Cu-3 at. % Ca alloy at 800°C. The resultant Mg-Cu solution was then transferred away from the reduced insoluble uranium. In an actual processing situation, this Mg-Cu alloy, which would contain nearly all of the plutonium in the system, would subsequently be processed for plutonium decontamination.

The simulated fuel assemblies that were dissolved in these experiments consisted of $\frac{3}{8}$ -in. ID, 0.035-in. wall tubes of type 304 stainless steel. Thirteen tubes, 12.5 in. long, were welded to three $\frac{1}{4}$ -in. spacer plates to form a bundle. The assemblies each contained 2.5 kg of UO_2 (95% as $\frac{3}{8}$ -in. dia by $\frac{1}{2}$ -in. long pellets and 5% as fines). The assemblies were immersed in 14 in. of zinc (84.5 kg) at 800°C in each experiment. A salt layer (about 2 in. deep) was present on top of the zinc to prevent zinc vaporization and to collect oxide fines. The tubing dissolved in 30 min, but about 4 hr were required to dissolve the spacer plates. The waste zinc was transferred away and was subsequently shown to contain very little entrained UO_2 (0.01% of the uranium charged

in one run). Most of the remaining zinc was vacuum distilled through the salt layer and collected in a condenser outside the furnace. Some salt, but very little uranium, was entrained in the evaporated zinc. (No special provision had been made to avoid entrainment in these experiments.)

After the zinc was removed, additional salt and a Mg-42 at. % Cu-3 at. % Ca reduction alloy were added to the crucibles, and the systems were agitated at 800°C for about 6 hr. The reductions in both experiments were shown to be >99% complete.

Mixer-settler investigation. Mixer-settlers have been selected for use in the plutonium decontamination steps of the process. A seven-stage unit appears to be capable of greater than 10^6 decontamination of the plutonium from the rare earth and noble and refractory metal fission products. The mixer-settler design selected incorporates a solid-rotor agitator-pump. Full-scale plastic models have been operated with a water-organic system to study fluid flow. A mixer-settler is under construction that will operate at 650°C with liquid Mg-Cu and molten salt phases.

Plutonium and uranium retorting. An existing induction furnace has been modified for use as a vacuum retort to evaporate solvent metals from solutions containing plutonium. Current experiments are directed toward selecting a suitable material for a still-pot crucible for use with plutonium.

Plutonium salt-transport facility. Preliminary bench-scale studies of the salt transport process have been performed with equipment located in a small walk-in hood. A new glovebox facility (called the Plutonium Salt Transport Facility) is being constructed. This facility will be capable of demonstrating the entire process with simulated fuel containing up to 1 kg of plutonium. Stainless steel assemblies containing (U,Pu) O_2 pellets and inactive fission products will be processed. The facility is designed to provide 99% recoveries of plutonium and uranium and a fission product element decontamination of 10^6 . The process equipment will be located in two gloveboxes having recirculated purified helium atmospheres. The gloveboxes are in position in the laboratory and services are being connected.

Materials testing. Corrosion testing has revealed that a number of materials including tungsten, tantalum, W-Mo, and several high-chromium steels possess acceptably low corrosion rates with the Mg-Cu and halide salt solutions of the salt transport process. The emphasis in the materials program is now on determining the best methods of fabrication and the expected service life for various process vessels and on investigating any interactions between dissolved plutonium and candidate construction materials.

Process technology. A facility has been operated to test a mixer-settler design. Experiments have been performed to demonstrate the transport of uranium via a salt phase from a metal alloy in one mixer-settler to another alloy in a second mixer-settler, and to determine if any of the metal phase is entrained in the salt. One run has been performed in which 0.8 kg of uranium was transported in 0.5 hr at a salt flow rate of 1.5 kg/min. Several operating difficulties were encountered. The equipment was modified to rectify the difficulties and has been reassembled in preparation for the next experiment.

The behavior of liquid metal-salt systems in packed columns was studied. One run was performed with a 1-in. dia, high-temperature extraction column packed with $\frac{1}{4}$ -in. Raschig rings. The column was operated under incipient flooding conditions. The extraction progressed at a low rate, with only 0.8 theoretical stage in the 33-in. long column compared with 2.2 stages in an earlier run with a lower salt flow rate.

Measurements of pressure drop, limiting flow rates, and holdup were made with a Wood's metal-water system in a 1-in. ID by 24-in. long column. The column was packed with either $\frac{3}{16}$ -in. metal saddles or $\frac{1}{4}$ -in. metal Raschig rings in various experiments. Discontinuous phase turbulence was observed to have an adverse effect on pressure drop and limiting flow rates. These effects have not been observed for ordinary fluids because the countercurrent columns usually flood before the discontinuous phase becomes turbulent.

Pyrochemical Purification of Plutonium-238

A pyrochemical process is under development for preparing high-purity plutonium-238 metal from impure $^{238}\text{PuO}_2$ feed material. A facility, designated as the Plutonium-238 Facility, was completed in early 1968 for development of this process. It consists of a 343-ft³ helium-atmosphere glovebox for pyrochemical work with an integral 86-ft³ air-atmosphere section for transfer operations and an attached 258-ft³ air-atmosphere glovebox for analytical work. The facility is now operating satisfactorily and runs are about to begin with plutonium-238.

Runs have been carried out with $^{239}\text{PuO}_2$ microspheres to demonstrate the main steps in the process. Spark-source mass-spectrographic analyses of the feed material and of the plutonium-239 metal products of two runs indicated successful removal of uranium and most of the light elements that result in (α ,n) reactions.

Fuel Cycle Facility Operations

Termination of FCF in-cell fuel production activities. At the close of 1968, after more than four years of essentially uninterrupted operation, the EBR-

II Fuel Cycle Facility (FCF) successfully concluded its hot-line operations for the remote reprocessing (pyrochemical process) and refabrication of fuel subassemblies for the EBR-II reactor at the National Reactor Testing Station (NRTS), Idaho. In this four-year period, the FCF provided the reactor with more than 400 subassemblies, of which some 280 contained refined fuel obtained from the processing of about 2300 kg of irradiated fuel from discharged subassemblies. Some of this fuel has made four complete cycles through the EBR-II and the FCF. The remainder of the subassemblies were prepared from unirradiated fuel. Also, in this period of hot-line operation, the major pieces of process equipment were operable or operated about 93% of the time, and the electric manipulators and cranes were operable about 90% of the time. All repairs, maintenance, and modification of in-cell equipment, manipulators, and cranes were performed by remote means. The hot-line operation successfully demonstrated the feasibility of the closed fuel cycle, in which metallic fuel from the breeder reactor is refined and refabricated in an adjacent fuel reprocessing plant, and recycled to the reactor. A final report describing the hot-line reprocessing and refabricating activities in the FCF is being written.

Alternative fuel sources. To supplant the hot line as the primary source of Mark-IA fuel for the EBR-II, two other sources of fuel are available. One source is the out-of-cell equipment (cold-line operations) that is installed in the FCF and has been used to fabricate unirradiated fuel elements for the assembly of 95 subassemblies. Subassemblies utilizing cold-line elements are being routinely used in the EBR-II. The other source is a commercial vendor, the Aerojet-General Corporation, San Ramon, Calif. The vendor fuel elements are being fabricated into subassemblies in the FCF cold line for irradiation in the EBR-II. Postirradiation evaluation of the elements will be conducted to determine their suitability as an alternative fuel. Fuel sub-

assemblies discharged in the future will be transferred to the Idaho Chemical Processing Plant, NRTS, Idaho, for recovery of the contained uranium.

Addition of silicon to EBR-II alloy. To determine how much the specification limit for silicon in driver fuel alloy (uranium-5 wt % fissium) can be extended beyond the current 400 ± 120 ppm, the performance of irradiated driver alloy containing up to 1000 ppm silicon is being evaluated in postirradiation examinations. Beneficial effects (relatively low swelling) were found in postirradiation tests of Mark-IA fuel elements containing more than 200 ppm silicon (tests included elements with 920 ppm silicon). The preparation of fuel alloys containing controlled amounts of silicon for this program required the development of a method for introducing the silicon into the alloy. Adding the silicon in the form of a master alloy of depleted uranium-2 wt % silicon during fuel-alloy preparation resulted in alloys of the desired silicon content in which the silicon was uniformly dispersed.

Future role of the FCF in the AEC Liquid Metal Fast Breeder Reactor Program. The AEC's Liquid Metal Fast Breeder Reactor Program to develop large, commercial fast breeder reactors is heavily dependent upon the irradiation tests of reactor fuels and structural materials, which are conducted in the EBR-II. The increasing demands of the irradiation program led, in 1968, to the increasing employment of the FCF for the examination and evaluation of irradiated specimens or for cleaning and packaging them for shipment to the experimenters. Since the demonstration of the remote fuel-processing and fabrication program utilizing the FCF hot line has been successfully completed, the hot line has been shut down to make space available in the cells for carrying out other FCF experimental and evaluation activities. This transition is under way. In-cell test equipment, presently installed and planned for, will provide for interim (nondestructive) and final (destructive) examination of irradiated specimens.

II. Fluidization and Volatility Processes (pages 47 to 76)

Laboratory-Scale Investigations

Fluorination of UO_2 - PuO_2 -fission product pellets. A 2-in. dia fluid-bed reactor is being used to study the fluorination of uranium and plutonium from simulated thermal light water reactor (LWR) fuels and fast breeder reactor (LMFBR) fuels containing nonradioactive fission product oxides. In these studies, the fuel is first oxidized to U_3O_8 - PuO_2 fines with oxygen. Uranium is then fluorinated to the volatile hexafluoride

with BrF_5 or dilute fluorine, and plutonium is subsequently fluorinated with concentrated fluorine at temperatures of 300 to 550°C.

The final experiments with simulated LWR fuels were Purse-25 and -26. In Run Purse-25, AlF_3 fines (-325 mesh) were added to the regular alumina bed (-40 to $+170$ mesh) (1) to precoat the fluid-bed filter and thereby reduce the amount of plutonium in the fines recovered from the upper parts of the reactor after a

run and (2) to avoid the caking that was encountered when Al_2O_3 fines were added. This procedure was unsuccessful.

About 3.9% of the plutonium charged was contained in fines recovered from the upper parts of the reactor after Run Purse-25, and an agglomerate weighing 15.7 g was removed from the bed. These results were in agreement with previous results, which indicated that the addition of 6 to 10% fines material generally does not reduce the amount of plutonium and leads to agglomeration of 1.5 to 5.8% of the bed. In Run Purse-26, two BrF_3 fluorination steps, one at 300°C and the second at 550°C, were used to investigate the possibility of a complete, selective fluorination of uranium and neptunium. After the high-temperature BrF_3 step, the fluidized bed contained about 0.25% of the uranium charged and about 20% of the neptunium charged. Also, the high-temperature BrF_3 step appeared to affect the subsequent fluorination of neptunium and plutonium with fluorine and is not recommended for a fluid-bed fluoride volatility process.

Fast breeder reactor fuels were simulated for another investigation by using a solid solution UO_2 -20.0 wt % PuO_2 powder combined with a mixture of nonradioactive oxides of fission product elements representative of FBR core fuel with a burnup of 100,000 MWd/metric ton. A fractional factorial series of five experiments was performed to determine how the plutonium concentration in the final fluidized bed was affected by two levels of the fuel-to-alumina ratio (0.3 and 0.6), two fluorination temperatures (350 and 450°C) with 10 vol % fluorine, and two recycle-fluorination sequences (10 and 20 hr). An acceptable plutonium concentration in the final bed is considered to be 1% or less of the initial charge of plutonium. For the five experiments, Runs FF-A1 to FF-A5, the fraction of plutonium charged remaining in the final bed ranged from 0.51 to 3.19%. Only one experiment, Run FF-A2, was significantly above the acceptance criterion of 1%. The conclusions drawn from a statistical analysis showed that an increase in the fuel-to-alumina ratio from 0.3 to 0.6 and an increase in the temperature of fluorination with dilute fluorine from 350 to 450°C increase the fraction of plutonium charge remaining in the final bed; the longer recycle-fluorination sequence reduces the fraction of plutonium charge remaining in the bed. The variables studied had no effect upon the quantity of fines recovered or the fraction of uranium and plutonium charge remaining in the fines.

Analysis of NaF in the product traps (which were used to collect UF_6 and PuF_6 products during the fluorination step with dilute fluorine) showed that an initial separation of uranium from plutonium may be

possible by fluorination with fluorine. Since the U/Pu ratio in the fuel is initially 3.96, a decontamination factor (DF) of about 1×10^3 can be obtained by a suitable choice of operating conditions. Higher U/Pu product ratios are promoted by use of the higher fuel/alumina ratio of 0.6 and the lower temperature of fluorination with dilute fluorine of 350°C.

With one exception, Run FF-A4, the highest rates of plutonium fluorination were obtained during the initial portion of the recycle-fluorination sequence. The low rate during this period in Run FF-A4 apparently resulted from the combination of fluorination with dilute fluorine at 450°C followed by initial recycle-fluorination with 90% fluorine at 300°C. In the other experiments, the production rate for PuF_6 averaged 1.2 to 3.0 lb/(hr)(ft²) while the reactor operated from 17.2 to 55.4% of equilibrium for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$. The diminishing-sphere reaction model was tested and appeared to correlate the data for plutonium fluorination during the initial recycle-fluorination period. Rate constants for the initial portion of the recycle-fluorination period were $0.7 \times 10^{-3} \text{ min}^{-1}$ at 300°C (Run FF-A1) and $4.4 \times 10^{-3} \text{ min}^{-1}$ at 450°C (i.e., average for FF-A2, FF-A3 and FF-A5), which correspond to an apparent activation energy of 10.2 kcal/mol.

Fission product chemistry: ruthenium. A laboratory-scale study of the absorption of ruthenium fluorides on LiF and other absorbents (NaF, nickel metal, and NiF_2) was performed to evaluate this procedure for the separation of ruthenium from PuF_6 . The experimental work involved the preparation of a mixture of UF_6 (as a stand-in for PuF_6) and ruthenium fluoride, collection of these fluorides in a cold trap (the product U-trap), and the transpiration of this mixture, using fluorine as the transporting gas, through a trap containing the absorbent.

The UF_6 -ruthenium fluoride mixture was prepared by the fluorination of UF_4 and either RuO_2 or a mixture of ruthenium metal and RuO_2 ; ^{106}Ru was used as a tracer to permit monitoring ruthenium movement and concentration. The fluorination conditions were varied: the temperature was from 350 to 600°C, and the gas-phase composition was 100% fluorine or 75% fluorine-25% oxygen. The latter gas mixture was used to favor the production of RuOF_4 . The product U-trap was maintained, in turn, at -78, 0, 50, 100, and 150°C during the transpiration period. These experiments were designed primarily to determine the ruthenium loading capacity of LiF and to identify the ruthenium fluoride species present.

The results led to the following general conclusions:

- 1) No ruthenium fluoride other than RuF_5 was pro-

duced by the fluorination of the UF_4 -ruthenium metal or UF_4 - RuO_2 mixture. This was indicated by the absence of significant transport of ruthenium during the periods when the product trap was at -78 , 0 , or 50°C .

2) These experiments indicate that, by transpiration at 0°C , a decontamination factor from ruthenium greater than 10^4 could be expected.

3) The ruthenium sorption capacity of LiF at 350°C was about 23 mg Ru/g LiF , in comparison with the ruthenium sorption capacity of NaF at 100°C of about 22 mg Ru/g NaF .

4) Nickel fluoride at 300°C was shown to be a poor absorbent for ruthenium; nickel, in the form of fine strands, did not retain ruthenium at 150°C .

Decontamination of PuF_6 . Separation of plutonium fluoride from ruthenium fluoride was demonstrated experimentally. The reaction of PuF_6 - RuF_5 -fluorine mixtures with solid LiF at 200 – 500°C resulted in the preferential fixation of ruthenium by the solid phase with decontamination factors of 10^2 to 10^3 . The separation was most efficient with the LiF at 300 – 400°C and was least efficient at 500°C .

Plutonium hexafluoride reacts with LiF at 300°C to form the solid phase $\text{LiF}\cdot\text{PuF}_4$. Fluorination at 400°C of this solid phase resulted in the intermediate formation of $4\text{LiF}\cdot\text{PuF}_4$ and finally in the complete removal of plutonium from the solid phase. It is suggested that the solid phases formed in the reactions of PuF_6 with LiF can be predicted by assuming that the system LiF - PuF_4 is analogous to the LiF - UF_4 system.

Reaction of NpF_6 with NaF . The reaction at 150 to 250°C of an excess of NpF_6 at 150 to 300 Torr with NaF can be represented by the equation

The partial pressures of fluorine and NpF_6 in equilibrium with the solid phase formed by this reaction were obtained by measurements of total pressure and ultraviolet absorbance of the gas phase. At a fixed temperature (350°C) over a tenfold variation of fluorine pressure, the values of $\log(p_{\text{NpF}_6})$ were found to depend linearly on $\log(p_{\text{F}_2})$ with a proportionality coefficient of 0.49 , comparable to the value of 0.50 expected for the above reaction. Equilibrium constants, $K_p = (p_{\text{NpF}_6})/(p_{\text{F}_2})^{1/2}$, for the reverse of the above reaction at 250 to 400°C , were expressed by the equation

$$\log K_{p(\text{atm}^{1/2})} = -3.147 \times 10^3/T(^{\circ}\text{K}) + 2.784$$

Plutonium hexafluoride safety. The hydrolysis of PuF_6 and the filtration, with fiber filters, of the aerosol formed by the hydrolysis have been measured. Of the variables studied, gas velocity through the filter was

found to have the most significant effect on filter penetration; a preliminary correlation is presented. The equation used to fit the results was

$$P = e^{cv^n}$$

where P is the fraction of the released plutonium that penetrates the first filter and is collected on the following filters and v is the gas velocity at the filter medium surface. The constants c and n are determined by least-squares fitting.

Electrostatic effects involved in the high penetration of the second filter of a series of filters were analyzed theoretically and experimentally. The results obtained with a charged-aerosol collector showed that a sufficiently high percentage of aerosol particles were positively charged to account for the observed penetration of the second filter.

Engineering-Scale Investigations

Kilogram-scale production of PuF_6 . A total of 2.3 kg of PuF_4 was fluorinated to PuF_6 with elemental fluorine in a fluidized bed of alumina to provide information pertinent to fluoride-volatility process flowsheets. The fluorination program was divided into three campaigns, each campaign consisting of three separate fluorination runs followed by a fluorination-cleanup step in which any plutonium deposited in the lines and equipment was recovered. Each run involved 260 g of -325 mesh PuF_4 powder. A single bed of alumina, about 6.5 kg of nominal 48 – 100 mesh , was used in each campaign. A 93% fluorine– 7% nitrogen gas mixture, on recycle, served as the fluidizing gas and reactant.

The temperature of the fluidized alumina bed was increased incrementally (about 25°C every 15 min) to 550°C from initial temperatures of 300°C (Campaign 1), 375°C (Campaign 2), and 450°C (Campaign 3). The total fluorination time for each run was 5 hr in the first and second campaigns and 3 hr in the third campaign. The significant results are as follows:

1) Plutonium material balances were 97 , 101 , and 99% , values that are within the expected range.

2) Production rates of PuF_6 averaged $2.4 \text{ lb PuF}_6/(\text{hr})(\text{ft}^2)$ for the first and second campaigns and 4.1 for the third campaign. Rates above $6 \text{ lb PuF}_6/(\text{hr})(\text{ft}^2)$ were attained in the initial 30-min fluorination periods.

3) Overall fluorine utilization efficiencies (defined as the amount of fluorine reacted to that which could theoretically react based on equilibrium considerations) averaged 22 , 17 , and 28% for the successive campaigns. Demonstrated efficiencies near 100% were attained in earlier portions of a run when large quantities of plutonium were present.

4) Less than 2% of the PuF_6 was decomposed to PuF_4 by radiation decomposition, and this was re-fluorinated and recovered without difficulty.

Conceptual process for fast-reactor fuels. Conceptual design studies of a large fluoride volatility plant (one metric ton of actinides per day) for processing fast breeder reactor fuels are in progress. Such a facility would service power plants with a total capacity of about 15,000 MW(e). The reference fuel is stainless steel-clad $\text{UO}_2\text{-PuO}_2$.

The objectives of this study are to present the current technological basis for such a plant in the form of process and engineering flowsheets and to define process uncertainties (problem areas). From this study, a research and development program will be developed and executed that will demonstrate the flowsheet and develop engineering information needed to establish the technical feasibility of the process.

Conceptual process and engineering flowsheets have been prepared using fluorine as the sole fluorinating agent. Major design features are a mechanical head-end step that separates oxide fuel from cladding and converts the oxide to powder, continuous fluid-bed fluorinators, and (for nuclear criticality safety) a slab geometry for vessels containing significant quantities of plutonium. The products are (1) particulate $\text{PuO}_2\text{-UO}_2$ material that is suitable for refabrication into fuel and (2) excess UF_6 for use in other reactors (after conversion to oxide).

Major areas that need confirmation or demonstration are the mechanical head-end step, continuous fluorination at the desired process levels and with acceptably small actinide losses, fission product behavior, hexa-fluoride-to-oxide conversion, and total containment of wastes. Successful demonstration of the flowsheet appears feasible on the basis of current technology.

Pulsed-bed studies. Exploratory tests were made with pulsed and fluidized beds using operating conditions and particle sizes similar to those used in the fluoride volatility process. (In pulsed beds, the bed expands during a pulse, then contracts during the interval when the gas flow is shut off.) The objectives were to compare bed behavior for the two modes of operation and to determine the type of feed-gas distributor needed for pulsed-bed columns.

Five sizes of granular alumina with particle sizes from 2380 to 2 μm were charged to the fluid-bed vessel in layers; the largest sized alumina was charged first, then the next smaller size, and so on. The fluidizing gas was air.

Data were obtained on bed expansion, particle mixing in the bed, and pressure drop across the feed-gas distributor for seven runs with pulsed beds and three

runs with fluidized beds. At similar gas flow rates, bed expansion was consistently higher for pulsed beds than for fluidized beds. In the pulsed-bed runs, the layers, which initially were completely segregated, mixed thoroughly within a few minutes of the start of the run and remained well mixed for the remainder of the 6-hr operation. In the fluidized-bed runs, however, mixing occurred in the top layers, but the two lower layers remained intact for the entire period.

Bed expansion, bed mixing, and pressure drop across the gas distributor were compared for a simple cone distributor and a sintered-metal distributor. Results suggest that a simple cone gas distributor can be used in the process application of the pulsed beds.

The dynamics of bubbles in a fluidized bed. A theoretical study was made to determine the interaction effects, on particle movement and gas flow, of bubbles rising through a fluidized bed in a "two-dimensional" column and a three-dimensional column. The effect on particle mixing of bubble spacing was studied, as were the effects on gas mixing of bubble spacing and ratio of bubble velocity to minimum fluidization velocity. Particle mixing was improved when passage of a bubble caused the length of particle trajectories to increase; the larger the volume of gas cloud surrounding each bubble, the better was gas-solids contacting.

For the two-dimensional case, the area enclosed by the particle trajectories caused by the passage of one bubble in a chain of bubbles is approximately doubled when the center-to-center bubble separation decreases from infinity to about 2.8 bubble radii. For the three-dimensional case, the volume enclosed by particle trajectories is approximately doubled as the center-to-center bubble separation decreases from infinity to 2.5 bubble radii.

For ratios (U) of bubble velocity to minimum fluidizing gas velocity greater than one, a gas cloud (a region in the particulate phase surrounding the bubbles across whose boundary there is essentially no gas interchange) envelops the bubbles in both the two- and three-dimensional cases. At high values of U and/or large bubble separations, an individual cloud surrounds each bubble. For low values of U and close bubble spacings, the gas clouds contact and gas flows from one bubble to another. The gas circulates from inside each bubble into the particulate phase and then back into the bubble, but also flows from one bubble into the bubble above.

In the three-dimensional case for values of U greater than 1.4, the cloud volume per bubble decreases with increasing bubble separation. However, at lower values of U , general trends are not easily described. At $U = 1.1$, the cloud volumes for center-to-center bubble separations of 6.0 bubble radii and infinity (where the

clouds are not contacting) are greater than for separations of 2.6 and 4.0 bubble radii (where the clouds are contacting). Although for the case of contacting clouds the cloud volume per bubble increases with decreasing

U , the rate of increase is not as large as for the case of separated clouds; thus at the lower values of U , cloud volumes are larger for separated clouds than for contacting clouds.

III. Materials Chemistry and Thermodynamics (pages 77 to 129)

High Temperature Thermodynamic and Physical Property Studies

Phase diagram and vapor pressure studies. A mass-spectrometric, Knudsen effusion study of the vaporization of plutonium oxides is in progress. Measurements have been made of samples with compositions near that for apparent congruent vaporization ($\text{PuO}_{1.83}$ at 2219°K) and in the two-phase system ($\text{Pu}_2\text{O}_3 + \text{PuO}_{1.61}$). The pressures were determined from the temperature dependence of ion intensities and rates of effusion calibrations. For single-phase $\text{PuO}_{1.83}(\text{s})$, the partial pressures of $\text{PuO}(\text{g})$ and $\text{PuO}_2(\text{g})$ are given by the equations

$$\begin{aligned}\log P_{\text{PuO}}(\text{atm}) &= - \frac{(27,810 \pm 600)}{T} \\ &\quad + (6.710 \pm 0.270) \\ \log P_{\text{PuO}_2}(\text{atm}) &= - \frac{(30,330 \pm 240)}{T} \\ &\quad + (7.750 \pm 0.110)\end{aligned}$$

The corresponding apparent partial molar enthalpies of vaporization are $\Delta\bar{H}(\text{PuO}) = 127.2$ kcal/mol and $\Delta\bar{H}(\text{PuO}_2) = 138.3$ kcal/mol. The plutonium, plutonium monoxide, and plutonium dioxide pressures measured over the two-phase system are assumed to result from the reactions

The tentative enthalpies of reaction to produce $\text{PuO}_2(\text{g})$, $\text{PuO}(\text{g})$, and $\text{Pu}(\text{g})$ are 126.2, 118.1, and 110.2 kcal/mol, respectively.

An investigation of the plutonium-oxygen phase diagram has been started. Initial studies revealed a liquid miscibility gap with a monotectic temperature between 1800–1850°C. The two immiscible liquids have tentative compositions of $\text{PuO}_{0.1}$ and $\text{PuO}_{1.0}$.

Carbon activities and total pressures are being investigated over the uranium-carbon system where measurements of hydrogen-hydrocarbon concentrations establish the activity of carbon. The results for $\text{UC}_{0.9}$ -

UC_2 at 2255°K are in reasonable agreement with the phase diagram and mass spectrometrically determined carbon activities. Measurements have been extended to higher temperatures and free energies of formation have been computed for various carbon concentrations.

The new transpiration equipment for studies of plutonium compounds is ready for initial tests. Oxygen activities and total pressures are to be measured for the Pu-O system.

The ultrahigh-vacuum Knudsen effusion system is being modified for plutonium studies. The alterations include provisions for the addition of a quadrupole mass spectrometer and quartz microbalance. These instruments will be used to obtain relative ion cross sections and to carry out mass-spectrometric studies of plutonium compounds.

Enthalpy, migration, and other physical property studies. The electron-beam-heated calorimetric system for the measurement of high temperature enthalpies relative to 25°C has been tested in the temperature range 1300–1900°K by obtaining enthalpy data for tungsten metal. Agreement with literature values is within $\pm 0.5\%$. Currently, work is under way on enthalpy measurements of UB_2 powder. The resistance-heated calorimetric system has been modified and is being used to determine enthalpies of Na_3Bi . In addition, enthalpies of UB_2 were measured over the temperature range from 579 to 1486°K in conjunction with the work employing the electron-beam-heated calorimetric system.

Work is continuing on the program to determine the heat capacity of liquid uranium dioxide. As part of the initial testing of the equipment, measurements were made of the enthalpy of pure tungsten. Enthalpy data to 3600°K are presented, thus extending the temperature range of experimental information by about 250°K. Measurements of the enthalpy of solid UO_2 are essentially complete, and initial measurements of liquid uranium dioxide enthalpies are presented.

Work is also in progress to measure other safety-related high-temperature physical properties of reactor materials. Initial experimental efforts in this area are to measure the vapor pressure of liquid uranium dioxide by transpiration methods. Construction and testing of equipment have begun. Current analytical work has in-

volved calculations of some properties of liquid uranium dioxide by the scaled-particle theory. An examination is also being made of a technique to calculate surface tension from frozen uranium dioxide menisci.

Studies of migration of plutonium in a thermal gradient ($\sim 1000^\circ\text{C}/\text{cm}$) for metal oxide fuels are continuing. Electron microprobe analysis of a pellet heated for 1020 hr at a temperature of 1970°C at the top of the pellet and another pellet heated for 123 hr at a temperature of 2350°C at the pellet top gave about a 10 wt % increase (relative) in the PuO_2 concentration at the hotter end. Oxygen analyses performed on these samples indicated loss of oxygen from the pellets with the smaller O/M ratios at the hotter end of the pellets.

Chemistry of Irradiated Fast Reactor Fuels and Materials

The program to study the chemical behavior of irradiated fast reactor fuels and materials is continuing. Construction of an inert-atmosphere cave facility in the Chemistry Division has been completed. This facility will be used for sampling and mounting specimens of irradiated fuel. Operation with irradiated fuels is expected to begin in early 1969. The analytical facility in the Chemical Engineering Division has also been completed and is now in use. Installation of a pneumatic tube for transferring samples between the two facilities is expected to be completed in early 1969.

Studies of fuel materials are being carried out by several techniques. Microsampling by laser-beam vaporization is being used to sample specimens of stainless steel (a common cladding material) that have been exposed to sodium. A spark-source mass spectrometer has been installed in the analytical facility and is now in use. Methods are being developed to improve the precision of mass-spectrometric data.

Electron microprobe studies have continued. A detailed study has been made of a cross section of a UO_2 -20 wt % PuO_2 fuel pin irradiated in EBR-II to 2.7 at. % burnup. The radial distribution of fuel constituents and fission products is described, and a discussion of the chemical behavior of these elements in relation to the microstructure of the fuel is presented.

A program is under way to develop methods of identifying the position in an operating reactor of a subassembly in which fuel failure has occurred. Specific radiochemical or isotopic tags will be used for individual subassemblies; in the event of fuel-element failure, the tag would be released to the sodium coolant, and its detection in the sodium would identify the subassembly containing the failed fuel. Present studies involve the development of methods for analyzing the trace element content of EBR-II sodium.

A small-scale experimental loop has been designed to test the stability of selected tags in circulating sodium. Construction of the loop is under way with completion expected in mid-1969.

The concept of using unique mixtures of the light isotopes of xenon as tags is presented. This method of tagging is intended to be a complement to the sodium-soluble tagging technique. The feasibility of applying this method of failed-fuel identification to EBR-II is discussed in a separate section (III.C).

Xenon Tagging of Fuel Elements in EBR-II

A xenon-tag method of failed fuel identification is being developed for application to EBR-II experimental fuel elements. Each fuel element in a subassembly will be tagged with 1 ml of a mixture of xenon isotopes which is unique for that subassembly. In the event of cladding failure, mass-spectrometric analysis of the reactor cover gas will permit rapid identification of the affected subassembly and its location in the reactor. This rapid identification should enhance the EBR-II plant factor.

Series of xenon tag mixtures will be prepared by mixing light-isotope enriched xenon with natural xenon or with reactor-produced ^{128}Xe . Tests with simulated fuel elements have shown that the rate of diffusion of xenon from an element plenum is sufficiently low to permit a simplified method of tag addition. Potential detrimental effects of tagging and effects which might hamper tag identification were studied and appear inconsequential. Tag mixture procurement has begun, and in the near future all unencapsulated gas-bonded elements entering EBR-II should be xenon-tagged.

Calorimetry

Standard enthalpies of formation, ΔH_f° , of uranium diboride and beta uranium disulfide were determined by fluorine bomb calorimetry. The values derived are $\Delta H_f^\circ(\text{UB}_{1.979}, \text{c}) = -39.1 \pm 2.6 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(\text{US}_2, \beta) = -124.2 \pm 2.1 \text{ kcal mol}^{-1}$.

Oxygen bomb calorimetry was used to determine the enthalpies of formation of plutonium dioxide and plutonium mononitride. The values derived are $\Delta H_f^\circ(\text{PuO}_2, \text{c}) = -252.35 \pm 0.17 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(\text{PuN}, \text{c}) = -71.51 \pm 0.62 \text{ kcal mol}^{-1}$. This method is being used to determine the enthalpy of formation of plutonium monocarbide.

A series of calorimetric combustions of fluorine in excess hydrogen has been completed. The uncertain correction for the nonideality of $\text{HF}(\text{g})$ was avoided by saturating the bomb with $\text{HF}(\text{g})$ so that the product of combustion was $\text{HF}(\text{l})$. A preliminary value of $\Delta H_f^\circ(\text{HF}, \text{l}) = -71.8 \pm 0.2 \text{ kcal mol}^{-1}$ was derived.

The reaction of iodine with excess fluorine was studied

in a bomb calorimeter. By varying the fluorine pressure, it was possible to produce IF_5 - IF_7 mixtures containing as little as a few tenths of a per cent of IF_7 to as much as 80% IF_7 . The enthalpies of formation of both products were derived, namely, $\Delta H_f^{\circ}(\text{IF}_5, \text{l}) = -210.6 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta H_f^{\circ}(\text{IF}_7, \text{g}) = -227.4 \pm 1.4 \text{ kcal mol}^{-1}$.

Combustions of germanium in fluorine were undertaken to resolve a discrepancy of $\sim 10 \text{ kcal mol}^{-1}$ in literature values for the enthalpy of formation of $\text{GeF}_4(\text{g})$. The preliminary value derived from this work is $\Delta H_f^{\circ}(\text{GeF}_4, \text{g}) = -284.5_8 \pm 0.2_1 \text{ kcal mol}^{-1}$.

Measurements were made of the enthalpies of dissolution (298°K) in water of crystalline and amorphous boric oxides according to the reaction $\text{B}_2\text{O}_3(\text{s}) + 686 \text{H}_2\text{O}(\text{l}) \rightarrow 2(\text{H}_3\text{BO}_3 \cdot 341.5 \text{H}_2\text{O})(\text{l})$. From the values obtained, -3.54 ± 0.04 and $-7.98 \pm 0.06 \text{ kcal mol}^{-1}$, respectively, the enthalpy of transition is $4.44 \pm 0.07 \text{ kcal mol}^{-1}$. The enthalpy of combustion of crystalline boric oxide in fluorine was redetermined with a new sample of B_2O_3 . The new value derived for $\Delta H_f^{\circ}(\text{B}_2\text{O}_3, \text{c})$, $-304.50 \pm 0.59 \text{ kcal mol}^{-1}$, is $1.48 \text{ kcal mol}^{-1}$ more negative than the previously reported value (ANL-7225) and is recommended to supersede it.

Previous estimates (ANL-7425) for the enthalpies of formation of CeF_3 , PrF_3 , NdF_3 , and PmF_3 were based on the lattice energy calculated for LaF_3 from the experimental value for $\Delta H_f^{\circ}(\text{LaF}_3)$. Recently published information raises some question about this value and, therefore, about the estimates derived from it. The estimates are being reexamined.

Extended Hückel molecular orbital calculations for the chalcogen hexafluorides show considerably more charge transfer in TeF_6 than in SF_6 or SeF_6 . This result is in accord with qualitative rationalizations and chemical evidence.

Thermodynamic functions were calculated by the formulas of statistical mechanics for the ideal gas states of the chalcogen fluorides and of P_2 , P_4 , PF , PF_2 , PF_3 , PF_4 , PF_5 , P_2F_4 , As_4 , As_2 , AsF , AsF_2 , AsF_3 , AsF_4 , AsF_5 , Ge_2 , GeF , GeF_2 , and GeF_4 .

Chemistry of Liquid Metals

An attempt is being made to detect complexes in liquid alloys for which complex formation has been claimed. Three such alloys, Hg-18 at. % Na, In-33 at. % Bi, and Hg-50 at. % In, were examined by ultrasonic absorption spectrometry. The absorption spectra for frequencies between 45 and 165 MHz did not show any features characteristic of liquids containing dissociable complexes. Further studies will be made over a considerably broader frequency range.

The thermodynamic activity of sodium in liquid Na-Cs solutions was determined at $\sim 140^\circ\text{C}$ by atomic

absorption spectrophotometry. Significant positive departures from ideality were observed. Comparison with previously studied systems shows that these departures are smaller than those for the Na-Rb system but larger than those for the Na-K system.

Stepwise multiple regression analysis was used to correlate selected properties of pure metals with the heats of mixing of binary liquid alloys at the equiatomic composition. Eight parameters were used, each a function of one or more physicochemical properties, e.g., electronegativity, heat of vaporization, Fermi energy, valence, etc. A regression equation was derived that predicts the correct sign and, within a factor of two, the magnitude of the heat of mixing for 33 of 34 binary systems for which reliable data are available.

Carbon transport between steels in contact with molten sodium is being studied with the aid of radio-carbon-14 tracing. The species involved in transport of carbon through liquid sodium has been deduced from the ^{14}C -containing products obtained on hydrolysis of the sodium. Acetylene was found to be the major hydrolysis product, and its likely precursor, disodium acetylide (Na_2C_2), is suggested as the main species responsible for carbon transport. It is postulated that sodium can react with carbon (e.g., Fe_3C) in steel to form Na_2C_2 .

To test the tendency of carbon dispersed in liquid sodium to carburize steels, the preparation of stable carbon dispersions is being attempted. The initial experiments are being made with NaK eutectic, a liquid at room temperature. Dispersions of up to 4 wt % carbon in NaK were prepared ultrasonically. The stability of the dispersions was found to depend on the concentration of dispersed carbon. Marked changes in viscosity and wetting characteristics were observed with dispersions containing more than 1 wt % carbon.

The solubilities of sodium cyanide and nitrogen gas in liquid sodium have been measured and can be represented by the equations

$$\log S_{\text{CN}} = 13.5 - 9140 T^{-1} \quad (400-565^\circ\text{C})$$

$$\log S_{\text{N}_2} = -7.18 - 2780 T^{-1} \quad (450-600^\circ\text{C})$$

where S_{CN} is the cyanide solubility in parts per million, and S_{N_2} is the nitrogen solubility in grams of nitrogen per gram of sodium per atmosphere of pressure. The heats of solution calculated from these equations are 42 ± 5 and $13 \pm 3 \text{ kcal/mol}$, respectively. The nitrogen was shown to dissolve diatomically, in contrast with other diatomic gases, which dissolve monatomically in liquid metals. Cyanide in liquid sodium was found to be quite effective in simultaneously carburizing and nitriding stainless steel.

The behavior of iron and of type 304 stainless steel immersed in sodium is being studied to determine whether or not surface diffusion is an important mechanism of mass transport in sodium systems. The phenomenon is being observed by interferometric measurement of the rate of decay of grain-boundary grooves and surface scratches.

Experiments have been undertaken to determine the partition of copper at 650°C between type 304 stainless steel, which may contain up to 0.5% tramp copper, and liquid sodium.

Preparation of Reactor Materials: Ceramic Fuels

Carbide preparation by metal-methane reaction. The preparation of ceramic fuels for fast reactors is being studied to develop processes that economically fit into appropriate fuel cycles. A previously developed fluidized-bed process (ANL-7325, p. 113; ANL-7375, p. 119; and ANL-7425, p. 114) for preparing carbide from metal was used to prepare 400-g batches of (U, 15 wt % Pu)C powder containing fully enriched uranium. The metal feed material was hydrided and dehydrided twice in a fluidized-bed reactor to produce a fine powder. The powder was then reacted for 5 to 8 hr with H₂-6.2 vol % methane fluidizing gas at 800°C and two atmospheres pressure to produce the carbide. Results of similar experiments with uranium and (U, 20 wt % Pu)C indicated that the rate of carburizing increases with increasing plutonium concentration from 0 to 20 wt % plutonium. The carbon content of the product can be adjusted to near-stoichiometric monocarbide with a final hydrogen treatment after sintering.

The typical oxygen and nitrogen contents of the product were 500 ppm each. These levels resulted primarily from impurities in the metallic feed materials.

The product powder was pressed and sintered into 0.25-in. dia pellets suitable for irradiation testing. A sintering temperature of 2100°C is required to obtain the desired sintered density of 11.6 g/cm³ (85% of theoretical). The sintered pellets were ground in a specially developed centerless grinder to a uniform and predictable diameter within the limits of accuracy for measurements that could be made in the glovebox (± 0.0005 in.).

Synthesis of carbides by conversion from oxides. A fluidized-bed process was studied for converting UO₂ to UC. The process involves making composite particles of UO₂ and graphite and reacting them at 1450 to 1800°C in a 2-in. dia fluidized-bed reactor, using an inert gas (helium or argon) for fluidization. The rate of reaction was relatively high in all of the twelve runs made in the study. Projections indicate that at least 30 kg per day of UC could be produced in a 12-in. dia fluidized-bed reactor. However, some or all of the particles sintered together in each of the runs, and prevented rapid removal of the product. Although the fluidized-bed process is capable of high production rates and gives a product of acceptable purity, bed sintering has not been eliminated at temperature levels where low oxygen content can be attained (>1550°C). Therefore, work on the fluidized-bed process has been suspended, and the effort has been directed toward development of a plasma-torch process for carbide production.

IV. Reactor Safety (pages 130 to 135)

Thermal Reactor Studies

Analyses of loss-of-coolant accidents. A computer program, CHEMLOC-II, has been devised for the case of emergency coolant failure; it describes core heating and cladding-steam reactions from the end of blowdown through core heat-up, core slumping, melting, and movement, and ends with the heat-up of the bottom grid plate.

Laboratory experiments were made with single Zircaloy-clad, UO₂-pellet-core simulated fuel rods. These were inductively heated in a flowing steam atmosphere to simulate a loss-of-coolant condition, and were subsequently quenched at predetermined cladding temperatures to simulate emergency core cooling. Failure of the rods depended mainly upon the extent of oxidation. All rods failed when the average extent of oxidation was 18.4% or greater.

Studies relating to the analyses of excursion accidents. Additional photographic experiments were conducted in TREAT to study the high-temperature behavior of Zircaloy-2-clad fuel rods during a reactor transient. Five experiments were carried out with sintered UO₂ pellets and six with vibrationally compacted UO₂ powder. Two patterns of failure were observed: prompt and delayed. Prompt failure generally occurred during the power transient and was manifested by rapid pressurization in the cladding, a vigorous rupture of the cladding, and injection of some of the fuel into the coolant. Delayed failure occurred after the transient and resulted from a weakening of the cladding due to excessive temperatures and reaction with water and UO₂ fuel. Computational procedures have been established which enable reasonable definition and prediction of fuel-rod failure thresholds.

Pressure generation due to particle-water energy transfer. Experimental and theoretical studies of pressure generation due to reactions of hot or molten core materials with water were continued. Two techniques were used in the experimental work: (1) the swinging-arm method to measure the boiling heat transfer between small moving particles and water, and (2) the pressure-pulse method, a technique employing a pressure transducer which measures the forces produced, as a result of void formation, when small hot particles fall into a column of water.

In the swinging-arm method, $\frac{1}{4}$ - and $\frac{1}{2}$ -in. dia silver spheres and $\frac{1}{2}$ -in. dia stainless steel spheres were used. Velocities ranged from 2.5 to 25 ft/sec; water temperatures from 20 to 90°C; and sphere temperatures from 100 to 800°C. Heat-transfer rates with silver spheres depended largely on the heat-transfer coefficient at the surface film. Heat-transfer rates of the stainless steel spheres depended largely on heat conduction within the sphere, and were relatively independent of the heat-transfer coefficient at the surface film. The experiments again showed that for transient heat transfer from the interior to the surface of a sphere, a small radius compensates for low thermal conductivity.

In the pressure-pulse column studies, silver and stainless steel spheres as well as molten bismuth were dropped into water columns, and the pressure pulses measured. The dynamic pressures are inversely proportional to the cross-sectional area of the water column and directly proportional to the depth of the water over the spheres or bismuth, as predicted by simple theory. The dynamic pressures are greatest at transition from quiet to violent boiling. Under similar conditions, the pulses are greater for molten bismuth than for the metal spheres. This results from the dispersal of bismuth into fine particles with a larger surface area and, thus, a greater heat-transfer rate.

Fast Reactor Safety Studies

Interaction of fuel, cladding, and coolant. An accident in a nuclear reactor could result in the contact of large quantities of molten fuel materials with the reactor coolant. If the materials break up into small droplets with a large surface area, explosive pressures could develop.

In a survey study, the water-tin system was employed to determine the effects of velocity and acceleration on fragmentation. The extent of fragmentation depended on the relative velocity of tin and water and was enhanced by the acceleration effects resulting from violent boiling on the surface of the tin.

Pressure generation due to violent meltdown.

The first TREAT meltdown experiment in a sodium-filled piston autoclave was conducted. A double-containment autoclave containing a cluster of five stainless steel-clad, UO_2 -core fuel rods and four dummy rods was subjected to three transients (energies of 214, 330, and 340 cal/g UO_2). Although all rods were warped, only the center rod in the cluster failed.

The possibility of generating high-pressure waves by rapid heating of sodium under acoustic constraint, as, for example, by the interaction of molten fuel with sodium, is of principal interest in this study. To provide a basis for understanding the pressure-generation effects, a one-dimensional calculational model for "steam" explosions was developed for the water system and applied to the SPERT-1D excursion tests. Application of the model to the sodium system is being undertaken.

Violently sprayed sodium-air reaction. A mathematical model was developed to predict the burning rate and burning temperature of a single spherical sodium particle moving through an oxygen-nitrogen atmosphere. The model was based on the assumption that the reaction rate is controlled by the diffusion of oxygen to a vapor-phase combustion zone surrounding the particle. A correlation was made between the reaction rates of individual particles in a spray and the burning rate of the spray itself. The pressure rise in the volume enclosing the spray was also calculated.

Rates of pressure rise occurring when sprayed sodium reacts with air were measured as functions of ambient oxygen concentration, orifice size of the spray injector, and spray velocity. Experimental pressure-rise rates for two orifice sizes as a function of initial oxygen concentration were compared with calculated rates.

Fuel failure propagation. The variables that govern the modes of transport of fuel element failure from the initial element failure to failure of neighboring fuel elements were studied in cooperation with other Argonne Divisions. Preliminary water-loop tests of the behavior of fission gas released from a breached fuel element were carried out. The feasibility of an in-pile sodium package loop was established, and initial in-pile tests were defined.

Detailed Report on Reactor Safety Work

The Chemical Engineering Division's work on Reactor Safety will be reported in detail in an ANL annual report that will bring together all the safety work performed at Argonne during 1968. It should be noted that responsibility for much of the safety work that was being carried out by the Chemical Engineering Division was transferred to the Reactor Engineering Division in September 1968.

V. Energy Conversion (pages 136 to 169)

Thermally regenerative galvanic cells and electrically rechargeable (secondary) cells continue to hold interest as devices for the conversion of thermal energy (as from a nuclear reactor or radioisotope heat source) to electrical energy, and for the storage of electrical energy (for use in various applications including off-peak energy storage for central power stations). Both lithium and sodium are attractive as anode materials for thermally regenerative and secondary cells. A broadly based research program is being carried out to investigate the thermodynamic, electrochemical, and physicochemical properties of the systems which show promise.

Cells with Lithium Anodes

The lithium-tin system is of interest for possible application in a thermally regenerative galvanic cell. The vapor pressures and vapor-phase compositions for the lithium-tin system have been determined for the full composition range at 1200°C (a likely thermal-regeneration temperature) and for selected compositions at lower temperatures. The critical pressure for the onset of solid deposition from the vapor phase has been determined as 0.42 Torr. Activity coefficients of lithium and tin as a function of alloy composition have been determined from the vapor-pressure data.

The emf measurements for the lithium/tellurium cell have been completed. The emf varies from 1.78 to 1.69 V over the composition range 8.6 to 33.2 at. % lithium and is a weak function of temperature over the range 400 to 570°C. These results have provided activity coefficients of lithium in lithium-tellurium alloys which will be subjected to a thermodynamic analysis.

The tellurium-rich portion of the phase diagram of the lithium-tellurium system has also been determined. There is a distinct parallelism between the sodium-tellurium and the lithium-tellurium phase diagrams, with the latter system having the higher-melting-point intermetallic compounds.

Phase-diagram studies of lithium halide-containing systems have continued, with interest in some mixed-cation systems such as LiCl-LiI-KI, which correspond to portions of reciprocal-salt systems. The conformal ionic solution theory (ANL-7425, pp. 176-179) has provided a useful basis for the prediction of phase diagrams and for the guidance of experimental investigations by minimizing the amount of data required to accurately locate the temperature and composition of the eutectic. In the studies of the LiCl-LiI-KI system, only eight experiments were required to determine the eutectic temperature (265°C) and composition (8.5 mol % LiCl, 59 mol % LiI, 32.5 mol % KI).

Raman spectroscopic investigations of a number of intermetallic compounds dissolved in lithium halides, and of various halide melts have given additional insight into the structure of these molten systems. The compounds Li₂Se and Li₂Te dissolve as monatomic species, yielding no detectable Raman spectra. Magnesium chloride-potassium chloride melts present a complex system of several species such as (MgCl₂)_n polymer, MgCl₄²⁻, and MgCl₃⁻. Similar behavior is found for MgBr₂-KCl melts. The presence of UO₂⁺² in MgCl₂-KCl melts has a strong influence on the structure of the melt, probably forming U-Cl-Mg bridges. The main polyatomic species in the HgI₂-LiI-KI system is HgI₂ with small amounts of HgI₃⁻ at high I⁻/Hg⁺² ratios. The Raman spectrum of Al₂Cl₆ vapor has been determined, and a complete normal coordinate analysis has been performed, using the Raman data and infrared data from the literature.

A mathematical analysis has been performed of the simultaneous heat-, mass-, and momentum-transfer in a lithium-tin regenerator. The results indicate that, with a heat-source temperature of 1300°C and with a regenerator design that minimizes the vapor-phase pressure drop, regeneration rates equivalent to 13 to 35 A/cm² should be achieved. In the operation of lithium/tin cells with paste electrolyte, short-circuit current densities of up to 1.8 A/cm² and maximum power densities of about 0.35 W/cm² have been achieved.

A lithium/selenium cell with a liquid LiF-LiCl-LiI electrolyte operating at 375°C has delivered power densities of 6.3 to 7.8 W/cm² at 1.2 V and has been recharged in less than fifteen minutes. These performance data, when combined with a reasonable battery design, yield a predicted specific power of 380 W/lb (fast discharge) and specific energy of 130 W-hr/lb (slow discharge). A lithium/sulfur cell with a liquid LiF-LiI-KI electrolyte has delivered 4 W/cm² for short periods of time at 347°C and has been recharged in less than fifteen minutes. These results correspond to a predicted battery performance of about 500 W/lb (fast discharge) and 160 W-hr/lb (slow discharge). A lithium/phosphorus cell with a liquid LiF-LiCl-LiI electrolyte operating at 425°C yielded a maximum power density of 0.36 W/cm² at 0.4 V. It is possible that the cathode was solid under these operating conditions. Higher performance is expected from a cell with a liquid cathode.

An important phase of the development of practical cell configurations is the immobilization of one or more of the three liquid phases. The electrolyte phase has

been immobilized in the form of a rigid paste by incorporation of a filler material of high specific area, such as lithium aluminate. Various methods of lithium aluminate preparation are being investigated, as are the various crystalline modifications and stoichiometries of lithium aluminates. The α (low-temperature) modification of LiAlO_2 has exhibited the best behavior in cells so far. Investigations are being carried out to determine the optimum composition, particle size, and particle shape for the filler. A paste electrolyte of α - LiAlO_2 (particle diameter, $\sim 0.03 \mu\text{m}$) combined with 60 wt % LiF-LiCl-LiI eutectic has shown the best performance in a lithium/tin cell.

Cells with Sodium Anodes

The quasi-ideal solution theory has now been successfully applied to both emf and vapor-liquid equilibrium studies of the sodium-bismuth system. The activity coefficients of sodium and bismuth have been calculated accurately over the full range of compositions, for temperatures of 550 and 1173°K, using as parameters the equilibrium constants for the formation of Na_3Bi and NaBi ; these constants, which were determined from the experimental data, were also used

to calculate vapor-liquid and liquid-solid phase equilibrium diagrams. New data for the sodium-bismuth liquid-solid phase diagram are also reported.

Materials Stability

The principal factor in the selection of suitable insulators and paste-electrolyte fillers for lithium-containing cells is the stability of the material toward liquid lithium. Only a few materials have stabilities that make them worthy of serious consideration. Various double oxides have been examined, but only LiAlO_2 is stable enough for use in cells with lithium anodes. The double oxides Li_2ZrO_3 and CaZrO_3 are both attacked by liquid lithium at 450°C.

Metals that are stable to tellurium and selenium are also required for use in laboratory cells. Of the metals examined, only tungsten is stable to tellurium at 480°C, and only niobium and some niobium-containing alloys are stable to selenium at 375°C. A wider selection of metals and alloys has been found for use with tin at 1300°C (a possible regeneration temperature): tungsten, Mo-30 wt % W, and Re-50 wt % W all showed no corrosion after 125 to 211 hr of exposure to tin at 1300°C.

VI. Nuclear Constants (pages 170 to 176)

Measurements of neutron cross sections for materials of interest to the fast reactor program are continuing. Capture cross sections as a function of neutron energy have been completed for the reactions $^{51}\text{V}(n,\gamma)^{52}\text{V}$, $^{50}\text{Ti}(n,\gamma)^{51}\text{Ti}$, $^{89}\text{Y}(n,\gamma)^{90\text{m}}\text{Y}$, $^{85}\text{Rb}(n,\gamma)^{86\text{m}}\text{Rb}$, and $^{87}\text{Rb}(n,\gamma)^{88}\text{Rb}$. Measurements are in progress for the reactions $^{86}\text{Sr}(n,\gamma)^{87\text{m}}\text{Sr}$, $^{84}\text{Sr}(n,\gamma)^{85\text{m}}\text{Sr}$, and $^{87}\text{Sr}(n,n')^{87\text{m}}\text{Sr}$.

Integral (reactor-spectrum) cross sections are being obtained by irradiation of materials in EBR-II. An irradiation of specimens of type 304L stainless steel in various positions in EBR-II has provided the data necessary to calculate, as a function of radial position, the neutron flux of EBR-II and the cross sections of important (n,p) , (n,γ) , and (n,α) reactions in stainless steel. An irradiation of samples of Ti, V, S, Fe, Ni, Co, Sc, Cu, and Au in EBR-II has been completed, and analysis of the reaction products is in progress.

Determination of capture-to-fission ratios (α) in EBR-II for various uranium and plutonium isotopes is continuing. Alpha measurements for ^{233}U are nearly complete and those for ^{235}U and ^{238}U are in progress.

An experiment has been designed to measure the fast-fission yields of tritium, hydrogen, and helium as functions of neutron energy. The low-mass particles produced in the fast fission of various uranium and plutonium isotopes will be detected and identified by means of a three-detector telescope array. Equipment for the experiment has been completed and will be tested with a ^{252}Cf source, which produces low-mass particles by spontaneous fission. Experiments are scheduled to begin upon completion of the ANL high-flux fast-neutron generator, which is now under construction.

VII. Determination of Burnup of Fast Reactor Fuels (pages 177 to 180)

The program for the development of analytical methods for the determination of burnup of fast reactor fuels is continuing. Evaluations were made of the suitability of molybdenum, technetium, and the rare earths

as burnup monitors for oxide fuels. The studies showed that neither molybdenum nor technetium was completely retained in oxide fuel, and that neither would be a satisfactory monitor. Cerium, a typical rare earth,

was completely retained; the rare earths are, therefore, considered to be excellent candidates for burnup monitors for oxide fuels.

In the development of a method for the determination of total rare earths by photometric titration with EDTA, minor modifications of the previously reported procedure have resulted in improved separations from interferences. Development work on this method is now complete.

A method for determining rare earths by X-ray

spectrometry is also under development. Good precision has been demonstrated in determining individual rare earths by an internal-standard technique. The sensitivity of the method has been increased by determining the sum of the four major fission product rare earths. Present work is focused on the development of a procedure for separating the rare earths from elements that emit interfering X-rays and from such bulk constituents as uranium, plutonium, and cladding.

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I

Compact Pyrochemical Processes¹

(*R. K. Steunenberg, J. D. Arntzen*)

Compact pyrochemical processes employ high-temperature, nonaqueous separations for processing ceramic (oxide and carbide) and metallic fuels discharged from fast breeder reactors. Liquid metal and molten salt systems are used as solvents in the processes currently being investigated. The metal solvents are usually binary alloys of magnesium with zinc, cadmium, or copper. The salt solvents usually contain MgCl_2 in combination with alkali or alkaline earth chlorides.

Some of the technological and economic features of pyrochemical processes are particularly desirable for processing fast breeder reactor fuels. These features include (1) the ability to process short-cooled, high-burnup fuels, which results in a reduction of out-of-reactor fuel inventories, (2) the simplification or elimination of chemical conversions, (3) minimum requirements for shielded processing space because of the small process volumes and compact equipment used, and (4) the direct production of solid radioactive wastes.

The objectives of pyrochemical processes are to re-

¹ A summary of this section is given on pages 1 to 4.

move fission products from the spent fuel, extract the bred plutonium from the blanket, enrich the core with plutonium, and repair irradiation damage. These objectives require that the cladding material, uranium, plutonium, and fission products be separated from one another. The buildup of radioactive isotopes of uranium and plutonium in recycled fuel may require semi-remote or remote refabrication of the fuel, even if all of the fission products are removed. Current studies indicate that with little or no change in operating procedure the same pyrochemical process could handle both core fuel (containing approximately 10 to 20 wt % plutonium) and blanket material (containing 5 wt % or less plutonium).

Pyrochemical processes incorporating salt-transport separations are currently being investigated. In salt-transport separations, solute plutonium or uranium is transported from one liquid metal alloy (donor) to another (acceptor) by a molten chloride salt solvent acting as a carrier. Pyrochemical processes incorporating salt-transport separations show promise of good fission product removals and high plutonium and uranium recoveries.

A. LABORATORY-SCALE INVESTIGATIONS (*I. Johnson*)

The objectives of the laboratory-scale investigations are to provide basic chemical data of importance to pyrochemical processing and to originate and evaluate new process concepts. During the period covered by this report, the major effort has been devoted to the further development of a pyrochemical process for breeder reactor (FBR) fuels that employs a salt transport separation. Salt-transport separations are based on the selective transfer of a solute from one liquid alloy to another by the circulation of a molten

salt between the two alloys. Chemical studies in support of the process development include (1) measurements of the distribution of neptunium between molten salts and liquid metal alloys, (2) measurements of the solubilities of plutonium, chromium, and neptunium in liquid metal solutions, (3) determinations of the liquidus composition-temperature relations for the $\text{MgCl}_2\text{-MgF}_2$ and $\text{CaCl}_2\text{-CaF}_2\text{-CaO}$ salt systems, and (4) a determination of the activity of neptunium in liquid Cd-Np alloys.

1. Distribution of Elements Between Liquid Alloys and Molten Salts

In pyrochemical processes, the basic separations of plutonium, uranium, and fission product elements are effected through differences in the distribution behavior of these elements between molten salts and liquid alloys. In the current process flowsheet (see Fig. I-9, Section I.B.), separations by distribution between molten salts and liquid alloys are employed at four places: (1) the separation of a major fraction of the alkali and alkaline earth metal fission products from plutonium and uranium is achieved by contacting the $\text{CaCl}_2\text{-CaF}_2$ reduction salt and the Cu-Mg reduction alloy; (2) rare earth metal fission products are separated from plutonium by contacting a molten MgCl_2 -based extraction salt mixture with the liquid Cu-Mg alloy; (3) plutonium is separated from the noble metal fission product elements by contacting a molten MgCl_2 -based transport salt mixture and the liquid Cu-Mg alloy; and (4) plutonium is recovered from the transport salt by contacting the salt with a liquid Zn-Mg alloy. We have previously reported distribution data (starting with ANL-6569, 1963) for key elements in each of these systems.

Since neptunium is of interest as a by-product from

the operation of a nuclear power reactor, its properties are being investigated to provide information for the development of a procedure for its recovery. The procedure should be compatible with the pyrochemical process under development for FBR fuels. Results obtained to date indicate that neptunium will accompany plutonium in the pyrochemical process. Data are reported below on the distribution of neptunium between a molten MgCl_2 salt mixture and a liquid Zn-Mg alloy.

a. Distribution of Neptunium Between $\text{MgCl}_2\text{-30 mol \% NaCl-20 mol \% KCl}$ Salt and $\text{Mg-31 at. \% Zn}$ Alloy (J. B. Knighton, K. R. Tobias)

The effect of temperature on the distribution of neptunium between a $\text{MgCl}_2\text{-30 mol \% NaCl-20 mol \% KCl}$ salt mixture and a $\text{Mg-31 at. \% Zn}$ alloy was determined in a recent experiment. These measurements were made to determine if any differences in the distribution of neptunium and plutonium in this system could be used as the basis of a technique for separating the two elements.

The materials charged to this experiment included

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FIG. I-1. Distribution of Neptunium and Plutonium Between $\text{MgCl}_2\text{-30 mol \% NaCl-20 mol \% KCl}$ Salt and $\text{Mg-31 at. \% Zn}$ Alloy.

108.0 g of high-purity zinc (99.999%), 92 g of magnesium (99.97%), 1.05 g of NpO_2 , and 150 g of purified MgCl_2 -30 mol % NaCl -20 mol % KCl salt. The materials were charged to a baffled tantalum crucible that was contained in a furnace vessel with a purified helium atmosphere. The crucible was heated to the desired temperature, and the melt was mixed for at least 1 hr to achieve equilibration. Mixing was provided by a flat-bladed tantalum agitator turning at about 300 rpm. Then, following settling of the melt at temperature with no mixing for 15 min, the salt and metal phases were sampled. The samples were taken by pressure filtering through porous tantalum frits into tanta-

lum sample tubes. The equilibrations were made in the following temperature sequence: 800, 600, 425, 500, and 700°C.

The neptunium distribution coefficients [$D = (\text{NpCl}_3 \text{ in salt, mol \%}) / (\text{Np in metal, at. \%})$] calculated from the results of this experiment are compared in Fig. I-1 with plutonium distribution coefficients in the same system. These data show that the neptunium distribution coefficients are only slightly larger than those of plutonium throughout the temperature range investigated. Therefore, a neptunium-plutonium separation based on this system would require a multistage countercurrent extraction.

2. Solubilities in Liquid Alloys

The solubilities of plutonium, uranium, by-product actinides such as neptunium, fission product elements, and structural metals in liquid metal alloys are important factors in the choice of suitable liquid-metal solvents, in the determination of volumes of process streams, and for the evaluation of corrosion data for the pyrochemical process for FBR fuels. Data have been obtained on the solubility of plutonium in liquid Zn-Mg alloys, of chromium in liquid zinc, and of neptunium in liquid cadmium.

a. The Solubility of Plutonium in Liquid Zinc-Magnesium Alloys (*J. B. Knighton, K. R. Tobias*)

Knowledge of the phase relations of the zinc-rich region of the Zn-Mg-Pu system is required to specify the temperature and composition of the acceptor alloy for the salt transport step of the pyrochemical process. This alloy system is used in the process because of low values for the plutonium solubility and for the distribution coefficient (mol % Pu in salt/at. % Pu in alloy), which result in a low plutonium concentration in the transport salt after it has contacted the acceptor alloy.

An experiment was conducted to provide additional plutonium solubility data in zinc and Zn-low Mg alloys between 600 and 800°C. The initial charge consisted of 400 g of high-purity zinc rod (99.999%), 56.28 g of plutonium metal, and 100 g of purified MgCl_2 -30 mol % NaCl -20 mol % KCl salt. The magnesium content of the metal was adjusted by two magnesium additions (21 and 12 g) during the experiment. The salt was used to blanket the melt to hinder evaporation of volatile zinc and magnesium.

The melt was contained in a baffled tantalum crucible inside a furnace vessel with a purified helium atmosphere. Mixing was provided by a flat tantalum paddle. Samples were obtained by pressure filtering

through porous tantalum frits into tantalum sample tubes. The temperature of the melt was measured with a calibrated, stainless steel-clad chromel-alumel thermocouple that was protected from the melt by a tantalum thermowell.

The salt-metal system was equilibrated by mixing for at least 1 hr at each temperature and alloy composition. Filtered metal samples were taken after a 15-min settling period. The equilibrations were made on both rising and falling temperature sequences.

Figure I-2 indicates that the results of this study agree with previously reported results (ANL-7375, p. 25). They also agree with the plutonium solubility in zinc reported by Johnson and Chasanov.² The present study extends the measured range of plutonium solubility in zinc from 750 to 800°C.

The intermetallic compound $\text{Pu}_2\text{Zn}_{17}$ is believed to be the equilibrium solid phase present in the Zn-Mg-Pu alloys used in the present study and in Zn-Pu alloys above about 710°C (see ANL-7375, p. 31). The compound PuZn_{12} is believed to be the equilibrium solid phase present in (1) the Zn-Pu melt below about 710°C, (2) Zn-Mg alloys of less than 6.2 at. % Mg at 700°C, and (3) Zn-Mg alloys of less than 16.8 at. % Mg at 600°C. Although Cramer and Wood³ failed to confirm the existence of PuZn_{12} , they reported an unidentified plutonium solid phase of the $\text{Th}_2\text{Ni}_{17}$ (hexagonal) type on the zinc side of the $\text{Pu}_2\text{Zn}_{17}$ (rhombohedral) compound. Two other Pu-Zn compounds reported by Cramer et al.,⁴ Pu_2Zn_9 and PuZn_2 ,

² I. Johnson, M. G. Chasanov, *J. Inorg. Nucl. Chem.* **26**, 2059 (1964).

³ E. M. Cramer, D. H. Wood, *J. Less Common Metals* **13**, 112 (1967).

⁴ E. M. Cramer, F. H. Ellinger, C. C. Land, *Extractive and Physical Metallurgy of Plutonium and its Alloys*, pp. 169-180, Interscience Publishers, New York (1959).

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FIG. I-2. Solubility of Plutonium in Zinc-Magnesium Alloy. (Solid points are data from this study; open points are data reported in ANL 7375, p. 25.)

may be the equilibrium solid phases at higher magnesium and plutonium contents in the alloy.

b. The Solubility of Chromium in Liquid Zinc (J. B. Knighton, L. F. Dorsey)

The pyrochemical process for FBR fuels utilizes molten zinc to dissolve stainless steel cladding from

mixed $\text{UO}_2\text{-PuO}_2$ fuels. Because information on the solubility of the various stainless steel components (Fe, Ni, and Cr) in liquid zinc is required, a study was made to determine the solubility of chromium in liquid zinc over a temperature range of 425 to 800°C.

The charge to the experiment consisted of 15 g of carbon-free purified chromium, 500 g of reagent-grade

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FIG. I-3. Solubility of Chromium in Zinc.

FIG. 1-4. Solubility of Neptunium in Liquid Cadmium.

zinc, and 182 g of purified LiCl-KCl eutectic salt. The salt was added to prevent zinc evaporation. The charge was contained in a baffled tantalum crucible held within a furnace vessel containing a purified helium atmosphere. A calibrated chromel-alumel thermocouple in a tantalum thermowell was used to measure temperature.

Chromium was dissolved in the zinc by heating for 48 hr while mixing at 300 rpm. The melt was then thermal-cycled and equilibrated at various temperatures during the cycle (800, 700, 600, 500, 450, and 425°C during cooling and 475, 550, 650 and 750°C during heating). The length of the equilibrium period ranged from 2.5 to 16 hr. Duplicate filtered metal samples were taken at each equilibration.

The results of the experiment are presented in Fig. I-3. The change in slope of the line representing the chromium solubility in zinc indicates that a phase change may exist at about 568°C. The least-squares method was used to calculate equations representing

The results of the experiment are presented in Fig. I-3. The change in slope of the line representing the chromium solubility in zinc indicates that a phase change may exist at about 568°C. The least-squares method was used to calculate equations representing

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FIG. I-5. Partial Neptunium-Cadmium Phase Diagram.

the solubility of chromium in zinc above and below 568°C. These equations are

$$419.5\text{--}568^\circ\text{C: } \log (\text{at. \% Cr}) = 1.0286 - \frac{897.6}{T(^{\circ}\text{K})}$$

$$568\text{--}800^\circ\text{C: } \log (\text{at. \% Cr}) = 1.7638 - \frac{1512}{T(^{\circ}\text{K})}$$

The standard deviation of the data from the equations is 0.75% from 419.5 to 568°C and 6.3% from 568 to 800°C.

These values for chromium solubility are lower than those reported by Chiotti et al⁵ (1.2 wt % at 500°C compared with our value of 0.6 wt % at 500°C) and Lihl et al⁶ (0.6 wt % at 440°C). Weisse et al⁷ report a solubility of chromium in zinc at 415°C of 0.26 wt %, compared with our calculated solubility at 419.5°C of 0.43 wt %.

The compositions of the equilibrium solid phases have not been determined. However, Lihl et al⁶ report a CrZn₁₇ compound, and Stanton et al⁸ report a CrZn₁₀ compound.

⁵ P. Chiotti, G. R. Kilp, *Trans. Met. Soc. AIME* **215**, 892 (1959).

⁶ F. Lihl, P. Jenitschek, *Z. Metallkunde* **45**, 686 (1954).

⁷ E. Weisse, A. Blumenthal, H. Hanemann, *Z. Metallkunde* **34**, 221 (1942).

⁸ R. M. Stanton, R. F. Woerner, C. L. Vold, J. A. Kingston, J. F. Smith, "The Structure of Binary Intermetallic Compounds," USAEC report IS-1047 (1958).

c. The Solubility of Neptunium in Liquid Cadmium (M. Krumpelt, P. J. Mack, J. J. Heiberger)

The solubility of neptunium in liquid cadmium has been measured as part of a program to provide sufficient data on neptunium systems for the design of neptunium separation processes. Two different Cd-Np alloys were prepared, and the liquid phases were sampled at temperatures ranging from 328 to 626°C. The experimental procedure was essentially the same in both experiments (see ANL-7425, p. 28 for details).

The atom fraction of neptunium in the liquid alloy is shown as a function of temperature in Fig. I-4. The solubility data are represented by two straight lines, which intersect at about 485°C. The existence of two straight-line segments on a plot of this type indicates two different solid phases in equilibrium with the liquid phase.

The solid phases in the Cd-rich region of this system were identified by X-ray diffraction examination of alloys with neptunium-to-cadmium atom ratios of 1:11 and 1:6. The alloys were each prepared by melting the metals together at 800°C and then annealing them. The 1:11 alloy was annealed at 400°C, and the 1:6 alloy was annealed at 450°C. The X-ray diffraction patterns indicated⁹ the existence of two intermetallic phases: NpCd₁₁, isostructural with CeBaHg₁₁, and NpCd₆, isostructural with CeCd₆. The

⁹ R. Schablaske, Chemical Engineering Division, Analytical Group, made the X-ray studies.

lattice constants, a_0 , were 9.288 Å for NpCd_{11} and 15.614 Å for NpCd_6 . In both cases, the constants are larger than those found for the corresponding plutonium compounds.

The two straight lines in the plot of the solubility data (Fig. I-4) represent the neptunium content of the liquid phase in equilibrium with NpCd_{11} from about 321 to 485°C and the neptunium content of the liquid phase in equilibrium with NpCd_6 from 485°C to at least 626°C. At 485°C, the NpCd_{11} compound undergoes peritectic reaction to form NpCd_6 in equilibrium

with a liquid phase containing about 2 at. % Np. The two straight lines may be represented by the equations

$$321\text{--}485^\circ\text{C: } \log x_{\text{Np}} = 4.099 - \frac{4397}{T(^{\circ}\text{K})}$$

$$485\text{--}626^\circ\text{C: } \log x_{\text{Np}} = 0.459 - \frac{1636}{T(^{\circ}\text{K})}$$

where x_{Np} is the atom fraction of neptunium. These solubility and X-ray diffraction data were used to prepare the phase diagram for the cadmium-rich region of the Cd-Np system shown in Fig. I-5.

3. Molten Salt Systems

The major separation procedures employed in pyrochemical processes utilize differences in distribution behavior between molten salt mixtures and liquid alloys. The phase relations in most of the molten salt mixtures of interest have been reported by others. However, since the solubility of CaO (a product of the reduction step of the process for FBR fuels) in the $\text{CaCl}_2\text{--CaF}_2$ reduction salt had not been reported, the CaCl_2 -rich region of the $\text{CaCl}_2\text{--CaF}_2\text{--CaO}$ system was investigated. The liquidus curve for the $\text{MgCl}_2\text{--MgF}_2$ system was determined as part of a search for a low-melting, high- MgCl_2 -content salt mixture.

a. The CaCl_2 -Rich Region of the $\text{CaCl}_2\text{--CaF}_2\text{--CaO}$ System (D. A. Wenz, R. D. Wolson)

The $\text{CaCl}_2\text{--CaF}_2$ salt mixture, when used with a Cu-Mg-Ca alloy, has been found to be very effective in reducing UO_2 powder, as well as sintered UO_2 pellets, in the reduction step of the pyrochemical process. The relatively high solubility of the CaO product in the reduction salt is presumed to be one reason for the effectiveness of this system. Information was needed on the optimum $\text{CaCl}_2\text{--CaF}_2$ salt composition for reductions and on the solid phases that might precipitate as CaO is added to a $\text{CaCl}_2\text{--CaF}_2$ salt. Therefore, the CaCl_2 -rich region of the $\text{CaCl}_2\text{--CaF}_2\text{--CaO}$ phase diagram was investigated by thermal analysis techniques.

Various $\text{CaCl}_2\text{--CaF}_2$ mixtures contained in stainless steel crucibles were placed in a furnace well inside a helium-atmosphere glovebox. The salts were heated above their melting points and stirred to insure complete solution of the components. Calcium oxide was added in small increments to each halide mixture, and heating and cooling curves were obtained for each composition.

The $\text{CaCl}_2\text{--CaF}_2\text{--CaO}$ phase diagram drawn from the data obtained in these experiments is shown in Fig. I-6. The $\text{CaCl}_2\text{--CaF}_2$ -binary side of the diagram

is in good agreement with the literature. The $\text{CaCl}_2\text{--CaO}$ binary differs from previous diagrams in that a peritectic was found at 18.5 mol % CaO and 835°C. The incongruently melting compound is $\text{CaO} \cdot 2\text{CaCl}_2$. Previous work¹⁰ reported on the same portion of the diagram indicated the existence of a congruently melting compound, $\text{CaO} \cdot 4\text{CaCl}_2$, and a eutectic at about 22 mol % CaO.

The present $\text{CaCl}_2\text{--CaF}_2\text{--CaO}$ diagram (Fig. I-6) contains a ternary eutectic at $\text{CaCl}_2\text{--}17 \text{ mol \% CaF}_2\text{--}4 \text{ mol \% CaO}$ and 625°C, plus ternary peritectics at $\text{CaCl}_2\text{--}23 \text{ mol \% CaF}_2\text{--}10 \text{ mol \% CaO}$ and 660°C and at $\text{CaCl}_2\text{--}23 \text{ mol \% CaF}_2\text{--}13 \text{ mol \% CaO}$ and 670°C. The first phases that precipitate upon cooling salt compositions in the various regions of the ternary are indicated in Fig. I-6. The $\text{CaCl}_2\text{--}10 \text{ mol \% CaF}_2$ salt composition appears to be the optimum for reductions because it has essentially the maximum CaO solubility in the reduction system at 800°C, and if the temperature is kept above 775°C, CaO is the only component that will precipitate when its solubility is exceeded.

b. The $\text{MgCl}_2\text{--MgF}_2$ System (R. A. Sharma)

In the salt-transport step of the pyrochemical process, a molten MgCl_2 salt mixture is circulated between a donor alloy and an acceptor alloy. At the donor alloy, plutonium is oxidized from the alloy into the salt by the MgCl_2 dissolved in the salt. The extent of this oxidation depends on the activity of MgCl_2 in the salt. When the activity in the salt is large, less salt needs to be circulated between the two alloys to complete the transfer of plutonium. Pure MgCl_2 would be the best transport salt except for its high melting point (715°C).

Several binary salt systems were investigated in an

¹⁰ B. Neumann, C. Kröger, H. Jüttner, *Z. Elektrochem.* **41**, 725 (1935).

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FIG. I-6. Partial Phase Diagram of the CaCl_2 - CaF_2 - CaO System.

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FIG. I-7. Liquidus-Temperature Diagram of the MgCl_2 - MgF_2 Binary System.

attempt to find a salt mixture with a high MgCl_2 content and a low melting point. The MgCl_2 - MgF_2 system was found to have potential as a transport salt. The liquidus-temperature diagram for the MgCl_2 - MgF_2 binary, as determined by thermal analysis, is

shown in Fig. I-7. A eutectic containing 78.0 ± 0.5 mol % MgCl_2 was found at $628 \pm 2^\circ\text{C}$. It is anticipated that this salt mixture could be used at 650°C in the salt-transport step and that it would function very much like pure MgCl_2 .

4. Thermodynamics of the Np-Cd System (M. Krumpelt, J. J. Heiberger)

The thermodynamic properties of the Np-Cd system are being investigated to provide basic information that might be used to develop a neptunium recovery step in the salt transport process. A high-temperature galvanic cell of the form

was operated between 380 and 545°C . Preliminary data are shown in Fig. I-8.

The alloy consisted of the solid phase NpCd_{11} and saturated cadmium-rich liquid over the temperature range from 380 to 485°C , while from 485 to 545°C it consisted of NpCd_6 and the saturated liquid. The temperature of the intersection of the two straight lines corresponds to the peritectic temperature for the reaction

The 485°C peritectic temperature found in this investigation is in good agreement with the 485°C value from the solubility data (see Section 2.c, above).

The overall reaction taking place in these cells may

be written as

Therefore, the emf, ϵ , is given by the relation

$$-3F\epsilon = \Delta G_f^\circ_{\text{NpCd}_n} - nRT \ln a_{\text{Cd}}$$

where $\Delta G_f^\circ_{\text{NpCd}_n}$ is the standard free energy of formation of the intermetallic compound NpCd_n , and a_{Cd} is the activity of cadmium in the saturated solution. Since these solutions are dilute with respect to neptunium, the term $nRT \ln a_{\text{Cd}}$ has a small value compared with ΔG_f° , and, therefore, may be neglected in a good first approximation. Thus, the standard free energy of formation is equal to $-3F\epsilon$. The following equations for the temperature dependence of the standard free energy of formation were obtained:

$$\text{NpCd}_{11}: \Delta G_f^\circ (\text{cal/mol}) = -44,700 + 43.3T(^{\circ}\text{K})$$

$$\text{NpCd}_6: \Delta G_f^\circ (\text{cal/mol}) = -28,400 + 21.7T(^{\circ}\text{K})$$

The values of the slope and intercept in these linear equations correspond, respectively, to the standard entropy, ΔS_f° , and enthalpy, ΔH_f° , of formation. In

FIG. I-8. Emf Data for the cell: $\text{Np} | \text{NpCl}_3, \text{LiCl-KCl (eutectic)} | \text{Np-Cd (two-phase alloy)}$.

both cases, the values found for the neptunium compounds are close to the values found for the corresponding plutonium-cadmium compounds.¹¹ The en-

¹¹ I. Johnson, M. G. Chasanov, R. M. Yonco, *Trans. Met. Soc. AIME* **233**, 1408 (1965).

thalpy of formation of UCd_{11} ¹² is -27.2 kcal/mol and is, therefore, smaller than the values for either NpCd_{11} or PuCd_{11} .

¹² I. Johnson, H. M. Feder, *Trans. Met. Soc. AIME* **224**, 468 (1962).

B. ENGINEERING-SCALE PROCESS INVESTIGATIONS (R. D. Pierce)

1. Process Flowsheet Development (W. J. Walsh)

A conceptual pyrochemical process flowsheet for the recovery of fast breeder reactor fuels is shown in Fig. I-9. This process has the potential of handling greater than one ton per day of short-cooled fuel with plutonium and uranium recoveries exceeding 99% and decontamination factors greater than 10^6 . The process features include (a) dissolution of the stainless steel cladding in liquid zinc (eliminating the need for disassembly, sodium removal, chopping or shearing, etc.), (b) complete removal and collection of the volatile fission products in the head-end vessel, (c) incorporation of a high-performance cross-current extraction technique to achieve efficient rare earth and noble metal removal in a semicontinuous mixer-settler unit, (d) plutonium product isolation in a slab-geometry solvent-metal distillation unit, and (e) resynthesis of the fuel to mixed uranium and plutonium oxides in a fluid-bed converter. Plutonium and uranium accountability is readily achieved in the head-end vessel where both elements are obtained in liquid metal solutions, which may be sampled and accurately weighed. A brief description of the individual processing steps is given below.

Decladding and feed preparation. The following sequence of operations comprises the head-end portion of the process: (a) The trimmed fuel elements are immersed in liquid zinc at 800°C to dissolve the stainless steel cladding and structural material. (b) After the stainless steel dissolution is complete, the zinc-stainless steel solution is transferred from the system. (c) The residual zinc is vacuum distilled away from the fuel and is collected in a condenser along with the released volatile fission products and any sodium that is present. (d) The Mg-29 at. % Cu-34 at. % Ca and CaCl_2 -20 mol % CaF_2 reagents are charged to the vessel, and the fuel oxides are reduced at 800°C . (e) The reduction salt is removed and sent to waste. (f) The Mg-Cu-Pu solution is removed, and the precipitated uranium is washed with a fresh Mg-Cu solution. (g) The precipitated uranium is removed from the vessel by

dissolution in a Cu-6 at. % Mg-3.5 at. % U solution or in a Fe-U solution (deferred processing alternative not shown on flowsheet), and any residual plutonium that is present is extracted into a MgCl_2 salt and recycled to the reduction step for recovery.

Plutonium purification. The separation of plutonium from rare earth, noble metal, and refractory metal fission products is achieved in a semicontinuous mixer-settler battery (see Fig. I-9). Seven stages are required to achieve an overall decontamination factor of 10^6 . In this unit, a MgCl_2 -18 mol % NaCl -12 mol % KCl -3 mol % MgF_2 salt mixture is employed as the rare earth extraction salt in stages 1, 2, 3, and 4, and as the recirculating plutonium transport salt in stages 5, 6, and 7. The Mg-Cu-Pu solution from the feed-preparation step is continuously recirculated through stages 1, 2, 3, 4, and 5, which comprise a high-performance, cross-current extraction system for plutonium-rare earth separations. The operation of this unit is described in detail in Section I.B.2.b of this report.

Plutonium recovery. Zinc and magnesium are vacuum distilled from the plutonium product solution in a retort having a slab geometry. The Zn-Mg-Pu solution from the seven-stage extraction unit is intermittently charged to the retort, and the bulk of the Zn-Mg is evaporated leaving the plutonium in the vessel as a liquid. After the desired amount of plutonium has been charged (within criticality limitations), and the distillation has continued until the purity of the accumulated plutonium is high, the plutonium product is transferred from the system.

Uranium recovery. The requirements for uranium processing are uncertain, but the available options include (a) the processing method shown in the proposed flowsheet (see Fig. I-9) in which the uranium in the head-end vessel is dissolved in Cu-13 at. % Mg at 900°C and salt-transported to a Mg-Zn acceptor alloy, which would subsequently be transferred from the uranium. The balance of the solvent metal is removed by vaporization during vacuum melting of the

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FIG I-9. Conceptual Pyrochemical Process Flowsheet.

uranium and (b) an alternative system for deferred processing (not shown in Fig. I-9) in which the uranium is removed in compact form as a U-18 at. % Fe alloy and sent to storage or to a large central processing plant. In both of these processing schemes, any re-

sidual plutonium present is extracted into MgCl₂ and recycled to the reduction step.

Resynthesis. In the resynthesis step, the plutonium product is blended with uranium and converted to (U,Pu)O₂ in a fluid-bed reactor.

2. Process Flowsheet Experiments

a. Fuel Decladding and Feed Preparation (W. J. Walsh, I. O. Winsch, T. F. Cannon, J. J. Stockbar)

An experimental program was initiated to study the removal of stainless steel cladding from oxide fuels and the subsequent interfacing of this process operation with the reduction step.

Two experiments, Runs ZD-3 and ZD-4, were performed in which a simulated stainless steel fuel assembly loaded with UO₂ pellets and UO₂ fines was sub-

jected to a complete head-end processing operation including (a) dissolution of the stainless steel in molten zinc, (b) transfer of the zinc-stainless steel solution from the system, (c) vacuum distillation of the residual zinc (from beneath the salt phase), (d) reduction of the UO₂ pellets and fines, and (e) separation of the Mg-Cu solution from the precipitated uranium phase. In an actual reprocessing facility, the resulting Mg-Cu solution would contain the bulk of the pluto-

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FIG. I-10. Simulated Fuel Assembly.

mium present in the system and would be the feed for the seven-stage extraction unit.

The simulated fuel assemblies used in Runs ZD-3 and ZD-4 (see Fig. I-10) were constructed of type 304 stainless steel and consisted of an array of 13 tubes welded to three circular plates. The tubes were about 12½ in. long, with a ⅜-in. ID and a wall thickness of 0.035 in. The plates were 4 in. in diameter and ¼ in. thick. Each of the assemblies contained 2.7 kg of stainless steel and 2.5 kg of UO_2 , ~5% of which was fines. Each tube was filled with UO_2 pellets (⅜ in. in diameter by ½ in. long) and UO_2 fines (crushed pellets). The fines were loaded in the center of each tube. A stainless steel holding rod (33 in. long by ⅝ in. in diameter) was welded to the top plate of each assembly to position the assembly in the liquid zinc.

The decladding experiments were conducted in a 9⅜-in. ID pressed-and-sintered tungsten crucible con-

tained in a furnace vessel with an argon atmosphere. The crucible was loaded with 84.5 kg of zinc to provide a liquid metal depth of 14 in. About 6 kg of CaCl_2 -20 mol % CaF_2 (about 2 in.) was charged to the crucible to retard vaporization of the zinc and to collect UO_2 fines. The system was then heated to 800°C, and the assembly was completely submerged in the melt. After about 30 min of contact, the tubing was completely dissolved, but the rod and plates were relatively unaffected. An additional 7 hr of contact (with moderate agitation) was employed to insure dissolution of all of the stainless steel. Filtered samples of the zinc-stainless steel solution were taken to ascertain the rate of dissolution in both runs. The results are presented in Fig. I-11. The data indicate that the 0.035-in. tubing dissolved in less than 30 min, but about 4 hr were required for dissolution of the more massive spacer plates.

FIG. I-11. Kinetics of Simulated Fuel Assembly Dissolution in Molten Zinc.

Most of the zinc-stainless steel solution was removed through a transfer line at the conclusion of the decladding step in each run. The zinc-stainless steel ingots were subsequently dissolved in nitric acid. Analyses of the acid solution showed that the ingots contained very little entrained UO_2 ($\sim 0.01\%$ of the uranium charged in Run ZD-4).

After the bulk of the zinc-stainless steel solution had been transferred from the crucible, a water-cooled condenser was connected to the furnace vessel through the same opening used for the transfer line. The condenser provided for gas flow up out of the furnace and to the vacuum system. The gas flowed through a horizontal section of steel tube having internal flow baffles and external cooling coils. When the system was evacuated through the condenser, a high rate of zinc vaporization from the heel was observed. The zinc vapors had to pass through the 2-in. deep salt layer. The crucible contents were maintained at about 800°C throughout the vaporization step.

About 2.3 kg and 4.0 kg of zinc were collected in Runs ZD-3 and ZD-4, respectively. At the rates employed, and without provision for de-entrainment, there was some salt entrainment, but uranium entrainment was low ($< 0.1\%$ of the uranium).

Following the zinc distillation step in Runs ZD-3 and

ZD-4, the UO_2 was reduced with Mg-42 at. % Cu-3 at. % Ca. Reduction efficiencies greater than 99% were achieved in both experiments. A sludge, attributed to uranium nitride formation, was present with the precipitated uranium in Run ZD-3. Run ZD-4 was conducted with an improved atmosphere, and no sludge was observed.

b. Mixer-Settler Investigation (W. E. Miller, J. B. Knighton, G. N. Vargo)

The salt transport process (see Fig. I-9) incorporates a multistage, semicontinuous extraction battery for separation of fission products from plutonium. Design work and laboratory investigations are being conducted on mixer-settlers for this application. Unlike conventional multistage mixer-settlers, which employ countercurrent flow of two fluids, many different fluids and several different flow patterns are used in the proposed mixer-settler battery. The flow patterns for the unit being developed are illustrated in Fig. I-12, which is a plan view of a seven-stage extractor. This design was chosen after a review of many mixer-settler designs. Figure I-13 is a simplified drawing of a typical mixer-settler stage. An agitator-pump located in the mixing region mixes the fluids outside the rotor and pumps them by centrifugal force up from an opening

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FIG. I-12. Plan View of Seven-Stage Mixer-Settler Battery.

in the bottom of the rotor to outlets at the top. Any fraction of the flow can be refluxed by adjusting a beveled cylindrical shell surrounding the outlets at the top of the rotor (not shown in Fig. I-13). The balance of the flow is discharged into a collector ring and diverted to the settling region. In all stages containing a captive solvent, the captive solvent flows around a vertical baffle in the settling region and back into the mixing region (see Fig. I-12).

In the planned process, the Mg-Cu-Pu alloy containing fission products is circulated from a feed tank through stages 1 to 4 to extract rare earth fission products from the solution into captive salt solutions. In stage 5, plutonium is selectively stripped into the transport salt, and the depleted liquid metal (containing most of the noble and refractory metal fission product elements) is recirculated to stage 1. In stage 6, the plutonium-bearing salt stream is contacted with a captive Cd-Mg phase to scrub the transport salt for additional removal of noble and refractory metals and traces of Cu-Mg which may be entrained occasionally from stage 5. In stage 7, plutonium is stripped from the continuously recirculated transport

salt into a captive Zn-Mg acceptor solution. The acceptor alloy is transferred intermittently to the distillation unit for plutonium recovery and is replaced with recycled Zn-Mg condensate. When the plutonium concentration in the salt in stage 1 has been reduced to an acceptable level, the salt and metal flows are stopped and the salt in stage 1 is sent to waste. The salts in stages 2, 3, and 4 are sent to stages 1, 2, and 3, respectively, and fresh salt is charged to stage 4. A fraction of the Cu-Mg solution is also sent to waste, and the remainder is recycled to the decladding vessel. The levels of the noble and refractory metals and copper in stage 6 are expected to be sufficiently low to permit reuse of the captive Cd-Mg alloy for several cycles. The transport salt is not consumed or contaminated in this process and may be reused indefinitely.

Full-scale plastic models of a mixer-settler stage have been built and tested. One of these models is shown in Fig. I-14. The mixing region of this unit is 3 in. by 3 in. by 8 in. deep. Water and an organic liquid (1 part acetylene tetrabromide and 0.43 parts xylene) were used to determine flow characteristics in these

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FIG I-13 Mixer-Settler Stage with Agitator-Pump.

models. These fluids were selected because they have a ratio of density difference to density of the lighter phase equal to that of the Mg-Cu and salt system of the reference flowsheet.

A mixer-settler is being fabricated for testing at 650°C with Mg-Cu and salt phases.

c. Plutonium and Uranium Recovery by Retorting

(J. F. Lenc, I. O. Winsch, A. L. Chandler, T. F. Cannon)

In the proposed plutonium salt-transport process shown in Fig. I-9, final recovery of the plutonium and uranium products is achieved in separate steps. The purpose of these steps is to vacuum distill the volatile Zn-Mg solvent from the plutonium, and to remove residual Mg-Zn solvent from the uranium and melt the uranium into a metallic ingot.

An existing induction furnace was modified for use as a vacuum retort. The still and condenser were built in accordance with a design developed for the skull reclamation process (ANL-7225, pp. 47-53). The new retorting equipment was initially tested with the plutonium and uranium products from the exploratory plutonium experiment described in ANL-7425, pp. 30-33. Neither the retorted plutonium product nor the retorted uranium product from this experiment consolidated into a metallic ingot because of atmos-

pheric contamination from small leaks in the furnace. The furnace and its associated vacuum system were subsequently modified to ensure that a high vacuum could be attained. Following the modifications, two 1/2-in. dia uranium rods weighing a total of 364 g were melted at ~1200°C and 10 Torr into a consolidated ingot in the retorting equipment. A thixotropically cast beryllia crucible was used to contain the uranium. Visual inspection of the ingot revealed no evidence of atmospheric contamination, and the ingot was easily recovered from the beryllia crucible. On the basis of these test results, the retorting equipment was considered to be acceptable for later retorting experiments with plutonium.

Retorting experiments are currently being performed to select a suitable material for a still-pot crucible to be used with plutonium. Beryllia, which has performed well in uranium retorting, will probably be unacceptable because of its neutron-moderating properties. Crucible materials under consideration include tantalum, high-purity magnesia, magnesia-10 wt % titania, and magnesia-3 wt % yttria. Tantalum and magnesia crucibles have been tested to date. Good consolidation of the retorted plutonium product in ingot form was achieved in experiments with tantalum, but the plutonium ingot adhered tenaciously to the tantalum. In experiments conducted in high-purity

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FIG. I-14. Plastic Model of Mixer-Settler Unit.

magnesia crucibles, the retorted plutonium product was easily recovered but was not in a well-consolidated form. This failure to achieve good consolidation of the product may be due to the small scale of the ex-

periments (about 15 g plutonium). Larger scale (about 100 g plutonium) retorting experiments are planned to determine whether better consolidation of the retorted product can be achieved with magnesia crucibles.

3. Plutonium Salt Transport Facility (*W. E. Miller, I. O. Winsch, D. E. Grosvenor, J. O. Ludlow, T. F. Cannon, N. P. Quattropani, J. J. Stockbar*)

Preliminary bench-scale studies of the salt transport process were reported in ANL-7425 (pp. 30-33). These experiments were performed in a small walk-in-hood facility containing two heated furnaces and were limited to batch studies with a maximum inventory of 200 g of plutonium. A new glovebox facility (called the Plutonium Salt Transport Facility) is being constructed that will contain process equipment capable

of demonstrating all of the steps in the pyrochemical process flowsheet with a fission product decontamination factor of $>10^6$ and plutonium and uranium recoveries exceeding 99%. The equipment will be sized to handle a process charge of 5-10 kg of fuel containing as much as 1 kg of plutonium and will incorporate semicontinuous mixer-settler extraction and solvent-metal distillation units. The facility will be

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FIG. I-15. Plutonium Salt Transport Facility.

able to handle dummy, stainless steel fuel assemblies containing $(U,Pu)O_2$ pellets and inactive fission product elements.

Figure I-15 is a sketch of the facility that is being assembled. Two gloveboxes will house the pyrochemical processing equipment. One box will contain equipment for plutonium extraction and retorting, and the other box will contain equipment for decladding, reduction, and uranium recovery. The atmosphere in these two boxes will be purified helium so that if any of the processing vessels is inadvertently opened to the glovebox atmosphere, oxidizing gases cannot be introduced into the helium atmosphere within process equipment.

Both gloveboxes are connected by a pass-through so that ingots produced in the uranium recovery box

can be moved easily into the plutonium extraction and retorting box for further processing. The two boxes are equipped with cooling systems for removing the heat lost from the various processing vessels. Movable cantilevered trays that can extend into either glovebox are located in each lock and pass-through, and motorized cranes are provided for materials handling within the gloveboxes.

Processing equipment for the uranium recovery box is being designed and fabricated. Process demonstrations (decladding and reduction) in this glovebox are expected to begin in the latter part of 1969. Extraction equipment for use in the plutonium extraction and retorting box is still being developed (see Section I.B.2.b of this report).

4. Materials Testing (M. L. Kyle, V. M. Kolba, L. F. Dorsey, R. C. Paul)

A materials testing program is being conducted to evaluate the suitability of various materials of construction for process applications. Materials for crucibles, transfer lines, agitators, and associated components will be selected according to the specific application of each component. Corrosion rates of various materials are being obtained, and the interactions between the candidate container materials and the solute uranium and plutonium in liquid metal and molten salt processing solutions are being investigated.

The emphasis is currently being placed on materials to be used with Mg-Cu alloys, which are used as donor alloys in salt-transport separations, and zinc and Zn-Mg alloys, which will be used for fuel element decladding and acceptor alloys, respectively.

a. Containment of Copper-Magnesium-Uranium/Halide Salt Systems

Previous corrosion tests (ANL-7425, p. 35; ANL-7375, p. 33) have shown that several structural ma-

TABLE I-1. CORROSION OF RHENIUM AND Re-Mo-W ALLOY IN Zn-Mg/MgCl₂-NaCl-KCl SYSTEMS

Temperature:	800°C
Exposure time:	100 hr
Method of exposure:	rotating agitator blades
Salt phase:	555 g of MgCl ₂ -30 mol % NaCl-20 mol % KCl
Metal phase:	3900 g Zn or 3400 g Zn-12 at. % Mg
Sample size:	~1 in. by 0.4 in. by 0.020 in.

Material	Metal Phase	Observed Depth of Corrosion (mm)
Rhenium	Zinc	0.025 ^a
Rhenium	Zn-12 at. % Mg	0.025 ^a
Re-18 wt % Mo-47 wt % W	Zinc	<0.01
Re-18 wt % Mo-47 wt % W	Zn-12 at. % Mg	<0.01

^a Attack by surface dissolution.

terials, including niobium, tantalum, tungsten, molybdenum, molybdenum alloys of titanium and zirconium, silicon carbide, and high-chromium-content steels, possess corrosion rates low enough to allow their use for containment of Cu-Mg/halide salt systems. The usefulness of these materials varies, however. Materials such as tantalum and niobium are embrittled by the halide salts after long exposure; tungsten, molybdenum, and the molybdenum alloys are difficult to fabricate into the desired shapes; and steels appear to interact with solute uranium and plutonium to produce compounds that could cause excessive processing losses of plutonium.

The materials testing program for Cu-Mg-U/halide salt systems is concentrated on determining the best method of fabricating the more promising materials into process vessels and testing the service life of these vessels. This is accomplished by fabricating prototype process vessels and testing these vessels under simulated process conditions. For example, a niobium crucible tested for Cu-Mg/halide salt service exhibited a service life in excess of 1000 hr (see ANL-7425, p. 36).

Interactions of solute plutonium with potential materials of construction are also being investigated to determine the nature and extent of such reactions. Steels might be usable with Cu-Mg-Pu/halide salt systems if plutonium intermetallic compounds do not form, or if the steel surface can be protected by prior formation of another intermetallic compound (e.g., uranium-iron).

Vitreous carbon. Vitreous carbon exhibits good corrosion resistance to both Zn-Mg-U/halide salt systems and Cu-Mg-U/halide salt systems (see ANL-7225, p. 40). Vitreous carbon crucibles that were tested

with these systems were not wetted by the metal solutions and displayed only limited wettability by the salt solutions. Since the tests were performed with very small crucibles (1 $\frac{5}{8}$ in. OD by 1 $\frac{5}{8}$ in. high by 0.10-in. wall), larger crucibles (3.9 in. OD by 7.1 in. high by 0.10-in. wall) were obtained for testing. One of these crucibles failed during a test for containment of a Cu-Mg-U/MgCl₂ system. Analysis indicated that the failure was caused by thermal shock. Another run was made in which a vitreous carbon crucible was encased in a tight-fitting graphite secondary to reduce the exposure of the crucible to thermal shock. This assembly was exposed to a Cu-20.7 at. % Mg-0.23 at. % U/MgCl₂ system for 192 hr at 800°C. Examination of the crucible at the end of the run indicated failure by thermal shock.

It is concluded that although vitreous carbon has desirable chemical properties for a container material, its thermal shock resistance does not appear to be adequate for process use. No further testing of this material is planned.

b. Containment of Zinc/Halide Salt Systems

Rhenium and rhenium alloys. Zinc and Zn-Mg alloys are used in the current flowsheet of the salt transport process as the decladding medium and as the acceptor alloys, respectively. Of all candidate container materials for zinc and high-zinc alloys, only tungsten and certain tungsten alloys are known to possess adequate corrosion resistance in combination with desirable physical properties and a developed fabrication technology. Other alloys that may be promising for these applications are continually being sought and evaluated. Two rhenium alloys, Re-25 wt % W and Re-50 wt % Mo, were tested for corrosion resistance to Zn/MgCl₂-NaCl-KCl and Zn-Mg/MgCl₂-NaCl-KCl systems, and both appeared to possess adequate corrosion resistance (ANL-7425, p. 38).

Recently, pure rhenium and a Re-18 wt % Mo-47 wt % W alloy were tested for corrosion resistance to the Zn-Mg/MgCl₂-NaCl-KCl system. The duration of the tests was 100 hr; the temperature was 800°C. The results of these tests are presented in Table I-1. The 0.025 mm of attack caused by surface dissolution indicates that pure rhenium has a limited solubility in zinc and Zn-Mg alloys. The Re-Mo-W alloy appears to be more stable.

Although pure rhenium is the most expensive refractory metal (~\$780/lb), its use as an alloying ingredient with the other refractory metals (W, Mo) may be practical and is being investigated. Neither tungsten nor molybdenum is easily fabricated into process equipment, but the addition of rhenium to these materials greatly enhances their fabricability.

These alloys can be produced as thin sheet material and are weldable. From a process standpoint, they appear to be feasible materials for use in vessel and pipe-lining applications—probably as a separate lining rather than as a coating.

Vapor-deposited tungsten crucible. Tests are being made on a tungsten-coated crucible (5¾ in. in diameter by 14 in. high by ¼-in. wall) that was fabricated by vapor deposition of tungsten on a graphite substrate. San Fernando Laboratories¹³ produced the crucible by heating a Speer SX-4¹⁴ graphite crucible to about 700°C and reducing WF₆ with H₂ on the inside surface until a 30-mil coating of tungsten had been deposited. The coating produced by this process should have nearly theoretical density. The particular graphite used was chosen because its properties of isotropic thermal expansion were reported to be very close to those of tungsten. This method of fabrication

¹³ San Fernando Laboratories, Pacoima, California.

¹⁴ Speer Carbon Company, Division of Air Reduction, Inc., Saint Mary's, Pennsylvania.

is being investigated because of its potential for producing large tungsten-coated parts of almost any shape, such as mixer-settler boxes.

As a preliminary test, the empty crucible was thermal-cycled six times between 400 and 900°C in an argon atmosphere. After the third and sixth cycles, the crucible was returned to room temperature for examination. At the end of the sixth cycle, the crucible was leak-tested for both gas and water permeability. Two or three areas (each about ½ in. in diameter) on the crucible bottom appeared to be devoid of the tungsten coating. These areas proved to be permeable to gas but not to water. The crucible will be tested next with molten MgCl₂-NaCl-KCl salts to determine if the density and coverage of the tungsten coating is sufficient to prevent salt leakage. Following the test with salt, the crucible will be tested with metal containing uranium and salt to determine if the amount of graphite exposed to solute uranium and plutonium is sufficient to cause processing losses by UC and PuC formation.

5. Processing Technology

Efficient, high-capacity, liquid-liquid contactors are needed for the pyrochemical processes presently being developed. Fuel recovery plants are envisioned for separating 36 kg/day of fission products from 74 kg/day of plutonium and 400 kg/day of uranium. Mixer-settlers and countercurrent packed columns are being studied since they are considered to be the most applicable types of contactors for pyrochemical processes. Mixer-settlers seem most suitable where only a few contacting stages are required. However, where several stages are needed, countercurrent columns may have advantages.

a. Development of a Large-Scale Mixer-Settler (*T. R. Johnson, W. E. Miller, R. C. Paul, F. G. Teats, E. F. Johnston, A. L. Chandler, G. N. Vargo, W. J. Voss*¹⁵)

A facility to test mixer-settler components and to evaluate various design concepts under typical processing conditions was installed in the large inert-atmosphere enclosure in Building 310. The purposes of the initial experiments were to demonstrate the transport of uranium through a salt phase and to determine if there is any entrainment of the liquid metal phase in the salt.

The equipment (Fig. I-16) was described in detail in ANL-7425, pp. 38-39. It was fabricated from type

304 stainless steel and is resistance heated. About three gallons per minute of liquid salt (MgCl₂-30 mol % NaCl-20 mol % KCl) is pumped by a centrifugal pump from the sump tank into a constant-head tank. Most of the salt flows from this tank directly back into the sump tank. However, a fraction of the salt is diverted and flows by gravity through the two mixer-settlers, the weigh tank, and then back into the sump tank. This stream is controlled by the liquid head and a valve in the constant-head tank. The salt flow rate is measured by weighing the salt that collects in the weigh tank.

The first mixer-settler contains 18.1 kg of a Cd-Mg alloy (the donor alloy) and 3.0 kg of uranium. Before the extraction begins, the composition of the liquid metal phase is Cd-2.3 at. % Mg-0.9 at. % U. Uranium is extracted from this alloy into the flowing salt and is then extracted from the salt into 12.4 kg of Cd-45 at. % Mg alloy (the acceptor alloy) contained in the second mixer-settler. As the extraction of uranium proceeds, the magnesium concentration in the donor alloy increases, causing the uranium extraction rate to decrease. The estimated amount of uranium transported at various salt flow rates (assuming 100% efficiency in both mixer-settlers) is shown in Fig. I-17.

During the first experimental run, the test facility was held at 600°C for about 680 hr. However, because of a variety of mechanical problems, the total time during which salt was circulated through the mixer-

¹⁵ Central Shops.

Based on 308-1102

FIG. I-16. Schematic of Mixer-Settler Test Facility.

settlers was only 30 min. The average salt flow rate was 1.5 kg/min (0.2 gpm). About 0.8 kg of uranium was transported into the acceptor alloy in the second mixer-settler during this period. This quantity agrees with the predicted amount within the accuracies of the calculations and the measurements under the conditions of this preliminary run. Analysis of a sample obtained from the salt flowing between the mixer-settlers indicated that metal entrainment in the salt was negligible.

The facility was subsequently cooled, disassembled, and inspected. Metallographic examination revealed that the maximum depth of corrosion in the mixer-settlers was 0.1 mm (intergranular attack in the salt phase)¹⁶ and that the average corrosion depth was 0.05 mm. This rate of corrosion will not preclude the use of type 304 stainless steel in future component-development experiments.

¹⁶ Metallographic examination by M. L. Kyle and L. F. Dorsey.

The facility has been modified slightly to avoid the problems encountered in the first experimental run, and it has been reassembled in preparation for the next run.

b. Countercurrent Column Development (T. R. Johnson, F. G. Teats, E. F. Johnston, P. J. Mack, R. C. Paul)

The behavior of liquid metal-salt systems in packed columns is being studied.¹⁷ A Cd-Mg-Ce/chloride salt system was used in a high-temperature column (see ANL-7425, pp. 33-35) to demonstrate countercurrent contacting and to measure mass transfer rates between the metal and salt phases. A low-temperature column with a metal-water system that simulated the physical properties of metal-salt systems was used to measure the hydraulic behavior of packed columns. The low

¹⁷ T. R. Johnson, R. D. Pierce, F. G. Teats, E. F. Johnston, "Behavior of Countercurrent Liquid-Liquid Columns with a Liquid Metal," preprint 24F, 61st Annual Meeting A.I.Ch.E., Los Angeles, California (Dec. 1-5 1968).

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FIG. I-17. Calculated Uranium Transport Rate in Mixer-Settlers.

temperature column and earlier experiments have been described in previous reports.^{17, 18}

One additional run was made in the high-temperature column. The composition of the metal used was Cd-17 at. % Mg-0.35 at. % Ce, and the salt was MgCl_2 -30 mol % NaCl-20 mol % KCl. The metal flow rate was 790 g/min, and the salt flow rate was 670 g/min. The packed section of the column was 1.05 in. in ID by 33 in. long, and the packing was $\frac{1}{4}$ -in. Raschig rings. The operating temperature of the column was 520°C. During the first 20 min of counter-current flow, the pressure drop across the column fluctuated, indicating that the column was operating with incipient flooding. The number of theoretical stages was 0.8, and the height of a transfer unit (based on the metal phase) was 44 in. during the operating period. The rather low extraction rate, compared with earlier runs, may have been due to the near-flooding conditions. After about 20 min the column did flood.

The high-temperature column has been dismantled and moved to Bldg. 310 where it will be reassembled for further experimentation. All of the work performed to date indicates that packed columns can be used in pyrochemical processes for nuclear fuel recovery.

Measurements of pressure drop, limiting flow rates, and holdup have been made using Wood's metal¹⁹ and water in the low-temperature column. The packed section of the column was 1.05 in. in ID by 24 in. long,

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FIG. I-18. Limiting Flows in Metal-Water Column.

and the packing was either $\frac{3}{16}$ -in. metal saddles or $\frac{1}{4}$ -in. metal Raschig rings, depending on the experiment. The pressure drop of the continuous aqueous phase was correlated with an equation for pressure drop

¹⁸ ANL-7325, pp. 30-32.¹⁹ Bi-21 at. % Pb-19 at. % Cd-19 at. % Sn.

through a porous medium.²⁰ The effect of the discontinuous metal phase on the pressure drop could be accounted for by assuming that the column void fraction varied with the metal flow rate to the -0.4 power. At high water flow rates, near the flooding point, the effective column void fraction became a function of water flow rate as well as metal flow rate. This effect is believed to be caused by the metal phase becoming turbulent and dissipating a larger amount of energy. The turbulence of the metal phase was found to influence limiting flow rates also. The limiting flow data are plotted in Fig. I-18. They are plotted in the conventional manner as the square root of the superficial water flow rate against the square root of the metal flow rate. The data deviate from the usual straight line at high water flow rates because of the in-

²⁰ S. Ergun, *Chem. Eng. Progr.* **48**, 89 (February 1952).

creased drag of the continuous phase caused by turbulence in the discontinuous phase. Hu and Kintner²¹ found that fluid drops falling through stationary columns of water behave like solid spheres at low Reynolds numbers. Above some Reynolds number (3000 for Wood's metal drops), they found that the drag coefficient increased above that for a solid sphere and that distortion of the drops caused by turbulent motion within the drops became evident. The local Reynolds number of a metal drop in the metal-water column was estimated to be between 2000 and 3500. The effects of discontinuous phase turbulence on the behavior of packed columns have not been observed with ordinary fluids because countercurrent columns usually flood before the discontinuous phase becomes turbulent.

²¹ S. Hu, R. C. Kintner, *AIChE. Journal* **1**(3), 42 (1955)

C. PYROCHEMICAL PURIFICATION OF PLUTONIUM-238 (P. A. Nelson)

The program is directed toward the development of a pyrochemical process for preparing high-purity plutonium-238 metal from impure $^{238}\text{PuO}_2$, such as the scrap that results from the production of $^{238}\text{PuO}_2$ microspheres that are used as fuel for isotopic power sources. A principal aim of the process is to yield a product relatively free of the light elements (e.g., sodium, magnesium, and lithium) which contribute to the undesirable radioactivity of impure plutonium-238 through (α, n) reactions. The process should also

be capable of removing any impurities that may be introduced by corrosion of containers during prior aqueous processing.

As the program is now conceived, the process being developed does not depend on innovations in process chemistry or equipment concepts but is based on concepts that have evolved in more than a decade of work at Argonne on the development of pyrochemical processes for fast reactor fuels.

1. Research Facility Construction (J. Fischer, J. D. Schilb, J. R. Haley)

A facility, designated as the Plutonium-238 Facility, was completed during the first part of 1968 for development of the scrap-recovery process.

The Facility consists of two glovebox units (see Fig. I-19). The larger unit (Glovebox A), which is designed for the pyrochemical work, consists of a

343-ft³ helium-atmosphere section and an 86-ft³ air-atmosphere section. This unit is connected by a transfer tunnel to a second unit (Glovebox B), which is a 258-ft³ air-atmosphere glovebox for analytical and other aqueous work.

2. Demonstration Runs with Plutonium-239 (J. F. Lenc, A. L. Chandler)

Concurrently with the final preparations for experimentation with plutonium-238, two runs (runs PR-1 and PR-2) have been completed to demonstrate purification of $^{239}\text{PuO}_2$ microspheres obtained from Battelle Memorial Institute. In these runs, the three main steps

in the process were demonstrated: (1) reduction of the $^{239}\text{PuO}_2$ microspheres with a reduction-donor alloy in contact with a molten chloride salt system, (2) transport of the plutonium away from the impurities by cycling the salt between the reduction-donor alloy and

FIG. I-19. Schematic Diagram of Plutonium-238 Facility.

an acceptor alloy with a high affinity for plutonium, and (3) retorting of the acceptor alloy to recover the plutonium metal product.

The reduction and salt transport steps of the runs were conducted in a divided crucible in an induction-heated tilt-pour furnace. All of the components that contacted the salt and metal phases during reduction and transport steps (crucibles, agitators, and filter-equipped sample tubes) were made of tantalum. The reduction was carried out in one side of the crucible at 725°C for 3 hr with continuous agitation. After the reduction step, the salt-transport step was initiated by tilting the furnace so that only the salt poured from one side of the crucible to the other. The other side of the crucible contained the acceptor alloy. The

salt was then equilibrated with the acceptor alloy and poured back into the donor side of the crucible. Ten complete transport cycles were carried out. The salt and metal phases were sampled after the reduction, and both phases on each side of the crucible were sampled after the ten salt transport cycles.

The charge to each experiment contained 10 g of $^{239}\text{PuO}_2$, 75 g of Mg-8.5 at. % Cd reduction-donor alloy, and 143 g of Zn-47.3 at. % Mg acceptor alloy. The transport salt for both experiments was MgCl_2 -38 mol % CaCl_2 (150 g in Run PR-1 and 184 g in Run PR-2).

The plutonium was recovered from the acceptor alloy by vacuum retorting (the retorting crucible was made of tantalum in Run PR-1 and of magnesia in Run

TABLE I-2. MATERIAL BALANCE FOR PLUTONIUM IN DEMONSTRATION OF SCRAP RECOVERY PROCESS WITH PLUTONIUM-239

Plutonium Accountability Prior to Retorting			
	Plutonium Content (g)		
	PR-1	PR-2	
Plutonium charge	8.82	8.82	
Donor side			
Transport salt	0.405	0.253	
Donor alloy	0.815	0.311	
Acceptor side			
Transport salt	0.025	0.081	
Acceptor alloy	7.32	8.24	
Samples taken after reduction (metal and salt)	0.087	0.211	
	8.652	9.096	
Percent accountability	98.1	103.1	
Recovery of Retorted Product			
Run	% of Acceptor Alloy Retorted	Wt of Pu in Alloy Retorted ^a (g)	Weight of Pu Product (g)
PR-1	73.5	5.38	4.22
PR-2	85.4	7.04	6.89

^a Based on analysis of molten acceptor alloy at 725°C; segregation of the alloy may have occurred upon freezing prior to charging a portion to the retort.

PR-2). The solid acceptor alloy was chipped out of the salt-transport crucible and transferred to a retorting crucible. (In a production run, the alloy would be removed in the molten state through a transfer line.) The Zn-Mg distillate was condensed on a water-cooled copper cold finger that extends from the top flange of the retorting apparatus. The final temperature and pressure in the retort in both runs was about 850°C and 10⁻⁴ to 10⁻⁶ Torr.

The plutonium material balance for the reduction and salt transport steps of the two runs is shown in Table I-2 along with the product recovery for the retorting steps. In both runs, the bulk of the plutonium was transported to the acceptor alloy. The plutonium accountability after the salt transport step was 100% within the accuracy of the sampling and analytical procedures. Only part of the acceptor alloy was retorted, and the product recoveries are shown at the bottom of the table.

Results of spark-source mass-spectrographic analyses of the ²³⁹PuO₂ feed material and of the plutonium-239 metal products from Runs PR-1 and PR-2 are shown in Table I-3. Removal of the light elements and uranium was fairly successful. This is especially encouraging since removal of these elements is im-

TABLE I-3. SPARK-SOURCE MASS-SPECTROGRAPHIC ANALYSES^a OF IMPURITIES

Element	Concentration in ²³⁹ PuO ₂ Microspheres ^b (ppm)	Concentration in ²³⁹ Pu Metal Product ^c (ppm)	
		Run PR-1	Run PR-2
Ag		42-53	
Al	39-130	110-190	400-500
As		0.2-0.3	0.8-1.5
B	0.7-2.0	1.2-2.3	0.3-0.5
Be	0.02-0.02	0.6-1.5	3.6-5.2
Bi	9-48	0.8-1.4	
C	500-1100	9.7-11	12-24
Ca	70-130	2.6-13	7-18
Cd	3.9-3.9		0.6-1.1
Cl	29-45	29-64	22-35
Co	0.5-0.5	1.3-1.4	1.3-2.0
Cr	170-220	240-400	82-130
Cu	34-45	200-320	200-320
F	1.6-1.6		0.1-0.2
Fe	820-1100	800-1100	430-780
Ga	0.4-0.7	4.6-5.7	2.2-2.2
In	0.8-1.4	0.2-0.3	0.2-0.4
K	4.2-13	3.2-3.6	0.9-3
Li	0.06-0.11		0.03-0.05
Mg	16-32	2.3-3.3	4.7-8.8
Mn	8-14	120-150	120-150
Mo	27-27	6.5-12	12-12
N	1.4-2.4	4.8-4.8	0.7-0.9
Na	200-200	1.5-3.0	1.5-2.0
Nb		0.06-0.4	
Ni	33-48	130-180	30-55
Np		7.1-7.6	7-7
O	matrix	74-100	82-94
P	5.3-9.5	0.7-0.8	2.6-2.6
Pb	1.5-2.5	68-77	36-36
S	24-43	^d	0.7-1.2
Se		0.05-0.09	0.05-0.09
Si	51-139	120-220	195-220
Sn		6.7-9.8	
Ta	7-12	100-540	20-24
Th	160-160	8.4-15	12-12
Ti	3.1-5.4	0.8-2.4	0.3-0.4
Tl		0.7-1.1	
U	1500-2600	6.3-7.1	5-8
V	0.3-0.5	0.1-0.1	0.1-0.1
W			7-9
Zn	120-160	24,000-24,000	1.0-2.8
Zr	180-300	1.1-4.9	0.7-1.1

^a Performed by The Dow Chemical Company, Rocky Flats Division, Rocky Flats, Colorado. No value indicates element concentration below detectable limit.

^b Low and high values of four determinations.

^c Values of two determinations.

^d Zinc interference.

portant in minimizing the radiation hazard associated with plutonium-238.

Table I-4 shows the expected (α, n) contribution to the total neutron production rate for plutonium-238 metal with the same average purity as the plutonium-

238 product in Runs PR-1 and PR-2. Although the overall (α, n) contribution is satisfactory for many purposes, a great improvement could be effected by reducing the beryllium and aluminum concentrations in the product. Beryllium and aluminum were probably introduced into the process either in the magnesium charged to the acceptor alloy or from the magnesia crucible used in Run PR-2, since aluminum and beryllium in the PuO_2 microspheres would have been removed in the donor alloy. The effective uranium removal in both runs (Table I-3) was probably achieved

TABLE I-4. EXPECTED NEUTRON YIELDS FOR (α, n) REACTIONS IN PLUTONIUM-238 METAL

Impurity Element	Expected Concentration ^a (ppm)	Neutron/(g) (sec)
Be	3	400
B	1	40
C	10	2
O	100	10
F	0.2	4
Na	2	4
Mg	5	10
Al	300	300
		Total 770

^a Based on approximate average impurities in the products of Runs PR-1 and PR-2.

through reaction of the uranium with carbon, sulfur, or other impurities in the microspheres.

The overall purity of the plutonium-239 product was only a factor of two or three better than that of the feed material because the feed material was fairly pure initially and because impurities were inadvertently added with the processing materials. A comparison between the impurities in the magnesium charged to the acceptor alloys and the purity of the plutonium-239 metal products indicates that many of the impurities in the products came from the 99.95% pure magnesium. The impurities present in the magnesium could account for all of the chromium, copper, lead, manganese, nickel, and silicon and most of the iron present in the products. Magnesium and zinc of higher purity will be used in future runs.

The plutonium product from the retorting step contained approximately 2.4 wt % Zn in Run PR-1. This zinc apparently dropped off the condenser into the molten product during cooling. However, the low zinc concentration in the product of Run PR-2 and the low magnesium and cadmium concentrations in the products of both runs indicate that the processing alloys can be removed effectively in the retorting step. Improvements in the retort design and operating procedure should prevent recurrence of high zinc concentrations in the product.

3. Preparation for Experiments with Plutonium-238 (*J. Fischer, J. D. Schilb, J. R. Haley*)

The main effort at the present time is directed toward completing tests of equipment and procedures in the Plutonium-238 Facility prior to beginning experiments with plutonium-238. A purified helium atmosphere has been maintained in the helium-atmosphere section of Glovebox A for almost three months; the water concentration is less than 2 ppm and the oxygen content is less than 5 ppm.

Testing of the process equipment in the facility with process metals and salts is almost complete. The first plutonium-238 experiments will involve only the reduction step. Later experiments will include the salt-transport step and will be performed in a tilt-pour furnace that is now being tested.

A lithium-drifted germanium diode detector and associated gamma spectrometer equipment have been installed in the analytical glovebox. This equipment will be used for rapid determinations of the plutonium-238 content of analytical sample solutions from the experimental work. Tests indicate that plutonium-238 can be determined with reasonable accuracy in amounts of 1 μg or less. For cases where analyses are to be made by the Division Analytical Group in its own plutonium facility, a method has been devised for removing aqueous plutonium-238 samples from the plutonium-238 facility simply and quickly with little danger of contamination.

D. FUEL CYCLE FACILITY OPERATIONS (C. E. Stevenson,²² M. J. Feldman, D. C. Hampson, J. P. Bacca, N. R. Grant, V. G. Eschen)²³

1. Termination of In-Cell Fuel Production Activities

At the close of 1968, the EBR-II Fuel Cycle Facility (FCF) successfully concluded its program for the remote production (hot-line operations) of Mark-IA fuel²⁴ subassemblies for the EBR-II at the National Reactor Testing Station (NRTS), Idaho. The planned termination of this source of reactor fuel for the EBR-II came after more than four years of essentially uninterrupted hot-line operations, which had begun in September 1964. During this period, the two major objectives of the program were accomplished. These were as follows: (1) the development and demonstration of the equipment and procedures required for the remote pyrochemical processing of irradiated fuel from discharged EBR-II subassemblies and subsequent re-fabrication of the purified fuel into fuel elements for manufacture into subassemblies, and (2) supplying the EBR-II with reactor core (driver) subassemblies at a rate adequate to insure an uninterrupted schedule of reactor operation, and receiving discharged subassemblies from the reactor at a rate that insured sufficient storage and transfer capacity in the storage basket within the reactor primary tank.

In this four-year period, the hot line fabricated some 33,000 acceptable fuel elements for more than 400 subassemblies for the reactor. Some 280 of these subassemblies contained purified fuel material from the processing of discharged subassemblies (totalling about 2300 kg of irradiated fuel). Some of this fuel material made four complete cycles through the EBR-II and the FCF. For the remaining subassemblies, fuel was obtained from unirradiated alloy. A summary of total operations carried out in the FCF since hot operations were initiated in September 1964 is presented in Table I-5. Also presented in the table is a summary of the process operations carried out during the past 14 months in which 51 subassemblies were fabricated for return to the reactor.

Since March 1964, when the Air Cell and Argon Cell were closed up prior to hot operation, no personnel have entered these cells. Generally, repair, maintenance, and modification of in-cell equipment and manipulators have been accomplished by remote means. When this was not possible, the equipment

TABLE I-5. SUMMARY OF FUEL CYCLE FACILITY HOT-LINE
PROCESS OPERATIONS

Operation	No. of Units Processed	
	Nov. 1967 through Dec. 1968	Total through Dec. 1968
Irradiated subassemblies cleaned of Na and dismantled:		
For processing	137	410
For examination, or for shipment only	50	109
Fuel elements decanned, including process rejects	10,322	34,691
Melt refining ingots produced:		
From discharged reactor fuel	69	331
From newly prepared alloy	5	78
From recycled scrap	42	185
Injection-casting operations	118 ^a	484
Injection castings produced	6,660	43,797
Acceptable cast pins produced	5,464	36,331
Fuel elements assembled and welded	5,194	37,678 ^b
Fuel elements passing leak test	4,964	36,378 ^b
Fuel elements bonded and passing bond test	4,060	32,985 ^b
Subassemblies fabricated	51	409
Waste cans buried in pits (~5 ft ³ each)	80	350

^a Including 30 rejected (out-of-specification) casting batches sent to Idaho Chemical Processing Plant for reprocessing.

^b Including elements fabricated from ~2,000 Mark-IA fuel rods cast in Argonne, Illinois.

item was remotely removed for decontamination and repair. On the average, the major pieces of process equipment were operable or operated about 93% of the time, and the electric manipulators and cranes were operable about 90% of the time.

The successful hot-line operation of the FCF has demonstrated the feasibility of the closed cycle²⁵ for recycling of FBR fuel. Advantages offered by the closed cycle include minimum cooling time for the processing of discharged fuel, minimum overall fuel inventory required for the reactor, and elimination of the need for offsite shipping of the discharged fuel for recovery of the uranium. A final report describing the hot-line reprocessing and refabricating activities in the FCF is being written.

²² Formerly with the Idaho Division; now with the Chemical Engineering Division, ANL-Illinois.

²³ EBR-II Project.

²⁴ Mark-IA fuel pins [uranium (52% ²³⁵U)-5 wt % fission] are 13.5 in. long by 0.144 in. dia.

²⁵ In the closed cycle, the fuel subassemblies discharged from the reactor are transferred to an adjacent fuel-reprocessing plant where the fuel is purified and subsequently refabricated into fuel elements for manufacture into subassemblies, which are returned to the reactor.

2. Alternative Fuel Sources

As previously reported,²⁶ steps were completed to provide alternative sources for Mark-IA fuel elements, which will now completely supplant the fuel output from the FCF hot-line operations. These sources are as follows: (1) the FCF fabrication of unirradiated fuel elements and subassemblies in out-of-cell equipment (cold-line operations), using either cold-line-produced fuel ingots or commercially produced ingots, and (2) a commercial vendor, the Aerojet-General Corporation, San Ramon, California. In the period since the start of cold-line operations, September 1967 to the end of 1968, cold-line-produced elements have been used in the fabrication of 95 subassemblies. These subassemblies are accepted for use in the EBR-II to the established burnup limit of 1.2 at. %. Postirradiation examinations of cold-line fuel showed that it displayed the same characteristics as those observed for hot-line fuel. Currently, the cold-line process equipment is being modified to produce Mark-II alloy and elements.^{27, 28} Sufficient Mark-II elements will be produced to fabricate five subassemblies. These subassemblies will be irradiated in the EBR-II, and postirradiation evaluation of the performance of the fuel elements will be conducted.

Shipments of vendor fuel to the FCF, started in August 1968, are continuing. Quality control inspections of the vendor elements at FCF have established the vendor's ability to meet contractual specifications. Four subassemblies utilizing vendor elements have been assembled in the cold line and are undergoing irradiation in the EBR-II to various burnup levels. Postirradiation tests will be performed on these subassemblies to evaluate the acceptability of vendor elements for routine use in the reactor.

²⁶ ANL-7425, pp. 40 and 41 (1968).

²⁷ Mark-II fuel pins [uranium (64% ²³⁵U)-5 wt % fission] are 14.22 in. long by 0.130 in. dia.

²⁸ During 1968, the cold line, in addition to its primary use as a source of Mark-IA fuel alloy and fuel elements, has been used to prepare special fuel alloys.

TABLE I-6. SUMMARY OF FUEL CYCLE FACILITY COLD-LINE PROCESS OPERATIONS

Operation	No. of Units Processed
Subassemblies from FCF-Produced Elements (Sept. 1967 through Dec. 1968)	
Alloy-preparation runs	
New fuel	22
Remelts	67
Injection-casting runs	135 ^a
Injection castings produced	11,220
Acceptable cast pins produced	10,707
Fuel elements assembled and welded	9,619
Fuel elements passing leak test	9,308
Fuel elements bonded and passing bond test	8,538
Subassemblies fabricated from FCF-produced fuel elements	95
Fuel elements (FCF-produced) available for subassembly fabrication at end of period	0
Subassemblies from Vendor Elements (Aug. 1968 through Dec. 1968)	
Fuel elements received from vendor	4,097
FCF-inspected and accepted	3,398
FCF-inspected and rejected	699
Fuel elements (vendor) passing FCF inspection available for subassembly fabrication	3,038
Subassemblies fabricated from vendor fuel elements	4

^a Includes 53 runs made with commercially produced ingots.

A summary of the process operations carried out in the cold line since its initiation in September 1967 is presented in Table I-6. Also presented in this table are data relative to vendor-produced elements.

Future discharged fuel subassemblies from EBR-II will be transferred to the Idaho Chemical Processing Plant (ICPP), NRTS, Idaho, for storage and additional postirradiation cooling in the ICPP water basin prior to eventual reprocessing by an aqueous chemical process.

3. Addition of Silicon to EBR-II Fuel Alloy

A surveillance program is in progress to evaluate the performance of driver fuel alloy (uranium-5 wt % fission) containing up to 1000 ppm silicon. These data will be used to determine the feasibility of extending the specification limits (to a higher value) for silicon (currently, 400 ± 120 ppm) in driver fuel manufactured in the future. Postirradiation data obtained

on the surveillance of Mark-IA fuel elements show that, above burnup levels of 0.7 to 0.8 at. %, ²⁹ fuel containing more than 200 ppm silicon (tests included elements with 920 ppm silicon irradiated to 1.2 at. % burnup) is characterized by relatively low swelling

²⁹ The presently established maximum burnup limit for Mark-IA fuel is 1.2 at. %.

properties compared with fuel containing less than 200 ppm silicon.

To prepare driver alloys containing controlled amounts of silicon, two methods of introducing the silicon into the alloy were tested. In one, the direct addition of pure silicon, metallic silicides, or silicon dioxide during alloy preparation did not prove satisfactory because only 50 to 80% of the silicon charged

alloyed with the matrix alloy. In the other method, adding silicon in the form of a master alloy of depleted uranium-2 wt % silicon during alloy preparation gave excellent results. Essentially stoichiometric addition of silicon was achieved by this method, thus making it possible to prepare driver alloys of the desired silicon content. This method also resulted in a uniform dispersion of the silicon in the matrix alloy.

4. Future Role of the FCF in the AEC Liquid Metal Fast Breeder Reactor Program

The AEC's Liquid Metal Fast Breeder Reactor Program to develop large, commercial fast breeder reactors is heavily dependent upon the irradiation tests of reactor fuels and structural materials, which are conducted in the EBR-II. The increasing demands of the irradiation program led, in 1968, to the increasing employment of the FCF for the examination and evaluation of irradiated specimens or for cleaning and packaging them for shipment to the experimenters. Since the FCF hot line has successfully completed its demonstration of the remote fuel-reprocessing and re-fabrication program (see Section I.D.1. above), the shutdown of the hot line will make space available in the air cell and argon cell for carrying out other FCF experimental and evaluation activities, some of which are discussed below. The transition is under way.

Prior to shutdown of the hot line, some in-cell

examinations were already being conducted in the FCF. These included remote weighing and dimension measuring, gamma scanning, neutron radiographing, and eddy-current testing (for sodium-bond and sodium-level inspection). New in-cell testing equipment for interim (nondestructive) and final (destructive) examination of irradiated specimens will be installed; present in-cell processing equipment that is not needed for the new program will be removed to make room for the new equipment. New test equipment being considered for in-cell installation will make it possible to conduct the following examinations: surface examination for defects (stereomicroscope) and swelling (profilometer), measurement of fission product gas volume and pressure (including sampling of this gas) within a fuel element or a test capsule, and detection of leaks in an element or a capsule.

II

Fluidization and Volatility Processes¹

(A. A. Jonke, J. W. Simmons)

During the report period, the fluoride volatility development program on the reprocessing of light water reactor (LWR) fuels was discontinued, and the program was reoriented toward an evaluation of the fluoride volatility process for application to fast breeder reactor (FBR) fuels. Some of the work reported below was done prior to reorientation of the program. Much of it, however, is applicable to both FBR and LWR fuels.

The final experiments in a laboratory-scale investigation of the application of an interhalogen process to irradiated thermal fuels were completed. In the interhalogen process, pellets containing UO_2 , PuO_2 , and fission products are first oxidized with oxygen to U_3O_8 - PuO_2 fines with oxygen. Uranium is then fluorinated to UF_6 with BrF_5 , and plutonium is subsequently fluorinated to PuF_6 with fluorine.

The UF_6 and PuF_6 streams contain as impurities the volatile fission product fluorides formed during the fluorination steps. Two laboratory-scale studies to evaluate procedures for the separation of ruthenium fluoride (one of the principal contaminants) were performed. One procedure involved selective sublimation of UF_6 (stand-in for PuF_6) from less volatile ruthenium fluoride(s). The other procedure involved the preferential sorption of ruthenium fluoride(s) from the PuF_6 - RuF_5 gas stream by a bed of solid lithium fluoride.

A reference flowsheet for the fluoride volatility reprocessing of FBR fuels was designed on the basis of knowledge developed from earlier work on LWR fuels. The head-end step mechanically separates the fuel from the stainless steel cladding and converts the fuel to a homogeneous powder, which can be sampled for input accountability and fuel burnup determinations. The oxide powder is then fed continuously to fluidized-bed fluorinators where uranium and plutonium are

converted to hexafluorides by reaction with fluorine gas. The nonvolatile fission product fluorides of Groups I, II, III, and IV are discharged from the fluorinators with the alumina powder used as the fluid-bed medium. The mixed hexafluoride gases and fluorine are cooled in a partial condenser to about 15°C to condense the bulk of the volatile ruthenium and niobium pentafluorides. The uranium and plutonium hexafluorides, after condensation in refrigerated traps, are separated from each other by thermal decomposition of the PuF_6 to the nonvolatile tetrafluoride at about 350°C ; the PuF_4 is then refluorinated to PuF_6 . The UF_6 gas from the thermal decomposer is purified by fractional distillation to separate the remaining fission products. The hexafluorides of uranium and plutonium are then mixed in the desired ratio and converted to oxides by gas-phase reaction with steam and hydrogen.

In the engineering-scale alpha facility, 2.3 kg of PuF_4 was fluorinated to PuF_6 in campaign-type experiments to demonstrate that production, transport, and recovery of PuF_6 on an engineering scale are practical.

Conceptual design studies of a large fluoride volatility plant (one metric ton of actinides per day) for processing FBR fuels are in progress. The objectives of this study are to present the current technological basis for such a plant in the form of process and engineering flowsheets and to define process uncertainties (problem areas).

Three supporting studies are reported. In one, the effect of gas-phase reaction and surface reaction upon penetration of high-efficiency filters by plutonium aerosol is investigated. The second has the objective of comparing particle mixing in fluidized beds and pulsed beds. The third is directed toward determining the effects of bubble spacing and bubble velocity in a fluidized bed on particle mixing and gas-solids contacting.

¹ summary of this section is given on pages 4 to 8.

A. LABORATORY INVESTIGATIONS (M. J. Steindler)

1. Fluorination of UO₂-PuO₂-Fission Product Pellets in a 2-in. Dia Fluid-Bed Reactor (L. J. Anastasia, D. Raue, M. Haas)

A 2-in. dia fluid-bed reactor is being used to study the fluorination of uranium and plutonium from simulated discharged reactor fuels containing nonradioactive fission products corresponding to burnups of 10,000 MWd/metric ton for LWR fuels and 100,000 MWd/metric ton for FBR fuels. In these studies, the fuel was first oxidized from UO₂-PuO₂ to U₃O₈-PuO₂ fines with oxygen. Uranium was then fluorinated to the volatile hexafluoride with BrF₅ or dilute fluorine, and plutonium was subsequently fluorinated with concentrated fluorine at temperatures of 300 to 550°C.

For experiments with simulated LWR fuels, a typical charge to the reactor consists of 650 g of UO₂-

PuO₂-fission product pellets (0.5-in. dia by 0.4 in. high, forming a packed bed 2 in. deep) and 1100 g of -40+170 mesh alumina with a static bed depth of 12 in. The UO₂-PuO₂-fission product pellets were prepared by sintering blended UO₂, PuO₂, and fission product oxide powder in 6 vol % hydrogen in nitrogen for 6 to 8 hr at 1700°C. The pellets contained a nominal 0.5 wt % PuO₂ so that a typical pellet charge to the reactor contained 2.8 g Pu.

For experiments with simulated FBR fuels, similar quantities of alumina were used, along with powdered mixtures (-325 mesh) of 80 wt % UO₂-20 wt % PuO₂ in solid solution and fission product oxides. A typical charge to the reactor contained 325 or 650 g of UO₂-PuO₂ powder and 34.5 or 69 g of fission product mix, respectively, so that about 58 or 115 g Pu was in the reactor for each experiment. The simulated FBR fuel is compared with simulated LWR fuel in Table II-1.

The major components in the experimental system are the 2-in. dia fluid-bed reactor, a remote-head diaphragm pump for gas recycle, soda lime traps for disposal of excess chemical reagents and UF₆ produced during the BrF₅ step, activated alumina traps for the disposal of excess fluorine reagent, and sodium fluoride traps for the collection of the PuF₆ produced during the recycle-fluorination step. Detailed descriptions of these components and of the experimental procedures have been reported previously (ANL-6925, p. 116; ANL-7055, p. 110).

a. Experiments with Simulated LWR Fuels

The final experiments with simulated LWR fuels were Purse-25 and -26 (Table II-2). In earlier runs (Purse-18, -19, and -23, ANL-7425, pp. 48-49), Al₂O₃ fines were added to the alumina bed to precoat the fluid-bed filters and thus to reduce the amount of plutonium in fines accumulated in the upper, cooler sections of the reactor during a run. However, since caking occurred in these runs with Al₂O₃ fines, AlF₃ fines (-325 mesh) were added, instead, to the -40+170 mesh bed of Purse-25.

In Purse-26, the initial fluorination of U₃O₈ with BrF₅ at 300°C was followed by a second BrF₅ step at 550°C to investigate the possibility that uranium and neptunium would be completely and selectively fluorinated with no adverse effects upon the subsequent removal of plutonium with fluorine.

After Run Purse-25, about 3.9% of the plutonium

TABLE II-1. COMPARISON OF SIMULATED FBR CORE FUEL AND SIMULATED LWR FUEL

Simulated burnup: FBR fuel, 100,000 MWd/metric ton
LWR fuel, 10,000 MWd/metric ton

Compound	FBR Fuel Composition ^a (wt %)	R ₁ ^b	R ₂ ^c
PuO ₂	18.09	36.9	1.0
UO ₂	72.34	0.74	0.02
BaO	0.28	4.40	0.01
CeO ₂	0.81	7.4	0.02
Eu ₂ O ₃	0.02	11.0	0.03
Gd ₂ O ₃	0.0005	1.0	0.03
La ₂ O ₃	0.29	7.0	0.19
Nd ₂ O ₃	0.86	4.1	0.11
Pr ₂ O ₃	0.32	8.3	0.23
Sm ₂ O ₃	0.16	3.8	0.10
Y ₂ O ₃	0.07	3.3	0.09
ZrO ₂	1.05	5.8	0.16
MoO ₃	1.55	6.4	0.18
Ag ₂ O	0.18	358	9.7
CdO	0.09	440	11.9
In ₂ O ₃	0.005	25	0.68
Nb ₂ O ₅	0.02	170	4.6
PdO	0.90	65	1.8
RhO ₂	0.36	16	0.42
RuO ₂	1.31	6.2	0.17
SrO ^d	0.12	2.7	0.07
Sb ₂ O ₃ ^e	0.05	—	—
CsF	1.11	12.1	0.33
RbF	0.05	1.8	0.05

^a Mixed powders, all -325 mesh, with solid solution UO₂-20 wt % PuO₂ powders.

^b R₁ = (g compound/g fuel)_{FBR}/(g compound/g fuel)_{LWR}.

^c R₂ = (g compound/g Pu)_{FBR}/(g compound/g Pu)_{LWR}.

^d CaO substituted for SrO after first run to eliminate analytical interference.

^e Antimony not present in previous studies.

charged was contained in fines recovered from the upper parts of the reactor, and an agglomerate weighing 15.7 g and containing 0.1 g Pu was found in the reactor. Additionally, the plutonium content of the final bed, 0.014 wt % Pu, corresponded to 5.3% of the plutonium charged after a recycle-fluorination sequence that generally reduces residual plutonium to about 3% of that charged.

The results from Runs Purse-18, -19, -23 (ANL-7425, pp. 48-49), and -25 indicate that the addition of 6 to 10% of fine material to the alumina bed leads to agglomeration of 1.5 to 5.8% of the fluid-bed material. Neither addition of Al_2O_3 or AlF_3 fines nor pre-fluorination of the alumina bed provided a solution to the agglomeration problem. With one exception, the addition of fines to the initial fluid-bed material was not effective in reducing the quantity of plutonium in the fines adhering to the upper parts of the reactor after a run. The exception was Run Purse-23, in which a prefluorinated bed of alumina containing 10 wt % Al_2O_3 fines was used and 1.6% of the plutonium charged was in the fines recovered from the reactor.

In Run Purse-26, after the first BrF_5 step, the fluid bed contained 0.6 wt % U, which is typical of results obtained in previous runs. Fluorination with BrF_5 at 550°C reduced the uranium concentration to 0.12 wt %, indicating that at least 0.25% (1.3 g) of the uranium charged remained in the reactor. The subsequent fluorination with fluorine reduced uranium to about 0.01 wt % so that the PuF_6 product contained about 30 wt % UF_6 even though a high-temperature BrF_5 step had been used. Additionally, after the second BrF_5 step, about 20% (8.8 mg) of the neptunium charged remained in the fluid bed. The distribution of fission products is uncertain. Apparently, most of the ruthenium was fluorinated during the second (high-temperature) BrF_5 step; ruthenium was below the limit of analytical detection of 0.003 wt % at the end of this step.

The high-temperature BrF_5 step appeared to affect the subsequent fluorination of both neptunium and plutonium with fluorine. The neptunium content of the final bed was about 0.005 wt % Np; in previous runs, neptunium was generally below the limit of detection, 0.003 wt % Np, before recycle-fluorination was completed. Similarly, the plutonium began to react only when the reactor temperature was increased to about 500°C. The final bed contained 0.054 wt % Pu (21.1% of the plutonium charged), while the fines recovered from the reactor contained an additional 7.3% of the plutonium charged.

Since uranium and neptunium are not completely fluorinated during a high-temperature fluorination step with BrF_5 and since the subsequent fluorination of

TABLE II-2. OPERATING CONDITIONS—EXPERIMENTS WITH LWR FUELS, PURSE-25 AND -26

Equipment: 2-in. dia fluid-bed reactor
Diluent gas: nitrogen
Reactor pressure: 950-1230 mm Hg

	Purse-25	Purse-26
Charge		
$\text{UO}_2\text{-PuO}_2\text{-F.P. pellets, g}$	642.4	648.7
Alumina		
1/4 in. -8 mesh, bed support, g	150	150
48-100 mesh ^a Alcoa T-61 alumina, g	990	1100
-325 mesh $\text{Al}_2\text{F}_6 \cdot 7\text{H}_2\text{O}^b$, g	110	—
RbF, g	0.16	0.15
CsF, g	0.6	0.6
$\text{NpO}_2, \text{ g}$	0.5	0.5
Oxidation with 20 vol % O_2 at 450°C		
Cumulative process time, hr	0-4	0-4
Superficial velocity, ^c ft/sec	0.8	0.7
Fluorination with 10 vol % BrF_5 at 300°C		
Cumulative process time, hr	4-6	4-6
Superficial velocity, ft/sec	0.7	0.6
Fluorination with 10 vol % BrF_5 at 550°C		
Cumulative process time, hr	—	6-7.9
Superficial velocity, ft/sec	—	0.9
Recycle-fluorination with 90 vol % F_2		
Cumulative process time, hr	6-17	7.9-18.9
Superficial velocity, ft/sec	0.4-1.0	0.5-0.9
Cumulative time at 300°C, hr	6-9	7.9-10.9
300 to 550°C, hr	9-14	10.9-15.9
550°C, hr	14-17	15.9-18.9

^a Screened to -40+170 mesh.

^b Water of hydration removed at 120 to 220°C [J. H. Perry, *Chemical Engineers' Handbook*, 3rd ed., p. 111, McGraw-Hill Book Co., New York (1950)].

^c Calculated for operating temperature and pressure.

neptunium and plutonium with fluorine is adversely affected, the high-temperature BrF_5 step is not recommended for use in a fluid-bed fluoride volatility process.

b. Experiments with Simulated FBR Fuels

Initial scoping experiments simulating the processing of fast reactor fuels by fluoride volatility methods consisted of a fractional factorial series of five experiments, Runs FF-A1 to FF-A5. In these tests the effects on plutonium in the final fluidized bed were determined for two levels of fuel-to-alumina ratio (0.3 and 0.6), two fluorination temperatures with 10 vol % fluorine (350 and 450°C), and two recycle-fluorination sequences (10 and 20 hr). Each experiment consisted of an oxidation step followed by fluorination of most of the uranium with dilute fluorine at 350 or 450°C and then fluorination (recycle-fluorination) of most of the plutonium with 90 vol % fluorine. The recycle-fluorination sequence of 20 hr consisted of 4 hr at 300°C, 3 hr each at 350, 400, 450, and 500°C, and 4 hr at 550°C, while the 10-hr recycle-fluorination sequence

TABLE II-3. OPERATING CONDITIONS—EXPERIMENTS WITH FAST BREEDER REACTOR FUELS, RUNS FF-A1 TO FF-A5

Equipment:	2-in. dia fluid-bed reactor				
Diluent gas:	nitrogen				
Reactor pressure:	910–1400 mm Hg				
Alumina bed:	1100 g Alcoa T-61 alumina, –40 +170 mesh				
Bed support:	150 g ¼-in. to 8-mesh alumina chips and one 0.5-in. dia alumina ball				
Oxidation step:	4 hr at 450°C with 20 vol % O ₂				
	FF-A1	FF-A2	FF-A3	FF-A4	FF-A5
Charge					
UO ₂ -20 wt % PuO ₂ , g	650.1	650.6	326.0	325.6	325.5
Fission product mixture, g	68.9	68.9	34.4	34.5	34.4
Fluorination with 10 to 15 vol % F ₂ ^a					
Cumulative process time, hr	4–7	4–7	4–7	4–7	4–7
Superficial velocity, ft/sec ^b	0.6	0.7	0.6	0.7	0.6
Temperature, °C	350	450	350	450	350
Recycle-fluorination with 90 vol % F ₂					
Cumulative process time, hr	7–27	7–17	7–17	7–27	7–17
Superficial velocity, ft/sec	0.3–0.9	0.6–0.8	0.4–0.6	0.3–0.6	0.3–0.6
Cumulative time (hr) at 300°C	7–11	—	—	7–11	—
350°C	11–14	—	—	11–14	—
400°C	14–17	—	—	14–16	—
450°C	17–20	7–10	7–10	16–19	7–10
500°C	20–23	10–13	10–13	19–22	10–13
550°C	23–27	13–17	13–17	22–27	13–17

^a Fluorine increased to 15 vol % after 2.5 hr of operation.^b Calculated for operating temperature and pressure.

was 3 hr at 450°C, 3 hr at 500°C, and 4 hr at 550°C. The latter sequence was chosen in an effort to obtain high fluorination rates for plutonium.

An acceptable plutonium concentration in the final bed is 1% or less of the initial charge of plutonium. The final bed weight is considered to be the sum of the weights of the initial charge of alumina and the added nonvolatile fission product fluorides.

The simulated FBR fuel used for these experiments consisted of a mixture of fission product oxides and solid solution UO₂-PuO₂ powder. The latter, made by the Numec Company, contained 17.8 wt % Pu and 70.3 wt % U and had a mean particle size of ~5 μm. The fission product mixture was made from chemicals having a minimum purity corresponding to reagent grade. The UO₂-PuO₂ and fission product mixture (Table II-1) were proportioned according to the FBR reference fuel for reprocessing studies and flowsheet planning. A single, intimate fission product mixture was made for all five experiments by blending the mixture overnight in a V-blender. All weighing and blending operations were carried out in a dry box.

The operating conditions for Runs FF-A1 to FF-A5 are summarized in Table II-3; the statistical design and the concentrations of plutonium in the final bed are shown in Table II-4. The statistical design is a quarter-replicate Plackett-Burman design, which

treats three independent variables at two levels.²⁻⁴ In this design, the first-order effects can be calculated together with an estimate of the experimental error from the replicated experiments.

The results given in Table II-4 for plutonium in the final bed represent the higher value obtained from two samples of the bed: one was obtained while the bed remained fluidized in the reactor and the other from a riffled sample of the final bed after it was dumped from the reactor. Plutonium concentration in the riffled sample was less than in the fluid-bed sample in only one case, Run FF-A5. A riffled sample is likely to contain plutonium-bearing fines that fell from the upper parts of the reactor when the reactor was being dismantled after a run. The plutonium concentrations in the final bed samples are compared in Table II-5. Analysis of variance for the two samples taken from the beds for replicate experiments FF-A3 and FF-A5 gives an F-ratio of 49, which is significant since a ratio of 40 with one degree of freedom in both the numerator and denominator will be exceeded (because of random errors) only 10% of the time.⁵ This significance can be

² R. A. Stowe, R. P. Mayer, *Ind. Eng. Chem.* **58**, 36 (1966).³ J. T. Holmes *et al.*, ANL-7425, p. 79.⁴ O. L. Davies, *The Design and Analysis of Industrial Experiments*, Hafner Publishing Co., New York (1954).⁵ E. B. Wilson, Jr., *An Introduction to Scientific Research*, McGraw-Hill, N. Y. (1952).

TABLE II-4. DESIGN OF INITIAL SET OF EXPERIMENTS WITH SIMULATED FAST BREEDER REACTOR FUELS

Run	Conditions			Statistical Design			Pu Charge (g)	Pu in Final Bed ^b (wt %)	Pu in Final Bed ^c (% of Pu charged)
	Fuel/ Al ₂ O ₃	Temp. of 10% F ₂ Fluorin. (°C)	Recycle- Fluorin. ^a (hr)	Fuel/ Al ₂ O ₃	Temp. 10% F ₂ (°C)	Recycle (hr)			
FF-A1	0.6	350	20	+	—	+	115.4	0.053	0.51
FF-A2	0.6	450	10	+	+	—	115.5	0.31	3.19
FF-A3	0.3	350	10	—	—	—	57.9	0.050	0.99
FF-A4	0.3	450	20	—	+	+	57.8	0.072	1.42
FF-A5	(Repeat of Run FF-A3)			—	—	—	57.8	0.031	0.61

^a 20-hr recycle-fluorination consists of 4 hr at 300°C, 3 hr at each of the temperatures 350, 400, 450, and 500°C, and 4 hr 550°C; 10-hr recycle consists of 3 hr at 450 and 500°C and 4 hr at 550°C.

^b Most conservative figure (i.e., higher of two analyses—see text).

^c Final bed weight calculated to be 1100 g Al₂O₃ plus 87 g F.P. fluorides for runs with a fuel-to-Al₂O₃ ratio of 0.6; final bed weight calculated to be 1100 g Al₂O₃ plus 43.5 g F.P. fluorides for runs with a fuel-to-Al₂O₃ ratio of 0.3.

TABLE II-5. EFFECTS OF PROCESS VARIABLES ON PLUTONIUM IN FINAL BED SAMPLES

Run	Pu in Fluidized-Bed Samples ^a		Pu in Riffled-Bed Sample ^b		Variance, ^c $\sigma^2 \times 10^4$
	wt %	% of Pu Charged	wt %	% of Pu Charged	
FF-A1	0.039	0.40	0.053	0.54	100
FF-A2	0.250	2.57	0.310	3.19	1900
FF-A3	0.029	0.57	0.050	0.99	880
FF-A4	0.060	1.19	0.072	1.42	265
FF-A5	0.031	0.61	0.028	0.55	18

Variable	Levels		Pu in Fluidized-Bed Samples		Pu in Riffled-Bed Samples	
	Low (—)	High (+)	Effect ^d (%)	t-Test ^e (%)	Effect ^d (%)	t-Test ^e (%)
Fuel/alumina ratio	0.3	0.6	+0.6	97	+0.7	70
Temperature of fluorination with dilute F ₂ , °C	350	450	+1.4	99	+1.5	87
Time for recycle-fluorination, hr	10	20	—0.8	98	—1.1	83

^a Taken at end of run from fluidized bed.

^b Taken at end of run from bed material removed from the reactor.

^c For % of Pu charged, $\sigma^2 = (\text{Pu in riffled-bed sample} - \text{Pu in fluidized-bed sample})^2/2$.

^d Effect of increasing the variable from its low to its high value on % of the Pu charge in the final bed.

^e The confidence level established by Student's t-Test as $100 \times (1 - \text{probability due to chance})$.

distributed to fines enriched in plutonium (7.3 wt % Pu) that fell into the static bed when the reactor was dismantled after Run FF-A3. Only 1.6 g of these fines falling into the final bed of 600 g (the actual bed re-

TABLE II-6. URANIUM AND PLUTONIUM IN FINES RECOVERED FROM UPPER PARTS OF REACTOR

Run	Total Fines ^a (g)	U or Pu in Fines (% of U or Pu Charged)	
		U	Pu
FF-A1	19.5	0.10	1.81
FF-A2	19.5	0.22	2.78
FF-A3	15.3	0.43	2.23
FF-A4	16.3	0.86	2.94
FF-A5	35.3	0.76	4.91
Average	21.2	0.47	2.95

Variable (low to high level)	Total Fines		U in Fines		Pu in Fines	
	Effect (g)	t-Test ^b (%)	Effect ^c (%)	t-Test ^b (%)	Effect ^c (%)	t-Test ^b (%)
Fuel/alumina ratio	+3.7	<<10	+0.5	70	+0.3	10
Temp. of fluorination with dilute F ₂ , °C	+0.5	<<10	+0.3	50	+0.8	20
Time for recycle-fluorination, hr	+0.5	<<10	+0.2	40	—0.1	<10

^a Removed from filters and the walls of disengaging and filter sections.

^b The confidence level established by Student's t-Test as $100 \times (1 - \text{probability due to chance})$.

^c Effect on uranium or plutonium concentration in fines (percent of uranium or plutonium charged).

maining after sampling) would increase the plutonium concentration from 0.029 to 0.050 wt %.

Since the return of fines to the final bed may influence any conclusions drawn from the statistical tests, the effects of the variables were determined also for the fluidized-bed samples. These results are compared in Table II-5. A higher level of confidence may be at-

TABLE II-7. URANIUM AND PLUTONIUM IN NaF PRODUCT TRAPS DURING 3 HOURS OF REACTION WITH 10-15 VOL % FLUORINE

Trap 1: used for first hour of reaction

Trap 2: used for subsequent 2 hr of reaction

Run	Fuel/ Al_2O_3	Temp ($^{\circ}\text{C}$)	% of Charge Fluorinated in 3 hr		Collected Product		
			U	Pu	U (g)	Pu (g)	U/Pu
FF-A1	0.6	350	84.0	0.6	Trap 1: 36.2 Trap 2: 346.8	0.042 0.650	860 530
FF-A2	0.6	450	77.8	2.0	Trap 1: 0.5 Trap 2: 355.1	0.003 2.334	135 150
FF-A3	0.3	350	75.7	9.0	Trap 1: 140.0 Trap 2: 33.6	0.024 5.217	5830 6
FF-A4	0.3	450	96.5	27.7	Trap 1: 127.7 Trap 2: 93.2	0.039 16.003	3280 6
FF-A5	0.3	350	69.7	6.7	Trap 1: 149.9 Trap 2: 9.6	0.033 3.857	4540 2

308-1802

FIG. II-1. Uranium and Plutonium in Fluidized Bed for Run FF-A1.

attached to results with fluidized-bed samples than to the results with riffled-bed samples (as would be expected). However, the conclusions are the same, i.e., an increase in the fuel/alumina ratio from 0.3 to 0.6 and an increase in the temperature of fluorination with

dilute fluorine from 350°C to 450°C will increase the fraction of plutonium charge remaining in the fluidized bed; also, increasing the recycle-fluorination time from the 10-hr to the 20-hr sequence will reduce the fraction of plutonium charge remaining in the bed.

The statistical analysis was also applied to test the effects of the variables on (1) the total quantity of fines recovered from the upper parts of the reactor and (2) the fraction of the uranium and plutonium charged retained in these fines. As shown by the results in Table II-6, the variables studied had no effect upon the quantity of fines recovered or upon the fraction of uranium and plutonium charged contained in the fines. For the five runs, FF-A1 to FF-A5, fines recovered from the reactor averaged 21.2 g and contained an average of about 0.5% of the uranium charged and about 3% of the plutonium charged. Recovery of plutonium from these fines has been demonstrated previously (ANL-7325, p. 61).

Uranium and plutonium fluorination with dilute and concentrated fluorine. The objective of a fluorination step with dilute fluorine is to fluorinate most of the uranium so that subsequent fluorination of plutonium with concentrated fluorine is not hampered by reactor temperature-control problems due to the large heat load from the uranium-fluorine reaction. The extent of uranium and plutonium fluorination for the initial fluorination step with dilute fluorine, as determined from the uranium and plutonium in the NaF product-collection traps, is shown in Table II-7. In each experiment, fluorine utilization was 100% during the first hour of operation according to analysis of the

off-gas with the thermal conductivity cell. In experiments with the high fuel/alumina ratio (Runs FF-A1 and FF-A2), little uranium and plutonium were collected during the first hour of operation (Table II-7), indicating that mostly solid fluorides rather than volatile hexafluoride products were produced. With the high fuel/alumina ratio, the fluorination temperature of 350°C was more favorable than 450°C because more UF_6 and less PuF_6 product was formed in this step. With the low fuel/alumina ratios, UF_6 was formed during the first hour of fluorination with very little PuF_6 formation; the U/Pu product ratios ranged from 3.3×10^3 to 5.8×10^3 . The results in Table II-7 suggest that an initial separation of uranium from plutonium is possible by fluorination with dilute fluorine. Since the U/Pu ratio in the fuel is initially 3.96, a decontamination factor (DF) of uranium from plutonium of about 1×10^3 can be obtained by a suitable choice of operating conditions. For this entire fluorination step, higher U/Pu product ratios are promoted by use of the higher fuel/alumina ratio and the lower fluorination temperature of 350°C.

The concentration of uranium and plutonium in the fluidized bed are shown in Fig. II-1 for Run FF-A1, which utilized a fuel/alumina ratio of 0.6 and the 20-hr recycle-fluorination sequence; Fig. II-2 shows similar data for Run FF-A5, which utilized a fuel/alumina ratio of 0.3 and the 10-hr recycle-fluorination sequence. The curves in Figs. II-1 and II-2 and similar data for Runs FF-A2, -A3, and -A4 indicate that portions of the recycle-fluorination sequences could be shortened without adversely affecting the plutonium concentration in the final bed. Additionally, the highest rates of plutonium reaction apparently occur during the initial recycle-fluorination period. A summary of these fluorination rates as calculated from plutonium concentrations in the fluidized-bed samples is given in Table II-8. In one experiment, Run FF-A4, plutonium fluorination rates were low during the initial portion of the recycle-fluorination period, which may have been the result of the low initial recycle-fluorination temperature (300°C) after fluorination with dilute fluorine at 450°C. In the remaining experiments, the average production rate for PuF_6 ranged from 1.2 to 3.0 lb/(hr) (ft²) while the reactor operated at 17.2 to 55.4% of equilibrium for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$.

As was done in previous studies of the fluorination of uranium from simulated thermal fuels,⁶⁻⁸ a dimin-

⁶ L. J. Anastasia, P. G. Alfredson, M. J. Steindler, 155th Meeting, San Francisco, Calif. (Apr. 1-5, 1968).

⁷ L. J. Anastasia, P. G. Alfredson, M. J. Steindler, Tripartite Chemical Engineering Conference, Montreal, Canada (Sept. 22-25, 1968).

⁸ L. J. Anastasia, P. G. Alfredson, M. J. Steindler, G. W.

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FIG. II-2. Uranium and Plutonium in Fluidized Bed for Run FF-A5.

ishing-sphere reaction model has been applied to the fluorination of plutonium from simulated fast fuel. The correlation for Runs FF-A1 and FF-A2 is shown in Fig. II-3, and the rate constants, k' , calculated for each run are shown in Table II-8. (These rates have been corrected for removal of plutonium from the fluid bed.) The rate constants of $4.4 \times 10^{-3} \text{ min}^{-1}$ at 450°C (i.e., average for Runs FF-A2, -A3, and -A5) and $0.7 \times 10^{-3} \text{ min}^{-1}$ at 300°C correspond to an apparent activation energy of 10.2 kcal/mole. This result is in reasonable agreement with activation energies between 10 and 12 kcal/mole reported by Steindler, Steidl, and Steunenberg⁹ for boat reactor experiments with PuF_4 and fluorine.

Sampling for material balance. An important quantity to be established for fast-reactor fuel proc-

Redding, J. G. Riha, M. Haas, "Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes, Part XVI. The Fluorination of $\text{UO}_2\text{-PuO}_2$ -Fission Product Pellets with Fluorine in a 2-inch Diameter Fluid-Bed Reactor," USAEC report ANL-7372 (1967).

⁹ M. J. Steindler, D. V. Steidl, R. K. Steunenberg, *Nucl. Sci. Eng.* 6, 333 (1959).

TABLE II-8. FLUORINATION OF PLUTONIUM WITH 90 VOL % FLUORINE DURING INITIAL PORTION OF REACTION PERIOD

Run	Fuel/Al ₂ O ₃	Dilute Fluorine Step, Temp (°C)	Initial Portion of Recycle-Fluorination Period					
			Time (hr)	Temp (°C)	Pu Reacted (g)	lb PuF ₆ /(hr)(ft ²)	% of Equilibrium ^a	k' × 10 ³ (min ⁻¹)
FF-A1	0.6	350	4	300	33.1	1.2	55.4	0.7
FF-A2	0.6	450	3	450	64.4	3.0	37.6	3.0
FF-A3	0.3	350	3	450	25.6	1.2	17.2	5.4
FF-A4	0.3	450	4	300	4.6	0.4	6.9	—
FF-A5	0.3	350	3	450	41.5	1.4	19.4	4.8

^a Based on the reaction, $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$, and the fluorine feed rate.

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FIG. II-3. Correlation for Plutonium Fluorination Rates.

essing is the material balance for uranium and plutonium. To maintain adequate material balances, the actinide input to a fuel processing plant must be determined by taking a representative sample of the fuel before fluorination. Representative samples might be obtained after oxidation has pulverized the fuel to fine particles, which are intimately mixed in the fluidized bed. To test this concept, samples of the fluidized bed were taken after the oxidation step in Runs FF-A1 to FF-A5. The average U/Pu ratio in the samples was 3.84 ± 0.50 at the 95% confidence level. This result was in good agreement with the U/Pu ratio in the fuel charge of 3.96. At the same level of confidence, the uranium balance was $92.0 \pm 13.8\%$; similarly, the plutonium balance was $92.0 \pm 11.8\%$. The U/Pu ratio, the uranium balance, and the plutonium balance are within the expected precision of the experimental results, based on sampling and analytical uncertainties.

c. Future Work

A second set of experiments is currently under way. In these runs, neptunium is added to the fluidized bed, and a fuel-to-alumina ratio of 0.6 is used. The effect of the oxidation step is being tested by fluorinating the fuel with and without a prior oxidation step. The fluorination steps consist of fluorination with 20 vol % fluorine at 350°C and recycle-fluorination with 90 vol % fluorine. Two recycle-fluorination schemes are being used: (1) 4 hr at 500°C and 4 hr at 550°C and (2) 4 hr at 400°C and 4 hr at 550°C. Additionally, the effect on plutonium concentration in the final bed will be determined for operating conditions in which the fluorine concentration is quickly raised to 90 vol % at the start of recycle-fluorination and for conditions in which the fluorine concentration is gradually in-

creased during the first hour. It is believed that this second set of experiments is a realistic approach to the

currently proposed engineering flowsheet for FBR fuels.

2. Fission Product Fluoride Chemistry—Chemistry of Ruthenium

(D. V. Steidl, R. L. Jarry)

Volatile ruthenium fluoride, formed along with PuF_6 in the fluoride volatility processing of reactor fuel materials, is one of the contaminants that must be removed in purifying PuF_6 . As part of the PuF_6 purification project, the absorption of ruthenium fluoride by LiF and other absorbents (NaF, nickel wool, NiF_2) has been studied. This work had two major goals: the first, to determine the ruthenium fluoride species formed in the fluorination reaction, and the second, to determine the sorptive capacity of LiF and other absorbents for ruthenium fluoride. Identification of the ruthenium fluoride species formed during fluorination is important for the prediction of the distribution of ruthenium in the fluid-bed fluoride volatility process. If the ruthenium fluoride species formed does not volatilize at 0°C , separation of plutonium from ruthenium can be effected by condensing the mixture of PuF_6 and ruthenium fluoride in a cold trap, then recovering the PuF_6 by transpiration at 0°C .

The procedure consisted of preparing a mixture of UF_6 (a stand-in for PuF_6) and ruthenium fluoride by the fluorination of a solid mixture containing UF_4 and either ruthenium metal or RuO_2 , condensing the mixture in a cold trap (the product U-trap) at -78°C , then transpiring the mixture by raising the cold trap temperature and sweeping with fluorine into a series of traps containing the several absorbents held at fixed temperatures. The ruthenium component was tagged with radioactive ^{106}Ru so that movement of the ruthenium fluoride could be monitored by counting. By monitoring the absorbent trap during the fluorination and transpiration periods and knowing the vapor pressures of the various ruthenium fluorides (RuF_6 , RuOF_4 , RuF_5), the fluoride species present might be identified.

Two sets of experiments were performed. In the first set, the activity level of the ^{106}Ru -spiked ruthenium was about 10^4 cpm/g Ru. In the second set, the activity level was about 10^6 cpm/g Ru. In these experiments, the principal absorbent was LiF, with NaF used as a backup absorbent to determine the breakthrough point of the LiF. A single experiment was performed in which nickel wool and nickel fluoride were tested as absorbents for ruthenium fluorides.

The reaction parameters were varied in these experiments. The ranges used were as follows: fluorination temperature, 350 – 600°C ; fluorination gas phase, 100%

fluorine or 75% fluorine-25% oxygen; transpiration temperature, 0 – 150°C ; LiF-trap temperature, 300 – 400°C ; and U/Ru ratio in solid, 1.9–9.4.

a. Materials

Ruthenium metal-ruthenium oxide mixture. The ^{106}Ru -tagged ruthenium metal was prepared by a standard exchange procedure followed by reduction of RuO_2 to the metal (ANL-7425, p. 55). The weight change indicated a conversion to the metal of about 75%.

The high-activity-level (10^6 cpm/g Ru) ^{106}Ru -tagged ruthenium used was also a mixture containing 75% ruthenium metal and 25% RuO_2 . This material was prepared by exchanging ruthenium with tracer in chloride solution, followed by reduction with magnesium metal. The solid was separated by centrifuging, then washed with HCl until free of magnesium, air-dried, and finally dried in flowing argon at 200°C for 3 hr.

The low-activity-level (10^4 cpm/g Ru) ^{106}Ru -tagged RuO_2 used was prepared as described in a previous report (ANL-7425, p. 55). The LiF used as absorbent was prepared by pressing Baker reagent-grade LiF into pellets and then quartering them to increase the available surface area. The NiF_2 was fused powder that was ground; the -325 mesh fraction used to prepare pellets did not pelletize well, and the resulting pellet fragments were easily powdered. The nickel wool used had a calculated surface area of 975 cm^2 for a 9.9-g charge. Grade F-1, 8–14 mesh activated alumina was used.

b. Apparatus

The horizontal tubular reactor and associated manifold used in these experiments were described in ANL-7375, pp. 59–60. Additional components installed downstream from the fluorination furnace (i.e., the reactor) were a product U-trap formed of $\frac{3}{8}$ -in. OD nickel tubing, vertical $\frac{3}{4}$ -in. OD traps containing the various absorbents, and finally an activated alumina trap to dispose of excess fluorine. The absorbent traps were loaded to a depth of approximately 5 in. The gamma counting equipment (described in ANL-7375, pp. 68–70) was adjusted to record both the 513- and the 624-keV gammas of the ^{106}Ru activity.

TABLE II-9. EXPERIMENTAL CONDITIONS—RUTHENIUM ABSORPTION EXPERIMENTS

Gas flow rate: 100 ml/min^a

LiF absorbent: ~ 30 g

Expt. No.	Solid Fluorination Charge ^b				Fluorination Step		Time (min) with Product U-Trap at Designated Temp. (°C)				
	Ru Species Present	Ru in Charge (g)	U/Ru Ratio	Specific Activity ^c (cpm/g Ru)	Gas-Phase Composition	Temp (°C)	-78 ^d	0	50	100	150
1	Ru-25% RuO ₂	0.779	9.4	4.59×10^4	100% F ₂	350	80	130	—	260	430
2	Ru-25% RuO ₂	0.933	4.3	4.82×10^4	75% F ₂ -25% O ₂	600	70	150	—	705	330
3	Ru-25% RuO ₂	0.988	3.6	5.16×10^4	75% F ₂ -25% O ₂	600	120	—	210	—	375
4	RuO ₂	1.190	3.1	4.45×10^4	75% F ₂ -25% O ₂	600	90	120	180	255	180
5	RuO ₂	0.725	4.9	4.84×10^4	75% F ₂ -25% O ₂	550	90	120	180	285	165
6	Ru 25% RuO ₂	1.087	3.4	1.16×10^6	75% F ₂ 25% O ₂	550	90	120	180	270	975
7	Ru-25% RuO ₂	1.014	1.9	1.24×10^6	75% F ₂ -25% O ₂	550	90	120	195	435	1555

^a Except in Expt. 1, in which the flow rate was 50 ml/min.^b The uranium compound used was UF₄.^c Measured in the same geometry as was used for counting the activity accumulated on the LiF trap.^d Temperature of product U-trap during the fluorination step.

c. Procedure

Seven experiments employing LiF as the absorbent and one experiment using nickel metal and NiF₂ as the absorbents were performed. In this study, ruthenium fluoride was removed from a gas phase containing UF₆ by absorption of ruthenium fluoride on a solid absorbent (Table II-9). In five of the experiments with LiF (Expts. 1 to 5), the ¹⁰⁶Ru specific activity ranged from 4.5×10^4 to 5.2×10^4 cpm/g Ru; in Expts. 1 to 3, the ruthenium used was the metal containing about 25% RuO₂, and in Expts. 4 and 5, RuO₂ was used. In Expts. 6 and 7, ruthenium metal containing about 25% RuO₂ and having a ¹⁰⁶Ru specific activity of about 1.2×10^6 cpm/g Ru was used.

The particulate reaction charge consisted of a ruthenium metal-RuO₂ mixture or RuO₂ (containing 0.7–1.2 g ruthenium) and 2.5–10 g of UF₄. When 10 g of UF₄ was used in one experiment, minor difficulties were encountered because of intermittent plugging in the product U-trap.

The specific activity of the sample was determined prior to each experiment. The scintillation detectors were placed 12 in. from the traps to scan the length of the 5-in. deep bed. The ruthenium metal-oxide mixture or RuO₂ was weighed, placed in a 3/4-in. OD nickel tube, and counted in the positions occupied by the absorbent traps during the experiment. Then the equipment and trap contents were prefluorinated at operating temperatures, the reactor was opened, and the nickel boat containing the particulate charge of UF₄ and either ruthenium metal or ruthenium oxide was placed in the tubular reactor.

The equipment was then brought to operating temperature, and the product U-trap was cooled to -78°C.

After a 10-min background count on the absorbent traps, flow of the fluorination gas through the tubular reactor and absorption train was started. The activity level of the absorbent traps was monitored at intervals during the ~2-hr fluorination step. In the transpiration step, the temperature of the product trap was raised to 0°C and subsequently to 50, 100, and 150°C with 100 ml/min of fluorine passing through the system until the transport of ¹⁰⁶Ru activity was complete or until the absorbents were saturated. The apparatus was then dismantled, and segments of the equipment were checked for ¹⁰⁶Ru activity.

d. Results and Discussion

LiF absorption experiments. In these experiments, results consisted of data on ¹⁰⁶Ru activity of the absorbents (LiF, NaF) and the elapsed time. Figure II-4, a plot of Expt. 5, which had results typical of the low-activity experiments, shows the absorption of ruthenium on LiF at 350°C and on the NaF back-up trap at 100°C. From the LiF activity plot, it can be seen that no ruthenium was transported during the fluorination period when the product U-trap was at -78°C or during the transpiration period when the trap was at 0 or 50°C. However, when the trap temperature was raised to 100°C, ruthenium was transported to the LiF trap. Ruthenium activity was not noted on the NaF trap until about 80% of the ruthenium absorption capacity of the LiF had been attained. In Expt. 5, the ruthenium absorption capacity of the LiF was 7 Ru/g LiF.

Since essentially no ruthenium was transported from the product trap when the trap temperature was -78, 0 or 50°C, the presence of RuF₆ or RuOF₄ in the fluo-

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FIG. II-4. Absorption of Ruthenium Fluoride on Lithium Fluoride at 350°C for Expt. 5. [Fluorine flow rate: fluorination step, 100 ml/min (3:1 fluorine-oxygen mixture); transpiration step, 100 ml/min (100% fluorine). Temperature of fluorination step: 550°C. Linear velocity of gas phase: approx. 2 cm/sec.]

ration product is unlikely. The vapor pressures of RuF_6 (Table II-10) at the pertinent temperatures indicate that some RuF_6 would be expected to have transpired during the -78°C fluorination period and all of the RuF_6 at a trap temperature of 0°C . On the same basis, transport of RuOF_4 would have started at a product trap temperature of 0°C and increased substantially at a trap temperature of 50°C . These data strongly suggest that the only ruthenium fluoride present was RuF_5 .

In Expt. 7 (a typical high-level-activity experiment) the ^{106}Ru specific activity was 1.24×10^6 cpm/g Ru, a factor of about 26 times greater than for Expt. 5. In Fig. II-5 are plots of ^{106}Ru activity versus transpiration time for the LiF traps and NaF trap for Expt. 7. The higher activity level was used to increase the activity transported during the periods when the product trap was at -78 , 0 , and 50°C , thus allowing measurement of the transpiration of very small quantities of ruthenium. The plots of Fig. II-5 show the same results as those obtained in the low-level activity experiments (Expts. 1-5), i.e., no apparent transport of

TABLE II-10. VAPOR PRESSURES OF RuF_6 , RuOF_4 , AND RuF_5 AT SELECTED TEMPERATURES

Temp. (°C)	Vapor Pressure (mm Hg)		
	RuF_6^a	RuOF_4^b	$\text{RuF}_5^{b,c}$
-78	0.020 ^d	3.9×10^{-6} ^d	5×10^{-13} ^d
0	23	0.063 ^d	1.3×10^{-5} ^d
50	540 ^d	2.39	0.01
100	>760 ^d	36.61	4.16
150	—	261.61	47.08

^a H. H. Claassen et al, *J. Amer. Chem. Soc.* **83**, 2390 (1961).

^b J. H. Holloway, R. D. Peacock, *J. Chem. Soc.* 527 (1963).

^c H. A. Bernhardt et al, USAEC Report AECD-2390 (1948).

^d Extrapolated.

activity during the -78 , 0 , and 50°C periods. During the transpiration periods at 100 and 150°C , ruthenium activity was transported onto the LiF and (after breakthrough) onto the NaF. The LiF trap at 350°C achieved a ruthenium loading of 21 mg Ru/g LiF. In this experiment, a trap containing activated alumina at 100°C was placed downstream from the LiF and

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FIG. II-5. Absorption of Ruthenium Fluoride on LiF at 350 and 450°C for Expt. 7. [Fluorination: (0-90 min) 550°C, 100 ml/min of 3:1 Fluorine-oxygen mixture. Transpiration: (90-2395 min) 100 ml/min of 100% fluorine.]

NaF traps. This trap did not show ruthenium activity until the NaF trap capacity had been reached at a loading of 22 mg Ru/g NaF. The data obtained from this terminal trap containing activated alumina indicated two facts: First, no ruthenium activity passed through the absorption train during the fluorination or transpiration periods, and second, contrary to experience with LiF, there was no breakthrough of the NaF until its capacity had been reached, indicating that NaF can be used as an absolute trapping agent for ruthenium.

The count level during the period when the product U-trap was at -78 , 0 , and 50°C is shown in Fig. II-5 as a straight line due to the large differences in count rate represented by scale units. This period for the LiF trap counting data is shown on an expanded scale in Fig. II-6. This plot shows the random nature of the count data during this period, indicating no upward trend of absorption of ruthenium on the LiF.

Regression analysis of the data obtained from the LiF absorption experiments during the period at -78 to 50°C was made to permit estimation of the maximum possible quantity of ruthenium that could have been transported. The mathematical treatment, for which we are indebted to Professor Koppel,¹⁰ is as follows:

The equation for the straight line fit to the data is

$$C_i = \bar{c} + b(t_i - \bar{t}) \quad (1)$$

in which C_i = the calculated value, cpm

$\bar{c}$ = the average experimental value, cpm

= $(1/N) \sum_{i=1}^N c_i$, in which c_i is the i 'th value, and N is the number of observations

t_i = the time at which the i 'th count was taken

$\bar{t}$ = the average value of time, min

= $(1/N) \sum_{i=1}^N t_i$

b = slope of the straight line through the data

The value of the slope, b , was determined by a least-squares solution using the following expression

$$b = \frac{\sum_{i=1}^N c_i t_i - \frac{1}{N} \left(\sum_{i=1}^N c_i \right) \left(\sum_{i=1}^N t_i \right)}{\sum_{i=1}^N t_i^2 - \frac{1}{N} \left(\sum_{i=1}^N t_i \right)^2} \quad (2)$$

The standard error, s , was calculated from the equation

$$s^2 = \frac{\sum_{i=1}^N (c_i - C_i)^2}{N - 2} \quad (3)$$

and the standard deviation, σ , of the slope is given by

$$\sigma_b = \frac{s}{\left[\sum_{i=1}^N (t_i - \bar{t})^2 \right]^{1/2}} \quad (4)$$

¹⁰ Consultant from Purdue University.

The confidence interval is $b \pm T_{\alpha}\sigma$, and the values of

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FIG. II-6. Absorption of Ruthenium Fluorides on LiF at 350°C for Expt. 7. (Scale is expanded relative to Fig. II-5.)

TABLE II-11. ABSORPTION OF RUTHENIUM FLUORIDES ON LITHIUM FLUORIDE: REGRESSION ANALYSIS OF DATA FOR TRANSPIRATION PERIODS AT 0 AND 50°C

Expt. ^a No.	Average Experimental Count Rate (cpm)	Standard Error of $\bar{c}$	Standard Error Based on Counting Statistics ^b	b^c (counts/ min ²)	σ_b (counts/ min ²)	$t_N - t_1$	Max. Ru Trans- ported, ^d 95% C.I.		Calc. Ru Trans- ported, ^e Based on RuF ₃ V.P. (mg)		DF	
							cpm	mg	0°C	50°C	Experi- mental ^f	Theoretical
1	5088	103	71	-0.169	1.048	210	418	9.1	1.03×10^{-5}	—	86	$\sim 8 \times 10^5$
2	7175	56	85	-0.180	0.499	205	174	3.6	1.19×10^{-5}	—	259	$\sim 9 \times 10^5$
3	9764	41	99	0.507	0.215	330	314	6.1	—	1.02	163	969
4	11296	36	106	-0.026	0.158	390	117	2.6	0.95×10^{-3}	0.88	458	1352
5	10572	27	33	0.083	0.117	390	126	2.6	0.95×10^{-3}	0.88	279	824
7	15802	57	40	-0.307	0.243	405	79	0.06	0.95×10^{-3}	0.95	1.7×10^4	1067

^a The quantity of ruthenium, ¹⁰⁶Ru specific activity, transpiration times, and general reaction conditions are listed in Table II-9.^b The standard error based on the counting statistics is the square root of the total count. In Expts. 1-4, 1-min counts were taken; in Expts. 5 and 7, 10-min counts were taken.^c Slope for the equation $C_i = \bar{c} + b(t_i - \bar{t})$.^d Calculated using the expression $(t_N - t_1)(b + T_\alpha \sigma_b)$.^e Vapor pressure of RuF₃ is 1.31×10^{-5} mm Hg at 0°C and 9.7×10^{-3} mm Hg at 50°C.^f The experimental DF's are minimum values; see text.

T_α for the 95 and 99 % levels are 2.06 and 2.78, respectively, from the statistical "t" test of significance.

The maximum possible increase in count level can then be calculated using the following expression:

$$\text{Maximum increase in count level} = (t_N - t_1)(b + T_\alpha \sigma_b) \quad (5)$$

The results of the regression analysis for Expts. 1-5 and 7 are listed in Table II-11. Experiment 6 was not

included in the analysis because of a plug that occurred during the fluorination period; subsequent release of this plug apparently caused an unusual release of ruthenium activity from the product trap.

From these results, it was possible to calculate the maximum conceivable quantity of ruthenium transported onto the LiF during the transpiration periods at -78, 0, and 50°C. A plot of typical counting data during these periods is shown in Fig. II-6. Using Eq. 5, in which $(t_N - t_1)$ is the transpiration time interval,

b is the rate of change of count rate, σ_b is the standard deviation of b , and T_α is the confidence interval (2.06 at 95%), and using the specific activities of the original ^{106}Ru preparations (see Table II-9), it was possible to calculate the minimum ruthenium decontamination factors (DF), which are also listed in Table II-11. For comparison, theoretical DF's based on the saturation of the carrier gas at the vapor pressure of RuF_5 are also listed.

Examination of these DF values shows that for Expts. 1-5, in which the original ^{106}Ru specific activity was $4-5 \times 10^4$ cpm/g Ru, the theoretical values are considerably higher than the values derived from the regression analysis results. However, for Expt. 7, in which the ^{106}Ru specific activity was 1.24×10^6 cpm/g Ru, the DF based on the regression analysis results (1.7×10^4) was greater than the theoretical value (1.1×10^3). These results indicate that the calculated value of the maximum amount of ruthenium transported is dependent on the specific activity level of the ^{106}Ru . The reason for the larger than theoretical value of the DF from the regression analysis results is not readily apparent. The vapor pressure data used in the calculations may be in error or, as is more probable, the transpiration conditions may have been less than ideal so that less than the theoretical amount transpired.

The above discussion was based on quantities calculated using Eq. 5. Due to the high confidence interval, the use of this equation tends to give a false picture of the amount of ruthenium transported. An alternative equation would be the following:

$$\text{Ru transported} = (t_N - t_1)^b \quad (6)$$

The use of Eq. 6 would result in the majority of the values of increase in count level being negative, indicating that in fact no ruthenium was transported.

TABLE II-12 RUTHENIUM SORPTION CAPACITY OF LiF

Flow rate:	100 ml/min
Gas phase:	100% fluorine
Linear velocity of gas phase:	~2 cm/min
Quantity of LiF:	~30 g

Expt. No.	LiF Trap Temp. (°C)	Sorption Capacity (mg Ru/g LiF)
1	300	12
2	300	13
3	400	9
4	300	9
	350	17
5	350	7
6	350	24
7	350	21

Finally, the conclusions based on these regression analyses are the following:

1) The only ruthenium fluoride species formed by the fluorination of ruthenium metal or RuO_2 under the reaction conditions of these experiments is RuF_5 . Had RuF_6 or RuOF_4 been present as a fluorination product, they would have been largely transported during the 0°C transpiration period and completely transported during the 50°C period.

2) The decontamination from ruthenium by trapping and then transpiring at 0°C would probably result in a DF value greater than 10^5 . Even at temperatures approaching 50°C , a DF greater than 10^4 could be expected.

Nickel metal and NiF_2 absorption experiment.

This experiment was performed using reaction conditions similar to those used in LiF absorption (Expts. 1 through 5). In this experiment, traps containing NiF_2 , nickel wool, and activated alumina were placed in series in that order. The NiF_2 and nickel wool traps, which were maintained at 300°C and 150°C , respectively, during the experiment, were prefluorinated at these temperatures. The activated alumina trap was not heated. The data show that NiF_2 is an inefficient absorbent for ruthenium, as indicated by the concurrent buildup of ^{106}Ru activity on the activated alumina. The data also show that there is essentially no retention of ruthenium on the nickel wool. After 300 min of transpiration, the activity level on the NiF_2 had risen by 3000 cpm, while the activity level on the activated alumina had risen by 4600 cpm. During the last hour of transpiration, the rate of increase of activity was much greater on the activated alumina than on the NiF_2 , being 45 and 20 cpm/min, respectively.

Ruthenium sorption capacity of LiF. The ruthenium capacity of the LiF at various temperatures for the several experiments are listed in Table II-12. The data of Expts. 1 through 4 indicate that a LiF trap temperature of 350°C was optimal, resulting in a capacity of about 17 mg Ru/g LiF. However, Expt. 5, in which the LiF trap was also at 350°C , had a low capacity of 7 mg Ru/g LiF; no reason for this low value is apparent. In the two high-activity-level experiments (6 and 7), an average value of the ruthenium capacity of LiF at 350°C of 23 mg Ru/g LiF was obtained. On the basis of these later results, 23 mg Ru/g LiF is recommended as the value for the sorption capacity of LiF at 350°C . Lithium fluoride, however, does not completely retain ruthenium up to its full absorption capacity; rather, ruthenium was observed to break through the trap starting at a point where about 70-80% of the absorption capacity had been reached.

3. Decontamination of Plutonium Hexafluoride (J. G. Riha, L. E. Trevorrow)

The recovery of plutonium from spent nuclear fuel by the fluoride volatility process includes a step in which oxidized nuclear fuel is reacted with fluorine, resulting in the production of PuF_6 and the gas-phase transport of PuF_6 away from fuel residue. Since the PuF_6 will be contaminated with volatile fluorides of fission product elements, procedures for the purification of PuF_6 from these contaminants must be developed. This report describes the testing of a procedure for separating PuF_6 from RuF_5 , a major contaminant.

Workers at ORNL¹¹ have reported that PuF_6 reacts with LiF to form a complex from which PuF_6 can be

mixture of ^{106}Ru tracer-ruthenium metal carrier and PuF_4 spread in a boat located in a tube reactor held at 350 to 550°C. The resulting gaseous mixture of fluorine, PuF_6 , and RuF_5 flowed out of the tube reactor and passed through a series of two connected traps. The first trap contained granulated LiF at 200–500°C to test the separation effect, and the second trap contained NaF pellets on which PuF_6 and RuF_5 that penetrated the LiF trap were fixed for recovery. In some experiments, as many as three separate NaF recovery traps were used, in turn, to obtain information on the amounts of materials penetrating the bed of LiF at various stages of the experiment.

TABLE II-13. SEPARATION OF PuF_6 - RuF_5 MIXTURES BY REACTION WITH LiF

Expt. No.	LiF Temp. (°C)	Total Fluorination Time (hr)	Charge to Reactor		Distribution of Materials in Apparatus						Decontamina- tion Factor ^a
					Fluorination Reactor		LiF Separation Trap		NaF Recovery Trap		
			PuF ₄ (mg)	¹⁰⁶ Ru (cpm)	PuF ₄ (mg)	¹⁰⁶ Ru (cpm)	PuF ₄ (mg)	¹⁰⁶ Ru (cpm)	PuF ₄ (mg)	¹⁰⁶ Ru (cpm)	
1885F109	200	7	188	91.7	3	0.34	22.8	41.5	156.8	0.32	2 × 10 ²
1885F121	300	7	211	447	4	2	2.5	205	210	1.8	2 × 10 ²
1885F101	300	7	185	91.7	10	<1	45.8	1	130.5	0.07	9 × 10 ²
1885F105	300	7	191	103	7	0.39	31.7	35.6	151.1	0.07	11 × 10 ²
1885F113	300	10	157	91.7	5	0.12	6.2	67.6	151	0.029	30 × 10 ²
1885F125	300–400	9	175	402	3	0.5	5.6	130	162	0.63	6 × 10 ²
1885F97	300–400	10	92	103	8	<1	0.5	53.6	53	0.23	3 × 10 ²
1885F139	400	5.5	191	447	4	0.26	3.1	267	188	0.39	1.1 × 10 ²
1885F131	400	7	199	447	1	0.25	4	243	192	0.48	9 × 10 ²
1885F147	500	4	198	402	2	1.2	15.3	146	178	17.2	0.02 × 10 ²

^a Defined by Eq. 1:

recovered by reaction with fluorine. Also, workers in the USSR¹² have reported that RuF_5 forms a complex with LiF. Therefore, experiments were performed to test the hypothesis that the stability of the two complexes might differ sufficiently at some optimum set of conditions so that separation of plutonium from ruthenium could be effected.

a. Separation of Plutonium Fluoride from Ruthenium Fluoride by Reaction with LiF

The experimental procedure in the separation tests was as follows: In a typical experiment, a gaseous mixture of plutonium hexafluoride and ruthenium fluoride was generated by passing gaseous fluorine at ~1 atm pressure and a flow rate of ~100 cm³/min over a

Before each experiment, the trap containing the LiF was evacuated at 25°C for several hours, then exposed to a fluorine stream at 300°C for ½ hr. At the end of each experiment, the fluorination residue, the entire bed of LiF, and the entire bed of NaF were removed from their containers, and each material was counted, at the same geometry, for ^{106}Ru activity using a GeLi detector and a multichannel analyzer. Plutonium analyses were obtained by dissolution of solid samples and alpha counting of plated aliquots.

The conditions and results of several experiments are listed in Table II-13. The distribution of ruthenium and plutonium in the apparatus indicates that ruthenium is preferentially fixed by the solid LiF. The separation of plutonium from ruthenium is assessed by an overall decontamination factor (DF) that compares the ruthenium contamination of the plutonium product (recovered in the bed of NaF) with the ruthenium

¹¹ S. Katz, G. I. Cathers, *Nucl. Appl.* **5**, 5 (1968).

¹² J. N. Prusakov et al, *Compt. Rend. Congr. Intern. Chim. Ind., Brussels*, 1966, Vol. 1, p. 787 (1967).

contamination of the sample of PuF_4 initially charged to the fluorination reactor:

$$\text{DF} = \frac{(\text{cpm } ^{106}\text{Ru}/\text{mg PuF}_4)_{\text{initial}}}{(\text{cpm } ^{106}\text{Ru}/\text{mg PuF}_4)_{\text{recovered}}} \quad (1)$$

This overall decontamination factor does not distinguish the separative effect of reaction with LiF from any other contributing separative effects inherent in the system. The overall DF values indicate that reaction with LiF offers a means of separating PuF_6 from RuF_5 with a decontamination factor of 10^2 to 10^3 . The separation was most efficient with the LiF at 300–400°C and was least efficient at 500°C.

One other criterion for assessing the value of the reaction with LiF as a means of separating PuF_6 - RuF_5 mixtures is the extent of retention of plutonium by the bed of LiF. Although minimization of plutonium retention by LiF was not studied in detail, the results indicate that the reaction can be carried out with retention of 1% or less of the plutonium charged.

Significant amounts of plutonium were found in NaF traps used in turn during a given experiment. The amounts observed might be interpreted as follows: During early stages of the experiment, the fluorination effluent is a gaseous mixture of PuF_6 , RuF_5 (both of which are fixed to varying extents on the LiF), and fluorine. During later stages of the experiment, after the fluorination of PuF_4 and ruthenium is complete, the gas flowing through the LiF trap is nearly pure fluorine, and plutonium fixed on the LiF as a complex is removed by the fluorination of the complex to form PuF_6 .

b. Lithium Fluoride-Plutonium Fluoride System

In order to determine the mechanism of temporary fixation of plutonium in the reaction of PuF_6 with LiF, experiments were performed in which LiF was exposed to PuF_6 -fluorine mixtures, and the species present in the resulting solid phase were identified by X-ray powder diffraction techniques. The following experimental procedure was used: Gaseous fluorine was passed at a flow rate of ~ 35 ml/min through a trap containing solid PuF_6 at 0°C, and the gaseous mixture of fluorine (750 mm) and PuF_6 (4 mm)¹³ issuing from the trap was passed over a weighed sample of powdered LiF. The LiF sample, contained in a boat located in a horizontal tube reactor, was kept at a temperature of 300°C. Complex preparation was done in a series of 5-hr periods. At the end of each period,

the boat was removed from the reactor; it was observed that the solid phase had gained in weight, formed a loose cake, and acquired an increasingly dark, reddish-brown color. The solid phase was broken up and stirred between reaction periods.

The weight of the solid increased linearly with total reaction time, an indication that the rate of reaction was constant and therefore that only one new compound had been formed during the entire reaction period. X-ray diffraction analysis of the solid showed the presence of only the complex compound $\text{LiF} \cdot \text{PuF}_4$. This compound and its homologs have been referred to variously in the chemical literature as 1:1 compounds or as 7:6 compounds; a recent paper¹⁴ argues in favor of the 1:1 ratio, which seems to have been accepted.^{15, 16} The identity of the solid product suggested that the net reaction of PuF_6 -fluorine mixtures with LiF probably occurs according to the equation

It is assumed that this reaction proceeded from left to right under the experimental conditions employed because the PuF_6/F_2 ratio (4/750) in the reactant mixture was greater than the equilibrium constant (unknown) for the reaction.

Experiments were also carried out to study the recovery of plutonium by fluorine treatment of the solid product of the PuF_6 -LiF reaction. The solid product was contacted with 100% fluorine at 300 to 450°C in a flow system. At these temperatures, no melting of the complex occurred. Samples of the solid phase contained in a tube reactor were fluorinated at a flow rate of ~ 100 ml/min for a series of periods of 1- to 2-hr length. Between reaction periods, the weight lost during the preceding fluorination was measured, and the solids were thoroughly mixed.

The rate of reaction changed abruptly after the mole ratio LiF/PuF_4 in the solid phase reached a value of about 4. Before this point, the color of the top layer of solid changed from reddish-brown to tan during each fluorination period; after this point, the color of the top layer of solid changed from tan to white during each fluorination period. Reaction was continued until the weight of the sample remained constant during two successive reaction periods, an indication of complete reaction. The discontinuity in the rate of fluorination and the change in color of the solid phase suggested that the identity of the solid phase had changed. This

¹⁴ G. Brunton, *Acta Cryst.* **21**, 814 (1966).

¹⁵ R. Schablaske, ANL, private communication (February 1968).

¹⁶ R. E. Thoma, ORNL, private communication (February 1968).

¹³ Average partial pressure determined experimentally from the weight of PuF_6 vaporized and the total volume of fluorine used.

hypothesis was confirmed by an X-ray powder-diffraction analysis, which indicated that the major phase present after the discontinuity in reaction rate was $4\text{LiF} \cdot \text{PuF}_4$.

The solid phase, $\text{LiF} \cdot \text{PuF}_4$, formed by the reaction of LiF with PuF_6 -fluorine mixtures at 300°C (Eq. 2), reacts with fluorine at a higher temperature (350 – 450°C) in a two-step reaction that can be summarized by the following series of expressions: Heating a mixture of LiF and $\text{LiF} \cdot \text{PuF}_4$ could result in the formation of $4\text{LiF} \cdot \text{PuF}_4$, i.e.,

At an overall composition of about 29 mol % PuF_4 , the resulting solid would be a mixture of $\text{LiF} \cdot \text{PuF}_4$ and $4\text{LiF} \cdot \text{PuF}_4$. The reaction of fluorine with this mixture could occur in two steps:

Thus, continued fluorination eventually results in complete removal of plutonium from the solid phase.

The net effect in the solid phase of the reaction of

PuF_6 with LiF therefore appears to be to increase the amount of PuF_4 in the condensed system $\text{LiF} \cdot \text{PuF}_4$. Although there is no recorded experimental investigation of the condensed phase diagram for the $\text{LiF} \cdot \text{PuF}_4$ system, reference to the condensed phase diagram¹⁷ for the system $\text{LiF} \cdot \text{UF}_4$ shows that the $\text{LiF} \cdot \text{UF}_4$ complexes contained therein are analogs of those found in the condensed phase resulting from the reaction of PuF_6 with LiF. In our laboratory, a sample of the solid phase formed by reaction of PuF_6 with LiF at 300°C (composition of solid phase: 29 mol % PuF_4 –71 mol % LiF) was heated; melting was observed at about 500°C . Therefore, we assume that 500°C is the approximate value of the eutectic temperature for mixtures of $\text{LiF} \cdot \text{PuF}_4$ and $4\text{LiF} \cdot \text{PuF}_4$. The analogous eutectic point in the $\text{LiF} \cdot \text{UF}_4$ system is 490°C . The condensed phase diagram for the $\text{LiF} \cdot \text{UF}_4$ system might therefore be used to predict the composition of the solid phase formed by the reaction of known quantities of PuF_6 and LiF at a given temperature.

¹⁷ C. J. Barton, H. A. Friedman, W. R. Grimes, J. Insley, R. E. Moore, R. E. Thoma, *J. Amer. Ceram. Soc.* **41**, 63 (1958)

4. Reaction of Neptunium Hexafluoride with Sodium Fluoride (T. J. Gerding, L. E. Trevorrow)

In the fluid-bed fluoride volatility process, a possible step will be passage of a gas stream containing UF_6 , NpF_6 , and other volatile fluorides through a bed of NaF pellets to fix neptunium preferentially. The equation representing the $\text{NaF} \cdot \text{NpF}_6$ reaction and the lattice constants of the complex formed, $3\text{NaF} \cdot \text{NpF}_5$, have been reported previously (ANL-7425, pp. 62–65). The equilibrium constant for the reaction of NaF with NpF_6 was since measured to permit quantitative prediction of the extent to which NpF_6 would be taken up or released by a bed of NaF. The results of this investigation have been published,¹⁸ and the abstract is as follows:

The reaction at 150 to 250°C of an excess of NpF_6 at 150 to 300 Torr with NaF can be represented by the equation

The X-ray powder-diffraction pattern obtained for $3\text{NaF} \cdot \text{NpF}_5$, sodium octafluoroneptunate (V), was indexed on the basis of a body-centered tetragonal unit cell with lattice constants $a = 5.449 \pm 0.001 \text{ \AA}$ and $c = 10.853 \pm 0.003 \text{ \AA}$.

The partial pressures of fluorine and NpF_6 in equilibrium with the solid phase formed by reaction of NpF_6 with NaF were obtained by measurements of total pressure and ultraviolet absorbance of the gas phase. At a fixed temperature (350°C) over a tenfold variation of fluorine pressure, the value of $\log(p_{\text{NpF}_6})$ was found to depend linearly on $\log(p_{\text{F}_2})$ with a proportionality coefficient of 0.49, comparable to the value of 0.5 expected for the above reaction. Equilibrium constants, $K_p = (p_{\text{NpF}_6}) / (p_{\text{F}_2})^{1/2}$, for the reverse of the above reaction at 250 to 400°C , were expressed by the equation

$$\log K_{p(\text{atm}^{1/2})} = -3.147 \times 10^3 / T(^{\circ}\text{K}) + 2.784$$

¹⁸ L. E. Trevorrow, T. J. Gerding, M. J. Steindler, "The Reaction of Neptunium Hexafluoride with Sodium Fluoride," *Inorg. Chem.* **7**, 2226 (1968).

5. Plutonium Hexafluoride Safety (R. W. Kessie, L. Marek)

The toxicity and volatility of PuF_6 require that a very high degree of air cleanup be provided in the event of an accidental release of PuF_6 in an enclosure. Previous work, which has been reported in detail,¹⁹ indicates that, with a normal moisture concentration in the atmosphere of the enclosure, hydrolysis occurs within the gas phase to produce a fine aerosol (PuO_2F_2 particles of $<0.1\text{-}\mu\text{m}$ diameter), but that with low moisture concentrations, reaction occurs at solid surfaces exposed to the reactants. In the previous work,

are to confirm the computed filter penetration due to surface reaction as well as to determine how each type of reaction (gas-phase reaction and surface reaction) affects filter penetration and to measure plutonium particulate penetration through a series of four filters.

Briefly, plutonium is removed from a gas stream by the combined process of (1) hydrolysis of PuF_6 in a gas mixer and (2) filtration of the resulting PuO_2F_2 aerosol through a series of pretested high-efficiency (AEC) filters. The quantity of plutonium on each

TABLE II 14 FILTRATION RESULTS FOR HYDROLYZED PLUTONIUM HEXAFLUORIDE

Filter disk diameter 10.0 cm
Temperature: 21 to 27°C
Run time 60.0 min

Run	Gas Velocity at Filter Surface (cm/sec)	$P_{\text{H}_2\text{O}}$ (Torr)	P_{PuF_6} (10^{-3} Torr)	Feed Rate (mg Pu/hr)	mg Pu on Designated Filter			
					1st	2nd	3rd	4th
PF-1	1.00	1.52	0.283	1.05	0.192	3.87×10^{-7}	6×10^{-10}	7×10^{-10}
PF-2	1.00	1.47	20.1	73.6	20.9	9.44×10^{-6}	1.9×10^{-9}	$<5 \times 10^{-10}$
PF-3	0.992	1.52	0.272	0.987	0.133	3.55×10^{-6}	$<3 \times 10^{-10}$	3.5×10^{-9}
PF-7	0.992	0.31	0.792	2.84	0.550	2.06×10^{-7}	3.1×10^{-10}	$<2 \times 10^{-10}$
PF-8	2.52	1.58	0.271	2.48	0.580	3.2×10^{-8}	3×10^{-10}	$<3 \times 10^{-10}$
PF-9	0.992	1.60	0.689	2.48	0.416	1.43×10^{-7}	$<4.8 \times 10^{-10}$	$<3 \times 10^{-10}$
PF-10	2.47	0.30	0.156	1.40	0.364	1.55×10^{-6}	$<3 \times 10^{-10}$	$<2 \times 10^{-10}$
PF-11	2.46	0.31	8.88	79.3	48.1	1.84×10^{-5}	2.1×10^{-9}	2×10^{-10}
PF-12	2.46	5.45	9.10	81.1	28.9	6.78×10^{-5}	6.2×10^{-9}	$<1 \times 10^{-10}$
PF-13	0.254	0.31	89.5	82.8	34.0	3.0×10^{-7}	3×10^{-10}	2.9×10^{-9}
PF-14	0.254	4.95	101	93.7	17.0	5.8×10^{-7}	$<1 \times 10^{-10}$	$<2 \times 10^{-10}$
PF-15	0.998	0.30	8.07	29.3	9.99	9.5×10^{-7}	$<3 \times 10^{-10}$	8.5×10^{-10}
PF-16	0.994	4.94	8.69	31.5	5.52	1.28×10^{-6}	$<3 \times 10^{-10}$	$<3.6 \times 10^{-10}$
PF-17	0.251	1.56	30.6	27.8	4.26	1.42×10^{-5}	8.4×10^{-10}	$<3 \times 10^{-10}$
PF-18	2.46	1.53	2.51	22.4	8.13	6.9×10^{-6}	1.5×10^{-9}	$<3.8 \times 10^{-10}$
PF-19	2.45	5.30	33.9	301	140	2.63×10^{-4}	6.22×10^{-8}	$<2.8 \times 10^{-10}$
PF-20	0.250	5.17	289	262	51.7	2.85×10^{-7}	1.9×10^{-9}	3×10^{-10}
PFE-1	2.51	5.14	9.84	89.8	27.4	2.74×10^{-5}	2.8×10^{-9}	—
PFE-2	2.50	5.34	5.35	48.6	14.3	1.13×10^{-6}	1.5×10^{-9}	—

solid aerosol was collected by two high-efficiency (AEC) filters in series at 40% of rated flow, and the fraction of the released plutonium penetrating the filters was less than 1 ppm. The kinetics of the reaction of PuF_6 and UF_6 with moisture on solid surfaces was measured in packed beds of glass spheres, and the data were used to compute filter penetration due to surface reaction effects. The computation indicates that less than 1 ppm of the released plutonium will penetrate the filter at moisture levels in excess of 0.25 Torr.

The objectives of the present series of experiments

¹⁹ R. W. Kessie, D. Ramaswami, "Removal of Plutonium Hexafluoride from Cell Exhaust Air by Hydrolysis and Filtration," USAEC report ANL-7066 (December 1965)

filter is determined by analysis. The filter material and the apparatus and procedure used for purification of PuF_6 and preparation of feed-gas mixtures are described in Ref. 19 (pp. 11, 37-39), and the gas mixer and filter series are shown in ANL-7325, p. 88.

The filtration-run part of the experimental program has been concluded, and the analytical work will be finished in several months. Preliminary correlation of results has started.

Correlation of plutonium penetration of the first filter with gas velocity through the filter was obtained from the results in Table II-14. The equation used to fit the results was

$$P = e^{c v^n}$$

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FIG. II-7. Charged-Aerosol Collector Used in Expts. PFE-1 and PFE-2.

where P is the fraction of the released plutonium that penetrates the first filter and is collected on the following filters and v is the gas velocity at the filter surface. The constants c and n , determined by least-squares fitting, are

$$c = -16.2 \pm 0.4$$

$$n = -0.09 \pm 0.03$$

The error limits are standard deviations and include the effects of other variables that have not been separately determined as yet. These other variables (P_{H_2O} , P_{PuF_6} , Pu feed rate) affect penetration to a lesser extent than does gas velocity over the ranges studied.

The value of n in the equation has some theoretical significance in indicating the mechanism of filtration. For a homogeneous aerosol collected in the filter by a purely diffusional mechanism, the value of n would be -1 . The previously reported experimental measurement¹⁹ of the surface reaction kinetics would also give a value for n of -1 if surface reaction controls filter penetration. A mechanism of interception alone would give $n = 0$. A mechanism of impaction alone would give $n = 1$.

Reaction of gaseous PuF_6 with moisture at the filter surface does not operate in parallel with the other mechanisms. Since the smallest value for n for all pairs of runs with any significant gas velocity differ-

ence is $n = 0.25$, it appears that surface reaction kinetics did not control penetration in any of the runs.

The other mechanisms operate in parallel on aerosol collection, with the interception mechanism predominating and the diffusion mechanism also effective to a smaller extent.

It has been observed that, in a series of two filters, the fraction of the incident plutonium aerosol penetrating the second filter is usually much greater than the fraction of the incident aerosol penetrating the first filter. Electrostatic charge effects might explain high penetrations of filters. Ion pairs, which are generated in an air- PuF_6 mixture by radiation from plutonium, have a diffusivity that is dependent on the sign of the charge. Positive ions attract and hold more neutral molecules, on the average, than do negative ions. Positive ions thus diffuse about 20% more slowly than do the negative ions. The solid walls of the equipment or ducts through which the aerosol is flowing collect more negative ions by diffusion and thus leave the aerosol with a net positive charge. Gas convection drives this charged aerosol through the filter, resulting in a positively charged filter. Thereafter, positive ions and positively charged aerosol particles penetrate the filter more readily than do neutral or negatively charged particles due to the charge repulsion force between particles and individual fibers of the filter. Even if the first filter reduces the radiation level in the gas to a low level, the excess positive ions and aerosol particles penetrating the first filter may be carried by gas convection through the successive filters, charging them, so that penetration of successive filters could theoretically approach 100%. This effect would

TABLE II-15. PLUTONIUM AEROSOL CHARGE DISTRIBUTION AFTER PASSING THROUGH AN AEC FILTER

	Run PFE-1	Run PFE-2
Collector voltage, kV	10.0	10.0
Collector current, pA		
Run start	2.1 ± 0.1	7.7 ± 0.2
Run end (max.)	2.3 ± 0.2	8.9 ± 0.2
Pu, ng		
Chamber walls	<0.0002	3.16 ^a
Positive electrode	0.248	0.0442
Negative electrode	1.00	0.374
Second filter	27.4	11.3
Positive aerosol, %	3.5	3.2
Negative aerosol, %	0.87	0.38
Neutral aerosol, %	96	96
Positive aerosol as a percentage of charged aerosol	79	89

^a High value probably due to contamination during handling in the glovebox rather than aerosol collection during the run.

be expected to be more significant in a burst-type release²⁰ in which most of the PuF_6 is released quickly and plutonium concentrations are higher than in the present series, which simulates continuous steady-state release (for example, a relatively constant leak continuing for more than 5 min). Burst-release penetrations of the second filter were observed to be as high as 80%, whereas for continuous release, second-filter penetrations rarely exceeded 1%. The greater reproducibility in the continuous-release experiments than in the burst-release group was considered to be an advantage in obtaining significant results on charged aerosol measurement although the fraction of charged particles in the aerosol from the former experiments may be much lower.

²⁰ R. W. Kessie, D. Ramaswami, "Removal of Plutonium Hexafluoride from Cell Exhaust Air by Hydrolysis and Filtration," USAEC report ANL-7066, pp. 23-29 (December 1965).

In runs PFE-1 and PFE-2, a charged-aerosol collector, the design of which is shown in Fig. II-7, was installed between the first and second filters. Three filters in series were used instead of the four filters normally used because of equipment space limitations. Analysis of the collection efficiency of the charged aerosol collector indicates that particles of minimum charge (single electronic unit, positive or negative) must be larger than 0.2 to 0.5 μm before collection efficiency decreases significantly below 100%.

The results obtained with the charged-aerosol collector (Table II-15), showing that a large fraction of the charged particles were positively charged, are consistent with the previous theory. In particular, the >3% of the aerosol that is positive is more than sufficient to account for the observed penetration (up to 1% of the incident aerosol) of the second filter. No additional work is planned on charged aerosol effects.

B. ENGINEERING-SCALE INVESTIGATIONS (*N. M. Levitz*)

1. Kilogram-Scale Production of Plutonium Hexafluoride by Fluorination in a Fluidized Bed (*N. M. Levitz, G. J. Vogel, E. L. Carls, D. Grosvenor, W. Murphy, B. Kullen, D. Raue*)

In fluoride volatility processes involving the recovery of plutonium from spent nuclear fuels, the conditions for the fluorination of plutonium to PuF_6 , for the transport of PuF_6 through the system, and for the collection of the PuF_6 are of particular interest. Also, since PuF_6 can be reduced to nonvolatile PuF_4 by alpha radiation, thermal decomposition, and reduction by compounds or metal surfaces of the equipment, the recovery of this PuF_4 from the equipment must be demonstrated.

A program of campaign-type experiments in which 2.3 kg of PuF_4 was fluorinated to PuF_6 in an engineering-scale alpha facility has been described recently.^{21, 22} A summary of the work follows.

Plutonium tetrafluoride was fluorinated to PuF_6

with elemental fluorine in a fluidized bed of alumina to provide information pertinent to fluoride volatility process flowsheets. Initial fluorination rates above 6 lb PuF_6 /(hr) (ft^2) and material balances near 100% were achieved.

The fluorination program was divided into three campaigns, each campaign consisting of three separate fluorinations (260 g of -325 mesh PuF_4 powder for each fluorination), followed by a fluorination-cleanup step in which plutonium deposited in the lines and equipment was recovered. A single bed of alumina, about 6.5 kg of nominal 48-100 mesh, was used in each campaign. A 93% fluorine-7% nitrogen gas mixture served as the fluidizing gas and reactant.

The fluorinator off-gas was passed through cold traps to collect the PuF_6 . Except for a bleed stream, the remaining gas was recycled to the fluorinator. Makeup fluorine was added to counteract the dilution effect of nitrogen added as instrument purges and as blowback gas for the fluorinator filters. The temperature of the fluidized alumina bed was increased incrementally (about 25°C every 15 min) to 550°C from the initial temperatures of 300°C (Campaign 1), 375°C (Campaign 2), and 450°C (Campaign 3). Previous work had shown that starting fluorination at lower

²¹ N. M. Levitz, G. J. Vogel, E. L. Carls, D. Grosvenor, B. Kullen, D. Raue, W. Murphy, "Production of Plutonium Hexafluoride by Fluorination in a Fluidized Bed," *Nucl. Appl.* **6**, 147 (1969).

²² N. M. Levitz, G. J. Vogel, E. L. Carls, D. Grosvenor, W. Murphy, B. Kullen, D. Raue, "Engineering Development of Fluid-Bed Fluoride Volatility Processes. Part 15, Material Balance Demonstrations, Production Rates, and Fluorine Utilizations in Fluorination of Kilogram Quantities of PuF_4 to PuF_6 with Elemental Fluorine in a Fluid-Bed Reactor," USAEC report ANL-7468 (July 1968).

temperatures decreased plutonium retention in the alumina bed. The total fluorination time for each run was 5 hr in the first and second campaigns and 3 hr in the third campaign.

The significant results from the campaigns are as follows:

1) Plutonium material balances were 97, 101, and 99% in successive campaigns, values that are within the expected range.

2) Production rates of PuF_6 averaged 2.4 lb PuF_6 /(hr)(ft²) for the first and second campaigns and 4.1 for the third campaign. Rates above 6 lb PuF_6 /(hr)(ft²) were attained in the initial 30-min fluorination period of each run.

3) Fluorine utilization efficiency (defined as the amount of fluorine reacted to that which could theoretically react based on equilibrium considerations) averaged 22, 17, and 28% for the successive campaigns. Demonstrated efficiencies near 100% were attained in the earlier portions of a run when large quantities of plutonium were present.

4) Less than 2% of the PuF_6 was decomposed to PuF_4 by radiation decomposition, and this was re-fluorinated and recovered without difficulty.

Other information developed from the data shows the following:

1) Elutriation from and heterogeneity of the bed affect the ability to sample effectively a fluid-bed system containing particles of widely differing sizes.

In the present work, with PuF_4 of -325 mesh size and nominal 48-100 mesh alumina as bed material, grab samples did not accurately reflect the inventory of the system, and the data could not be used to calculate PuF_6 production rates and fluorine efficiencies.

2) The cold traps for collecting PuF_6 from the process gas stream operated efficiently with -65°C coolant. The two in-series cold traps removed 98.7% of the PuF_6 passing through them, which is near the theoretical amount that could be removed as determined from extrapolated vapor pressure data.

3) Corrosion of the fluorinator is not a problem under our operating conditions. The corrosion rate, based on continuous operation for a 24-hr day, 365-day year, was less than 30 mils/yr.

4) Development of neutron counting techniques for monitoring (1) the movement of PuF_4 and PuF_6 during fluorination of PuF_4 in fluid beds and (2) the transfer of PuF_6 from one vessel to another shows considerable promise. The endpoints of both the fluorination and the transfer operations in the current campaign were clearly indicated on the recorder traces.

5) A straight-line, log-log correlation (Fig. II-8) was obtained when the neutron emission rate per gram of sample (a direct analysis of sodium fluoride pellets on which was sorbed PuF_6) was plotted against the plutonium concentration obtained by chemical analysis of this NaF material. The correlation held over a con-

FIG. II-8. Neutron Count Rate vs. Plutonium Concentration in Sodium Fluoride Sorber Samples.

centration range of about five orders of magnitude (26 wt % to about 0.001 wt %). Similar correlations were not obtained for samples from the final alumina bed, the fluidized alumina bed, or the fluorinator wall and filter. These samples contained americium, like plutonium an alpha emitter that contributes to the $F(\alpha, n)$ Na reaction.

6) Sodium fluoride efficiently sorbed PuF_6 from the

process gas streams. Loadings of up to 25% plutonium were obtained.

7) The concentration of americium (from ^{241}Pu decay) in the fluorinator bed increased in succeeding fluorination runs of a campaign. Monitoring of americium in the overhead product might be applicable to a filter efficiency determination, since its fluoride is a nonvolatile particulate solid.

2. Conceptual Fluoride Volatility Process for Fast-Reactor Fuels (N. M. Levitz, M. J. Steindler, L. J. Anastasia, E. L. Carls, A. A. Chilenskas, J. Graae, G. J. Vogel)

A long-range objective of the AEC's Division of Reactor Development and Technology is the development of an economically feasible nuclear fuel cycle for fast breeder reactors (FBR).²³ Recovery processes for FBR fuels represent a critical part of the fuel cycle because of the high value of the plutonium in discharged fuel, the need for short turn-around time, and the high burnups. The reprocessing method chosen may be aqueous, nonaqueous, or a combination of the two.

A current assignment of the Fluoride Volatility Section of the Chemical Engineering Division is assessment of the potential of fluoride volatility processes for reprocessing FBR fuels. Plans call for an examination of two conceptual cases: (1) a large central plant serving nuclear power plants with a total capacity of 15,000 MW(e) and providing a highly decontaminated product (decontamination factor²⁴ of 10^6 – 10^7) and (2) a small on-site plant serving a reactor park, 3000 MW(e), and providing an overall decontamination factor of about 10^3 . Attention is first being given the large-plant case in an assessment of the state of the art, delineation of process and engineering uncertainties, and a proposed development program to establish flowsheet feasibility. The large-plant case represents a processing load of about 1 metric ton of actinides per day from the combined core and blanket fuel.

a. Fuel Characteristics

The reference fuel characteristics are

Core specific power: 200 MW(t)/metric ton
Average core burnup: 100,000 MWd/metric ton
Average blanket burnup: 8000 MWd/metric ton

²³ See "Liquid Metal Fast Breeder Reactor Program Plan," ten sections numbered WASH-1101 through WASH-1110 (August 1968).

²⁴ Decontamination factor = quantity of contaminant in the feed/quantity of contaminant in the product.

Composition

Core:	20% $\text{PuO}_2\text{-UO}_2$
Blanket:	2% $\text{PuO}_2\text{-UO}_2$
Cladding:	stainless steel
Design:	axial blanket integral with core
Bonding:	gas, but it is assumed that 1% of the fuel is sodium-logged
Cooling time:	30 days

Key fuel characteristics are the high plutonium content, the high fission product content, and the high heat loads. Overall minimum recovery of 99% of the uranium and plutonium is specified.

b. Fluoride Volatility Flowsheet

The flowsheet under design is structured for the most part on known technology since fluoride volatility coupled with fluidization has been investigated or applied to a number of nuclear fuel cycle problems such as the following:

1) Refinement of uranium ore concentrates by continuous fluorination in fluid-bed reactors to produce UF_6 , followed by distillation to purify the UF_6 (used in a commercial plant by Allied Chemical Corporation^{25, 26} at Metropolis, Illinois).

2) Fluid-bed calcination of radioactive liquid wastes (full-scale demonstration in the Idaho Nuclear Corporation²⁷ plant).

²⁵ W. C. Ruch et al, "Production of Pure Uranium Hexafluoride from Ore Concentrates," presented at Nuclear Engineering and Science Conference, Cleveland, Ohio, April 6–9, 1959.

²⁶ A. H. Sutton et al, "Reduction and Hydrofluorination of Uranium Concentrates by Fluid-Bed Techniques," presented at 53rd National AIChE Meeting, Pittsburgh, Pa., May 17–20, 1964.

²⁷ R. E. Commander et al, "Operation of the Waste Calcination Facility with Highly Radioactive Aqueous Wastes, Report of the First Processing Campaign," USAEC report IDO-14662 (June 1965).

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FIG. II-9. Fluoride Volatility Process for Fast Reactor Fuels.

3) Pneumatic conveying of radioactive solids (demonstration of reliable operation in progress at Idaho Nuclear Corporation²⁸).

4) Processing of fully enriched uranium fuels (methods developed in the United States²⁹ and in Europe³⁰).

5) Fluorination of kilogram quantities of plutonium to the hexafluoride (performed at ANL³¹ and at the Dow Rocky Flats Laboratory,³² with a 12-kg/day prototype plant being designed at the latter).

6) Full-scale reprocessing of the uranium stream

²⁸ C. L. Bendixsen, G. E. Lohse, "Experience with Non-mechanical Solids Flow Control Devices in the Waste Calcining Facility," presented at Symposium on Storage, Flow, and Handling of Solids, Boston, Oct. 20-23, 1968.

²⁹ J. T. Holmes, H. Stethers, J. J. Barghusen, "Engineering Development of Fluid-Bed Fluoride Volatility Processes, Part 8. Pilot-Plant Development of a Process for Uranium Alloy Fuels," USAEC report ANL-6973 (August 1965).

³⁰ "Reprocessing of Fuel from Present and Future Power Reactors," Institut for Atomenergi report KR-126, p. 324 (September 1967).

³¹ N. M. Levitz et al, "Engineering Development of Fluid-Bed Fluoride Volatility Processes, Part 15. Material Balance Demonstrations, Production Rates, and Fluorine Utilizations in Fluorination of Kilogram Quantities of PuF_4 to PuF_6 with Elemental Fluorine in a Fluid-Bed Reactor," USAEC report L-7468 (July 1968).

³² J. M. Cleveland, M. A. Thompson, eds., "Proceedings of the Rocky Flats Fluoride Volatility Conference," CONF-680610 (1968).

(planned for use in the Midwest Fuel Reprocessing Plant³³ of the General Electric Company).

Process and engineering flowsheets for FBR fuels have been prepared, including (1) basic layouts of the process cell and the overall plant and (2) design of major equipment items. The conceptual flowsheet is shown schematically in Fig. II-9.

The mechanical head-end scheme³⁴ includes chopping the fuel pins and a step to separate the cladding and provide a powdered UO_2 - PuO_2 -fission product feed for the continuous, fluid-bed fluorinators. The major mechanical head-end steps are common to all current reprocessing schemes (aqueous, fluoride volatility, and pyrochemical). A major deviation for the fluoride volatility process is the need to assay the individual fuel pins to detect those that contain sodium because of cladding failure. The behavior of sodium in the process is presently unknown and is to be determined. It is known that NaF sorbs PuF_6 irreversibly, and it may be desirable to minimize the sodium content of the feed to the fluorination step. A method for handling fuel pins containing sodium might include

³³ "Reprocessing of Fuel from Present and Future Power Reactors," USAEC report K-126, p. 342 (September 1967).

³⁴ Portions of this head-end process are under development at ORNL and are described in the "Chemical Technology Division Annual Progress Report for Period Ending May 31, 1968," USAEC report ORNL-4272 (September 1968).

chopping, washing the fuel to remove the sodium, then combining the fuel with the main stream.

The main stream of chopped fuel sections ($\frac{1}{2}$ -in. to 1-in. lengths) passes from the chopper to a continuous ball mill, where the fuel is separated from the stainless steel hull sections and at the same time converted to powdered form. The hulls are monitored for residual fuel; the fuel-free hulls are discarded to waste, and the hulls that contain fuel are recycled for rework in the mill. Preliminary ball-mill tests at ANL with simulated chopped fuel sections ($\frac{1}{4}$ -in. OD, stainless steel tubes filled with porcelain rod and chopped by ORNL) have given encouraging results—about 97% separation in a 10-min residence period.

The conceptual design study starts basically after the fuel has been chopped. Two fluid-bed fluorination units in series provide bulk separation of the uranium and plutonium as well as partial decontamination. The two fluorination vessels are made of nickel and have slab configurations for nuclear criticality safety. The bulk of the uranium is recovered as volatile UF_6 in the first vessel and the volatile PuF_6 is recovered in the second vessel (a two-stage unit). Fluorine is the only fluorinating agent used. Recent fluid-bed studies (see Laboratory Investigations, Section II.A.1.b of this report) indicate that selectivity can be achieved by the control of temperature and fluorine concentration. A single-reactant system should be inherently simpler.

Uranium fluorination is conducted at 350°C with oxygen-~20% fluorine, and plutonium is fluorinated at 500°C and 550°C (first and second stages, respectively) with ~90% fluorine. Continuous operation and staging without the use of downcomer pipes appear feasible on the basis of recent exploratory studies at ANL.³⁵ Staging using several baffle arrangements was demonstrated earlier by Overcashier and coworkers.³⁶ An alumina stream, mixed with the fuel-oxide feed, cascades through the reactors and finally to waste receivers, carrying with it those fission products in the feed that do not form volatile fluorides. The gas streams from the fluid-bed fluorination units pass through fission product traps (partial condensers) and product collection cold traps, where separation from some fission products occurs.

The UF_6 product stream may contain sufficient plutonium to warrant recovery of PuF_6 from this stream. This is accomplished in the present flowsheet by recombining the hexafluoride product streams and carrying out a more nearly quantitative separation in a

fluid-bed thermal decomposition step³⁷ in which PuF_6 is converted to solid PuF_4 . This step also gives further purification of the plutonium from remaining volatile fission products. The UF_6 stream passes overhead and is purified using a combination of fractional distillation and sorption traps.

The PuF_4 produced by thermal decomposition is subsequently refluorinated to PuF_6 and combined with the desired proportion of the pure UF_6 product for feed to an Inconel fluid-bed converter, where a dense homogeneous $\text{PuO}_2\text{-UO}_2$ particulate solid is produced by simultaneous reaction of the hexafluorides with steam and hydrogen. The conversion process is based on work³⁸ conducted earlier on UF_6 alone. Excess UF_6 may be shipped off-site.

Many of the intermediate process vessels are installed in duplicate and are operated on a nominal 12-hr cycle. One is always on-stream, permitting continuous operation of the main fluorinators at the front end of the process and the stills and converter at the tail end of the process without need for a large number of intermediate holdup vessels.

Heat loads are most severe in the main fluorination vessels, which have large inventories of fission products, and particularly in the uranium fluorinator, which has in addition a large chemical heat load. Maximum heat fluxes are on the order of 11,000 Btu/(hr) (ft^2), and calculations indicate that satisfactory heat removal can be achieved with air cooling of a finned reactor surface. A slab design for the fluorination vessels appears to offer several advantages with regard to the heat-load problem. It provides a greater surface for heat transfer than would a cylindrical vessel of comparable volume and, in addition, presents a small dimension (4-in. thick vessels in the present design) across which the heat must be transferred.

Off-gas is passed through solid reactants to dispose of the excess fluorine, the HF (from conversion), and the volatile fission product fluorides. Oxygen is converted to water, which may be stored or disposed of depending on the activity level. The rare gases, xenon and krypton, are compressed and can be stored, allowing xenon to decay. Possibly, clathrates can be used for ultimate krypton disposal. Since fluorine is extensively recycled and wastes are primarily solids, the

³⁵ Reactor Development Program Progress Report, October 1968, USAEC report ANL-7513, pp. 119–120, Nov. 27, 1968.

³⁶ R. H. Overcashier, D. B. Todd, R. B. Olney, "Some Effects of Baffles on a Fluidized System," *AIChE Journal* 5(1), 54 (1959).

³⁷ L. E. Trevorrow, M. J. Steindler, "Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes, Part XV. Estimation of Rates of Thermal Decomposition of Plutonium Hexafluoride in Process Streams," USAEC report ANL-7347 (July 1967).

³⁸ I. E. Knudsen, N. M. Levitz, A. A. Jonke, "Engineering Development of Fluid-Bed Fluoride Volatility Processes, Part 6. Preparation of Dense Uranium Dioxide Particles from Uranium Hexafluoride in a Fluidized Bed," USAEC report ANL-6902 (December 1964).

design calls for essentially no release of noxious materials to the environment.

c. Criticality, Accountability, and Plant Safety

Overall plant problems such as criticality, accountability, and plant safety in the event of hexafluoride release have been considered in this preliminary evaluation. The approach to criticality control adopted for this volatility-plant concept is one that avoids neutron moderation and minimizes neutron reflection to obtain a low reactivity per unit mass of plutonium in the process system. Also, all vessels expected to contain significant quantities of plutonium are of a slab design, which lends itself to safe-by-shape geometry. Preliminary criticality calculations by the K-25 plant (ORGP) indicate that 100 kg of plutonium could be safely contained in a 4-in. thick slab reactor of nickel, 48 in. wide (the proposed fluorinator dimensions), containing PuF_4 at its theoretical density (7 g/cm^3), and reflected at the top and bottom by alumina bed material. The normal operating inventory in the present flowsheet is less than 50 kg of plutonium.

Water is excluded from the process,³⁹ both internally and as an external reflector. Other safety factors are incorporated into the plant design (e.g., vessel spacing and piping dimensions) to prevent external reflectors from complicating the criticality problem. Input of fissile material will be monitored by weight, and the inventory of plutonium in the key process vessels (e.g., the fluorinators) will be monitored by nuclear instrumentation. These monitoring procedures contribute additional criticality safety factors. For both normal and credibly abnormal situations, an acceptable overall factor of safety is predicted. The exclusion of moderators in plant design and an experimental demonstration of the process would assure its criticality safety.

Accountability and burnup analyses are accom-

³⁹ An exception is the use of steam in the conversion of hexafluoride to oxide, but criticality safety requirements are met by the slab design of the converter.

plished by sampling (1) fuel before it is fed into the first chemical process stage and (2) final waste streams (which establish loss levels). Fuel is conveyed from the mill to weighed containers and is sampled continuously by pneumatic techniques as the container contents are fed, also pneumatically, to the process. Blended samples of fuel batches processed over a specified time interval are prepared. Weights and analyses of (1) input material, (2) the final products (the mixed $\text{PuO}_2\text{-UO}_2$ product of the conversion step), and (3) the excess UF_6 provide the necessary information for accountability. Additional monitoring of plutonium inventories and plutonium movement in the intermediate process steps provides supplemental information for accountability. Monitoring appears to be feasible based on recent work at ANL in which neutron survey meters were used as plutonium monitors.

d. Objectives of a Demonstration-Development Program

On the basis of current technology, a successful demonstration of the flowsheet should be possible. The principal areas requiring confirmation by the demonstration include

- 1) separation of the fuel from the cladding and a method for identifying sodium-logged fuel pins (excluded from the current scope of this study are other mechanical head-end operations),
- 2) continuous fluorination at the desired production levels and with acceptably small actinide losses,
- 3) fission product behavior during product purification steps,
- 4) conversion of $\text{UF}_6\text{-PuF}_6$ mixtures to $\text{UO}_2\text{-PuO}_2$,
- 5) "total" containment of wastes,
- 6) satisfactory solids mixing and heat transfer in slab-shaped vessels.

Solutions lie primarily in a demonstration of the flowsheet. On the basis of current technology, successful demonstration of the flowsheet should be possible.

3. Pulsed-Bed Studies (*D. Ramaswami, M. Kobayashi,⁴⁰ W. T. Brazelton,⁴¹ C. Schoffstoll*)

Studies have been initiated on the use of pulsed beds for fluoride volatility processes as an alternative to conventional fluidized beds with steady upward flow of gas. In pulsed-bed operations, the bed expands during a pulse, then contracts during the interval when the gas flow is shut off. During each pulse cycle, the beds exist in four distinct states. With rapid transi-

tion the solids undergo pneumatic transport, behave as a fluidized bed, undergo hindered settling, and return to the static bed condition. Possible advantages of pulsed-bed operation for a fluoride volatility process are (1) capability of using wider ranges of particle sizes, (2) better solids-gas contacting with large as well as small particles and improved reactant utilization, (3) improved heat and mass transfer rates, (4) greater mean gas throughput rates and shorter fluorination periods, and (5) decreased elutriation of parti-

⁴⁰ Resident Student Associate from Northwestern University. Candidate for a doctorate in Chemical Engineering.

⁴¹ Faculty Associate from Northwestern University.

cles out of the bed. Evidence that these advantages will accrue was found in six papers in the open literature describing physical observations, solids mixing, heat transfer, drying, and chemical reactions. The aspects pertinent to fluoride volatility processing are summarized below.

Massimilla, Volpicelli, and Raso⁴² studied pulsed and fluidized beds in a cylindrical Lucite column with a 20-cm ID and in a two-dimensional glass column with 20 by 1.5-cm inside dimensions. Pressure drops were higher for pulsed beds than for fluidized beds for equivalent gas throughputs. They concluded that the uniformity of solids-gas contact peculiar to fixed-bed operation and the solid motion peculiar to fluidized-bed operation are, to some extent, combined in a pulsed-bed operation.

Berg and Miniscalco⁴³ described a commercial air-pulsed mixer of 5000-lb capacity that blends six ingredients (limestone, mica, talc, asbestos, clay, and casein or PVA binder) solely with intermittent blasts of air at the bottom of the bed. The mixer is 14.5 ft high, and its cylindrical section is 6 ft in diameter. The air-pulsed mixer gives better mixing than three mechanical blenders that it replaced.

Bokun and Zabrodskii⁴⁴ investigated heat transfer from a heater immersed in a bed of dry sand of narrow size range. The heat-transfer coefficients increased as the gas velocity was increased and were up to three times as high for pulsed beds as for fluidized beds at the same integral gas throughput in a range immediately above the minimum fluidization velocity. The maximum heat-transfer coefficient for this system, about 60 Btu/(hr)(ft²)(°F), was obtained at mean integral gas velocities smaller by 30 to 40% than the gas velocity giving maximum heat transfer for conventional fluidized beds. In another investigation,⁴⁵ when drying was attempted with a steady flow of air upward through a bed of moist tetracycline, channeling

occurred, resulting in irregular drying and poor utilization of the drying agent. However, with the pulsed flow of gas, channels did not form and the bed moved vigorously, resulting in better heat and mass transfer and good utilization of the drying agent. Evidence for improved heat and mass transfer coefficients between air and moist tetracycline with pulsed-bed operation was a lower moisture content of the tetracycline for pulsed than for steady gas flow (e.g., with pulsed gas flow, the moisture content decreased from 40 to 10 wt % in an hour; with steady gas flow, the moisture content decreased from 40 to 33 wt % in an hour).

Three years of experience in operating commercial pulsed-bed dryers was reviewed by Belik.⁴⁶ Organic products with particle sizes of 10 to 3000 μm and with moisture contents up to 25% were dried in batches up to 1000 kg. The pulse frequencies were 0.4 to 1.2 Hz depending on the bed height, and the on-period was ~33%. Gas was fed, in turn, through each of five ports located on the circumference of the gas distributor. Following introduction of a gas pulse through one port, the subsequent pulse was fed through a port diagonally across from the original port. The gas was allowed to expand after introduction into the bed. This pulsation procedure eliminated channel formation, even in deep beds. The drying time was about one-third to one-sixth that in a conventional vacuum drier.

Levey et al.^{47, 48} reported that conducting a number of gas-solid reactions in pulsed beds resulted in products with the desired physical and chemical properties, whereas conducting them in fluid beds, fixed beds, or rotary calciners was neither practicable nor yielded satisfactory products. Hydrogen reaction of U_3O_8 particles with diameters less than 100 μm was conducted for 1.5 hr with an integral gas velocity of ~2.0 ft/sec. The hydrofluorination of the resultant product was conducted for 6.5 hr with an integral gas velocity of ~1.5 ft/sec. When the same U_3O_8 was processed with a steady flow of gas, the maximum gas velocity attainable without packing the solid against the top of the reactor was 0.1 ft/sec, and the total time for reduction and hydrofluorination was 24 hr. Ammonium diuranate filter cake having a particle size distribution of ~1 to 5000 μm was successfully reduced and hydrofluorinated in pulsed beds. Massive uranium machine chips were reacted with hydrogen, then the hydride

⁴² L. Massimilla, G. Volpicelli, G. Raso, "A Study of Pulsing Gas Fluidization of Beds of Particles," *Chem. Eng. Progr. Symp. Ser.* **62**(62), 63 (1966).

⁴³ D. B. Berg, B. Miniscalco, "Product Uniformity up 300%—Capacity Doubled, Labor Cost Cut 20% as Air-Pulsed Mixer Replaces 3 Mechanical Blenders," *Chemical Processing* **31**(4), 30-31 (1968).

⁴⁴ I. A. Bokun, S. S. Zabrodskii, "Experimental Study of Heat Transfer between a Pulsating Bed and the Heating Surface," ANL-Trans-592 (March 1968); translated from *Investigation of Heat and Mass Transfer in Technological Processes and Apparatus*, pp. 27-32, edited by A. V. Lykov, Publishing House "Nauka i Tekhnika," Minsk (1966).

⁴⁵ S. S. Zabrodskii, I. A. Bokun, "Heat Transfer between a Pulsating Bed of Moist Tetracycline and the Heating Surface," ANL-Trans-593 (March 1968); translated from source given in Ref. 44, pp. 135-139.

⁴⁶ L. Belik, "The Impact-Turbulence Method for Drying Ground Solids," ANL-Trans-613 (March 1968); translated from *Chimie-Ingenieur-Technik* **32**(4), 253-277 (April 1960).

⁴⁷ R. P. Levey, Jr., "Gas-Solids Contacting Method," U.S. Patent No. 3164440 (Jan. 5, 1965).

⁴⁸ H. M. Heidt, R. P. Levey, C. E. Hamrin, "The Use of Fluid-Bed Equipment in Enriched Uranium Processing," *Chem. Eng. Progr. Symp. Ser.* **62**(65), pp. 43-51 (1966).

thermally decomposed to uranium powder. The particle size distribution of the product was such that 95% of it was less than 5 μm and 90% was less than 1 μm .

a. Current Work

The objectives of the ten exploratory runs (PB1 to PB10) performed in this investigation were to compare the behaviors of pulsed-flow beds and steady-flow beds for materials similar to those used in the fluoride volatility process and to determine the type of feed-gas distributor needed for pulsed-bed columns.

The apparatus consists of a 3-in. dia, 72-in. long Pyrex glass column with auxiliaries needed to pulse the feed-gas stream. The interior of the column has a conductive coating (a mixture of Sb_2O_3 and SnO_2) to reduce the effect of static charges. For Runs PB1 through PB6, a sintered-metal plate was used as the feed-gas distributor at the bottom of the column; for Runs PB7 through PB10, a simple cone bottom was used as the gas distributor. Two bayonet-type sintered-metal filters (9 in. long by 1½ in. wide, Type G, average porosity of 10 μm) were attached to the top flat cover plate of the glass column. The feed system consisted of ¾-in. or ⅜-in. orifice solenoid valves (1 or 4 units) in the feed-gas line, a surge tank (16 or 40 liters) in the feed-gas line, two humidifiers in series, and an integrating gas flow meter in the feed-gas line or off-gas line. Compressed air from the house supply was used as the feed gas.

Five sizes of Alcoa T-61 granular alumina with particle sizes of 2380 μm to 2 μm were used as the charge. The average particle sizes of the five fractions were 1327, 882, 420, 180, and 55 μm . Some runs had a total charge of 2.5 kg and the others a total charge of 5 kg, each charge consisting of five equal parts of the particle-size fractions. The bed was charged in layers. The largest-sized alumina was charged first, then the next smaller size, and so on. Each of the ten runs

(PB1 to PB10) was about 6 hr in duration. Three runs (PB2, 4, and 6) utilized a steady gas flow, and the other seven a pulsed gas flow.

Data on gas velocities, pulse conditions, pressure drop across the feed-gas distributor, and bed expansion are given in Table II-16. For conciseness, only five of the ten runs are included. The conclusions drawn from these data are also applicable to the data from the five other runs.

It was observed that the entire bed expanded with the pulsing gas flow, whereas only top layers expanded with the steady gas flow. Bed expansion was consistently greater for pulsed beds than for fluidized beds at the same integral gas flow rates (Table II-16).

The mixing of the wide-size-range particles was better with the pulsed gas flow than with steady gas flow for the same integral gas throughputs. Particle mixing at the end of a run was determined by sieve analysis of successive portions of the bed. Data on average particle size at various heights of the bed before and after a run are shown in Fig. II-10 for 10-in. deep beds and in Fig. II-11 for 20-in. deep beds. Visual observation of the pulsed beds revealed that the initial, completely segregated layers mixed thoroughly within a few minutes of the start of the run and remained well mixed for the remainder of the 6-hr operation. However, in fluidized-bed runs the two lower layers remained intact during the entire 6-hr period of operation.

Expansion of the alumina bed and mixing of particles in the bed were similar at the same integral gas throughput for pulsed-bed Run PB9 with a simple cone distributor and pulsed-bed Run PB5 with a sintered-metal distributor (see Table II-16 and Fig. II-11). The pressure drop across the cone distributor and bed was lower than for the sintered-metal distributor and bed for similar pulse frequency, pulse duration, and gas throughput. These results suggest

TABLE II-16. BED EXPANSION AND PRESSURE DROP DATA

Column diameter: 3 in.

Run No.	Alumina Charge (kg)	Av. Gas Flow Rate (scfm)	Integral Gas Velocity at Column Conditions (ft/sec)	Pulse On-period ^a (sec)	Pulse Frequency (Hz)	Pressure Drop Across Feed Gas Distributor After 6-hr Operation (psi)	Bed Expansion (in.)
PB1	2.5	1.0	0.31	0.36	0.49	0.8	16
PB2	2.5	1.0	0.31	—	—	0.6	8.5
PB5	5.0	2.7	0.6	0.5	0.46	4.0	34
PB6	5.0	2.7	0.7	—	—	2.2	23
PB9	5.0	2.6	0.54	0.5	0.46	1.5	35

^a This is the time the solenoid valve is open and is not necessarily equal to the gas-pulse duration in the bed.

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FIG. II-10. Mixing of Particles in Pulsed and Fluidized Beds. (Superficial gas velocity: 0.31 ft/sec. Integral gas velocity: 0.31 ft/sec. Static bed height: 10 in. Ratio of static bed height to column diameter: 3.3.)

that a simple cone gas distributor can be used in the process application of the pulsed beds.

b. Future Work

Heat-transfer coefficients between a heater surface and a pulsed bed will be determined using a 4-in. dia pulsed-bed column. Residence times of particles on

the heater surface will be measured using the same column. The experimental data on heat-transfer coefficients and particle residence times will be used to determine the mechanism of heat transfer in an attempt to obtain pulsing conditions (such as frequency of pulsation, pulse duration, and gas flow rate) that give higher heat-transfer coefficients in a pulsed bed than those attained in a fluidized bed.

308-1817

FIG. II-11. Mixing of Particles in Pulsed and Fluidized Beds. (Ratio of static bed height to column diameter: 6.7. Static bed height = 20 in.)

4. Interaction Effects on the Fluid Dynamics of Bubbles in a Fluidized Bed (J. D. Gabor, L. B. Koppel, J. Hepperly)

Information for the design and operation of fluidized-bed chemical reactors is largely empirical and is therefore limited to the systems from which the data are derived. The complex character of the particle and gas mixing in a fluidized bed is a result of gas bubbles that are formed when the fluidizing gas velocity is greater than the minimum fluidization velocity.

Recent theoretical work reported in the literature has laid the foundation for understanding the hydro-

dynamics of a freely bubbling fluidized bed. A model to describe the particle motion around a single bubble and also the gas flow associated with a single bubble was presented by Davidson⁴⁹ and subsequently refined by Jackson⁵⁰ and Murray.⁵¹ The model predicts that a gas cloud envelops the rising bubble, which is the

⁴⁹ J. F. Davidson, *Trans. Inst. Chem. Eng.* **39**, 230 (1961).

⁵⁰ R. Jackson, *Trans. Inst. Chem. Eng.* **41**, 13 (1963).

⁵¹ J. D. Murray, *J. Fluid Mech.* **22**, 57 (1965).

FIG. II-12. Geometry for Flow Past a Chain of Doublets in Three Dimensions.

308-1791

FIG. II-13. Effect of Separation Parameter b on Volume of Drift in Three-Dimensional Case; $a = 1$.

major source of gas bypassing in a fluidized bed; the model describes the particulate phase as behaving as an ideal fluid (incompressible and inviscid) flowing around a cylinder (i.e., a bubble). This work, though quite revealing, applies to a single bubble and does not indicate the effect of other bubbles, which are present in practical fluidization.

A theoretical examination has therefore been made of the interaction effects (on particle movement and gas flow) of bubbles in a chain rising through a fluidized bed inside a "two-dimensional" column⁵² and inside a three-dimensional column. Although a study of the interaction effects between bubbles in a vertical chain will not reveal the effect of horizontally adjacent bubbles, a first-order approximation on bubble interaction effects can be made since bubbles are most likely to be formed in chains.⁵³⁻⁵⁵ The results of this

⁵² A column of rectangular cross section for which the thickness is so small that a rising bubble is in simultaneous contact with two opposite walls.

⁵³ J. B. Romero, D. W. Smith, paper 30C presented at AIChE Meeting, Tampa, 1968.

⁵⁴ J. S. M. Botterill, P. D. Bloore, *Can. J. Chem. Eng.* **41**, 111 (1963).

308-1454

FIG. II-14. Effect of U and b on Gas Cloud Volume per Bubble; $a = 1.0$.

application have an important bearing on bubble coalescence, particle mixing, and gas bypassing in a chemically reacting fluidized system.

The objectives of the study were

1) to determine the effects on particle mixing of bubble spacing (particle mixing was improved when passage of a bubble caused the length of particle trajectories to increase), and

2) to determine the effects on gas-solids contacting of bubble spacing and ratio of bubble velocity to minimum fluidization velocity (the larger the volume of gas cloud surrounding each bubble, the better was gas-solids contacting).

⁵⁵ J. S. M. Botterill, J. S. George, H. Besford, *Chem. Eng. Progr. Symposium Ser.* **62**(62), 7 (1966).

a. Two-Dimensional Case

Work on interaction effects for a chain of rising bubbles in a two-dimensional medium⁵⁶ is summarized below:

A theoretical examination is made of the particle movement and gas flow associated with a rising chain of equally sized and spaced bubbles in a two-dimensional bed. When the bubble spacings are small and the ratios of bubble velocity to interstitial gas velocity are low, the gas clouds associated with adjacent bubbles come into contact and form a gas envelope. Within this envelope are two major gas flows: (1) flow from within one bubble upward to the leading bubble and (2) a circulating flow from within one bubble and back into the same bubble.

The area of particle drift caused by a bubble within a chain of bubbles and the area of the gas cloud per bubble in a chain of bubbles are generally greater than those caused by a single bubble in an infinite medium. The area enclosed by particle trajectories caused by the passage of one bubble in a chain of bubbles is approximately doubled when the center-to-center bubble separation decreases from infinity to about 2.8 bubble radii.

b. Three-Dimensional Case

Particle mixing. Summing up doublets uniformly spaced at a distance $2b$ apart with a superimposed fluid flow, U_B , yields the following expressions for the stream function, ψ_p , and the potential function for the particle movement, ϕ_p , in three dimensions:

$$\psi_p = -\frac{1}{2} U_B \left[(r \sin \theta)^2 - m \sum_{j=-\infty}^{\infty} \frac{\sin^2 \theta_j}{r_j} \right] \quad (1)$$

$$\phi_p = -U_B \left[r \cos \theta + \frac{m}{2} \sum_{j=-\infty}^{\infty} \frac{\cos \theta_j}{r_j^2} \right] \quad (2)$$

where

$$m = 1 / \sum_{j=-\infty}^{\infty} \left(\frac{1}{\sqrt{1 + 4j^2b^2}} \right)^3$$

The other variables in Eqs. 1 and 2 are defined in Fig. II-12.

Figure II-13 shows, for a range of bubble-to-bubble spacings, particle displacement caused by a rising bubble as determined from the stream function. The

⁵⁶ J. D. Gabor, "Interaction Effects on the Fluid Dynamics of Bubbles in a Fluidized Bed: Chain of Rising Bubbles in an Infinite Two-dimensional Medium," *Ind. Eng. Chem. Fundam.* **8**, 84 (1969).

volume enclosed by the initial and final positions of the fluidized particles decreases from 3.94 to 2.09 as b increases from 1.25 to 10.0. Closely spaced bubbles rising in a chain improve particle mixing in comparison with a single rising bubble.

Gas mixing. Murray's⁵¹ linear approximation was used to determine the potential function, ϕ_r , for the gas flow associated with a chain of rising bubbles in a three-dimensional medium:

$$\phi_r = x + \phi_p - \frac{r_e^4}{3m} \frac{1}{U} \frac{\partial \phi_p}{\partial x} \quad (3)$$

where r_e is the radial component at the leading edge of the bubble and U is the ratio of the bubble velocity to the interstitial fluidizing velocity.

The gas flow patterns indicated by Eq. 3 are as follows: At low values of U and small bubble separation, the gas clouds contact, resulting in a gas flow upward from one bubble into another, as well as a gas flow that circulates from inside each bubble into the particulate phase and then back into the bubble.

In Fig. II-14 the gas cloud volume per bubble as a function of U and b is shown. For $b = 1.3$, the gas clouds are in contact over the entire range of U shown here (1.1 to 3.5). For $b = 2.0$, the gas clouds are separated for values of U greater than 2.03, and for $b = 3.0$, the clouds are separated over the entire range shown here. For U greater than 1.4, the cloud volume per bubble decreases with increasing bubble separation. However, at the lower values of U , general trends are not easily described. At $U = 1.1$, the cloud volumes for $b = 3.0$ and ∞ (cases of separated clouds) are greater than for $b = 1.3$ and 2.0 where the clouds are contacting. Therefore, although the cloud volume per bubble increases for contacting clouds with decreasing U , the rate of increase is not as large as for separated clouds, and greater cloud volumes result for the separated clouds at the lower values of U .

For bubbles rising in a chain, particle mixing and gas-solid contacting per bubble are generally improved, in comparison with a single isolated bubble.

c. Future Work

Information obtained from the study on bubbles rising in a chain will be extended in new studies to determine the conditions of fluidized-bed bubbling that will optimize the operation of a chemical reactor. The effects on heater-to-bed heat-transfer coefficients of (1) bubble size, (2) bubble frequency, and (3) bubble distance from the heater surface will also be studied.

III

Materials Chemistry and Thermodynamics¹

A. HIGH TEMPERATURE THERMODYNAMIC AND PHYSICAL PROPERTY STUDIES (*P. E. Blackburn, A. D. Tevebaugh, J. D. Bingle*)

The objective of this program is to obtain phase-diagram, thermodynamic, and physical property data that can be used to interpret and evaluate the performance and safety of candidate fast-breeder reactor fuels. This information will aid in understanding and predicting (1) interactions among fuel, fission product, and cladding materials, (2) migration by diffusion or

vapor transport of fissile atoms, anion atoms, and fission products, and (3) melting, flow, and pressure rise rates in core and structural materials associated with possible coolant failure or nuclear excursions. In addition, these data will help to identify phases formed in fuel under operating conditions and to choose cation additives for controlling the chemical potentials of the fuel anions.

¹ A summary of this section is given on pages 8 to 11 .

1. Phase Diagram and Vapor Pressure Studies (*P. E. Blackburn*)

High-temperature investigations of the U-Pu-O and U-Pu-C systems have been initiated. These investigations include mass-spectrometric vapor pressure measurements, phase-diagram studies, and activity measurements by transpiration. In the mass-spectrometric study, both the Pu-O and Pu-C systems are being investigated before taking up the ternary systems. Phase-diagram studies of the metal-rich end of the Pu-O system have begun. Carbon activities and uranium pressures are being obtained by means of a transpiration technique. A new transpiration system for plutonium studies was assembled and is ready for some preliminary tests. An ultrahigh-vacuum effusion chamber is being converted for glovebox operation and modified to accept a quadrupole mass spectrometer and quartz vacuum balance. This apparatus will be used for congruent vaporization measurements and mass-spectrometric studies.

a. Volatilization Studies of Plutonium Compounds by Mass Spectrometry (*J. E. Battles, J. W. Reishus, W. A. Shinn*)

Mass-spectrometric studies of the volatilization of plutonium-containing materials (e.g., the systems Pu-O, U-Pu-O, Pu-C, U-Pu-C, Pu-P, Pu-S) are under way. Their purpose is to determine (1) the composi-

tion of the vapor phase in equilibrium with the condensed phase(s), (2) the partial pressures of the vapor species as a function of temperature, and (3) the thermodynamic properties of the vapor species and condensed phases.

(1) Plutonium-Oxygen System

The volatilization of the plutonium-oxygen system is being studied first, because mass-spectrometric data for this system are not available. Data relating to the apparent congruently vaporizing plutonia ($\sim \text{PuO}_{1.33}$ at 2219°K) and to the binary condensed phase $\text{Pu}_2\text{O}_3 + \text{PuO}_{1.61}$ are presented.

As previously reported (ANL-7425, pp. 95, 96), vapor species characteristic of the vaporization of tungsten or rhenium oxides were observed mass-spectrometrically when stoichiometric $\text{PuO}_2(\text{s})$ was heated at about 1450°K or higher in tungsten or rhenium diffusion cells. After the initial heating, the intensity of these vapor species was greatly reduced; however, some WO_2^+ and WO_3^+ or ReO_2^+ and ReO_3^+ were detectable in the vapor phase throughout the experiments. Because of the reaction of tungsten and rhenium with plutonia, additional experiments were conducted with effusion cells of iridium, which, according to available data, should be nonreactive. When samples of initially

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FIG. III-1. Intensities of PuO_2^+ and PuO^+ , and the Ratio $I_{\text{PuO}^+}/I_{\text{PuO}_2^+}$ as a Function of Time at 2225°K for Run PI-1.

TABLE III-1. MASS SPECTROMETRICALLY DETERMINED PARTIAL HEATS OF SUBLIMATION FOR THE VAPOR SPECIES OF PLUTONIA

Run No.	Cell Material	Ionizing Electron Energy (eV)	Temperature Range (°K)	Composition of Solid Material O/Pu	Partial Heat of Sublimation* (kcal/mol)	
					PuO_2	PuO
P-5A	Re	13.0	2011-2342	1.83	140.2 ± 1.8	125.1 ± 1.0
P-5B	Re	13.0	2008-2327	1.81	137.8 ± 1.6	123.5 ± 0.9
P-5B	Re	17.0	2008-2327	1.81	138.2 ± 1.9	128.5 ± 1.3
PI-1B	Ir	13.0	1955-2229	1.83 ₄	137.8 ± 1.2	130.4 ± 0.9
PI-1D	Ir	13.0	1946-2230	1.83 ₉	139.6 ± 1.3	128.9 ± 1.1
PI-2A	Ir	13.0	1937-2226	1.83 ₄	138.8 ± 1.4	125.9 ± 1.4

* The errors listed are standard deviations.

stoichiometric $\text{PuO}_2(\text{s})$ were heated above 1750°K in iridium effusion cells, a strong vaporization of oxygen was observed; however, the absence of iridium oxide species in the vapor phase confirmed that plutonia does not react with iridium.

Figure III-1 shows the variation of the ion intensity of PuO_2^+ and PuO^+ , as well as the ratio $I_{\text{PuO}^+}/I_{\text{PuO}_2^+}$, as a function of time when a sample of $\text{PuO}_2(\text{s})$ was heated at 2225°K in an iridium effusion cell. Since the

sample lost considerable oxygen during the heat-up, the actual composition of the material was unknown when heating at 2225°K was begun. The measured ion intensity of PuO_2^+ exhibited a gradual decrease with time, while that of PuO^+ and the ratio of $I_{\text{PuO}^+}/I_{\text{PuO}_2^+}$ increased.

After about 10 hr at 2225°K (point A in Fig. III-1), a sample was removed for oxygen analysis. The atom ratio of oxygen to plutonium was 1.88. The sample was then heated an additional 9 hr (point B in Fig. III-1) before measurements of temperature dependence and rate of effusion were begun. At point B, the atom ratio was 1.83. No further reduction of the atom ratio of oxygen to plutonium was observed during the subsequent measurements (see Runs PI-1B, PI-1D, and PI-2A in Table III-1). Similar behavior was observed when rhenium effusion cells were used.

The temperature dependence of the plutonium-bearing vapor species in equilibrium with condensed plutonia has been determined in several series of measurements using both rhenium and iridium effusion cells. The ionizing electron energy was 13 eV in all runs except Run P-5B, in which it was 17 eV. The variation of the ion intensity of PuO^+ and PuO_2^+ plotted as a function of reciprocal temperature ($\log IT$ vs. $1/T$) is shown in Fig. III-2 for a typical series of measurements. About half of the data points were taken as the temperature was systematically decreased (open points) and the others were taken as the temperature was systematically increased (solid points). The concurrence of the data

regardless of the direction of temperature variance gives assurance that equilibrium among the phases was achieved.

The partial heats of sublimation, determined from a least squares analysis of the temperature-dependency data, are summarized in Table III-1. The data were normalized at the mid-temperature and reevaluated by the method of least squares to obtain single values for the partial heats of sublimation: 127.2 ± 2.7 and 138.8 ± 1.1 kcal/mol for $\text{PuO}(\text{g})$ and $\text{PuO}_2(\text{g})$, respectively. The ion intensity ratios of PuO^+ to PuO_2^+ at 2219°K averaged 2.6. The concentration of $\text{Pu}(\text{g})$ in the vapor phase was too small ($\sim 0.1\%$ at 2219°K) for reliable temperature-dependency measurements. Table III-1 also shows the composition of the condensed phase.

Normally, in order to determine the composition of a vapor phase containing several species, the measured ion intensities for each species must be corrected for ionization cross sections, multiplier efficiencies, and energy differences. These corrections for the ion intensity are given by the relationship

$$I'_i = I_i / \sigma_i \gamma_i (E - AP_i) \quad (1)$$

where I_i is the measured ion intensity, σ_i is the ionization cross section, γ_i is the multiplier efficiency which is taken to be inversely proportional to the square root of the molecular weight, and $(E - AP_i)$ is the ionizing electron energy (E) minus the appearance potential (AP_i). The ionization cross sections of Pu^+ and O^+ reported by several investigators²⁻⁴ are listed below:

Species	Ionization Cross Sections		
	Otvos & Stevenson ²	Lin & Stafford ³	Mann ⁴
O^+	3.29	3.23	1.31
Pu^+	56.8	13.77	10.00
PuO^+	60.1	17.00	11.31
PuO_2^+	63.4	20.23	12.62

The additive rule of Otvos and Stevenson² has been used to evaluate the ionization cross sections for PuO^+ and PuO_2^+ . The values reported above are for ionizing electron energies several times larger than those used in this study and, therefore, the application of these values at low ionizing electron energies is subject to question. Also, considerable disagreement exists in the values for the ionization cross sections and in the ratio of these values (e.g., $\sigma_{\text{Pu}}/\sigma_{\text{PuO}}$). Because of these discrepancies

² W. Otvos, D. P. Stevenson, *J. Amer. Chem. Soc.* **78**, 546 (1956).

³ Sin-Shong Lin, F. E. Stafford, *J. Chem. Phys.* **48**, 3885 (1968).

⁴ J. B. Mann, *J. Chem. Phys.* **46**, 1646 (1967).

Based on 308-1267

FIG. III-2. Variation of Ion Intensities of PuO_2^+ and PuO^+ Observed over Plutonia as a Function of Reciprocal Temperature for an Ionizing Electron Energy of 13 eV.

and the small differences in the multiplier efficiencies for Pu , PuO , and PuO_2 , the measured ion intensities were corrected only for the energy differences, so that Eq. 1 becomes

$$I'_i = I_i / (E - AP_i) \quad (1a)$$

The validity of this correction for the energy difference in the linear portion of the ionization efficiency curve was experimentally verified. The appearance potentials were determined by the linear extrapolation method. The values are 9.4 ± 0.5 eV for PuO_2^+ , 5.8 ± 0.5 eV for PuO^+ , and 6.2 ± 0.5 eV for Pu^+ .

After applying the correction for energy differences and calculating a material balance assuming the composition of the vapor phase and solid to be equal, the vapor phase was computed to contain 53.6 wt % PuO , 44.0 wt % PuO_2 , 0.1 wt % Pu , and 2.3 wt % monatomic oxygen at 2219°K. The vapor phase composition reported will be subject to correction when accurate values are known for the ionization cross sections.

From knowledge of the composition of the vapor

Based on 308-1266

FIG. III-3. Temperature Dependence of the Vapor Pressure of Plutonia.

phase and the rate of effusion at a given temperature, the partial pressures of the vapor species were calculated from the effusion equation

$$P_i(\text{atm}) = 2.256 \times 10^{-2} \frac{wF_i}{AtK} \sqrt{\frac{T}{M_i}} \quad (2)$$

where w/At is the rate of effusion in $\text{g}/(\text{cm}^2)(\text{sec})$, F_i is the weight fraction of total vapor, K is the Clausing correction factor for molecular flow through short channels, T is the absolute temperature, and M_i is the molecular weight. The rate of effusion at 2219°K was determined by the weight-loss method using iridium effusion cells. The orifice area was corrected for thermal expansion, and the rate of effusion was corrected for the small weight loss of iridium that occurred during the run. After making the above corrections, the total rate of effusion obtained was $4.21 \times 10^{-5} \text{ g}/(\text{cm}^2)(\text{sec})$ at 2219°K .

The partial pressures of $\text{PuO}(\text{g})$ and $\text{PuO}_2(\text{g})$ over $\text{PuO}_{1.53}(\text{s})$ are given by the equations

$$\log P_{\text{PuO}}(\text{atm}) = - \frac{(27,810 \pm 600)}{T} + (6.710 \pm 0.270) \quad (3)$$

$$\log P_{\text{PuO}_2}(\text{atm}) = - \frac{(30,330 \pm 240)}{T} + (7.750 \pm 0.110) \quad (4)$$

The partial pressures of $\text{Pu}(\text{g})$ and O at 2219°K were calculated to be 2.6×10^{-9} and 2.6×10^{-7} atm, respectively.

The vapor pressure of plutonia has been measured by a number of investigators,⁵⁻⁹ and the results from these studies agree very well, except for the data of Phipps et al, who used tantalum effusion cells. A comparison of all the vapor pressure data, except those of Phipps et al, is shown in Fig. III-3. In all the previous studies, the vapor phase was assumed to be entirely $\text{PuO}_2(\text{g})$.

To study vapor pressures over two-phase material (assumed to be $\text{Pu}_2\text{O}_3 + \text{PuO}_{1.61}$),¹⁰ appropriate amounts of $\text{PuH}_3(\text{s})$ and $\text{PuO}_2(\text{s})$ were mechanically mixed and heated slowly to about 800°K in vacuum. After heating at 800°K for 12–16 hr, the material was then heated slowly to 1750 – 1850°K and maintained at this temperature for about 4 hr, or until all reaction was completed, as determined by mass-spectrometric observations. Chemical analysis showed that the material had an O/Pu atom ratio of 1.54.

Mass-spectrometric observation of the vapor phase over the $(\text{Pu}_2\text{O}_3 + \text{PuO}_{1.61})$ indicated the presence of $\text{Pu}(\text{g})$, $\text{PuO}(\text{g})$, and $\text{PuO}_2(\text{g})$. This result, coupled with X-ray diffraction data, indicates that vaporization to produce these species proceeds according to the reactions

These reactions are based on the assumption that the phase boundaries are Pu_2O_3 and $\text{PuO}_{1.61}$ and are independent of temperature as indicated on p. 18 of Ref. 8.

⁵ T. E. Phipps, G. W. Sears, O. C. Simpson, *J. Chem. Phys.* **18**, 724 (1950).

⁶ R. N. R. Mulford, L. E. Lamar, in *Plutonium 1960*, p. 411, E. Grison, W. B. H. Lord, and R. D. Fowler (eds.), Cleaver-Hume Press, Ltd., London (1961).

⁷ R. J. Ackermann, R. L. Faircloth, M. H. Rand, *J. Phys. Chem.* **70**, 3698 (1966).

⁸ R. Pascard, CEA, information submitted to a panel on Thermodynamic Properties of Plutonium Oxides held in Vienna, Oct. 24–28, 1966, Technical Reports Series No. 79, "The Plutonium-Oxygen and Uranium-Plutonium-Oxygen Systems: A Thermochemical Assessment," p. 43, IAEA, Vienna (1967).

⁹ D. R. Messier, "Evaporation of Hypostoichiometric Plutonium Dioxide from 2070° to 2380°K ," *J. Amer. Chem. Soc.* **51**, 710 (1968).

¹⁰ The Pu-O phase diagram at high temperatures and in this composition range has not yet been firmly established; A. E. Martin and F. C. Mrazek have recently initiated work on this system (see Section III.A.1.b of this report).

The temperature dependency of the vapor species in equilibrium with condensed ($\text{Pu}_2\text{O}_3 + \text{PuO}_{1.61}$) was determined in the temperature range of 1657 to 2148°K using both tungsten and rhenium effusion cells. An ionizing electron energy of 11 eV was used in all measurements of Pu^+ and PuO^+ , whereas 15 eV was used for PuO_2^+ measurements. The experimental procedures and treatment of the data were the same as those employed above in the study of the volatilization of plutonia ($\text{O/Pu} \sim 1.83$).

A summary of the heats of reaction, ion intensity ratios, and the composition of the condensed material is presented in Table III-2 for the several runs. Additional measurements are being made to obtain more accurate data on the heat of reaction for Reaction 7 and on the amount of PuO_2 in the vapor phase. The O/Pu atom ratios of the samples were determined both before and at the conclusion of the experiments. Because of the large samples (~ 1 g) and the small amount of material volatilized (~ 10 – 30 mg), the composition of the samples remained essentially constant during the measurements.

The temperature dependency data for each of the five series of measurements were normalized at the mid-temperature and reevaluated by the method of least squares to obtain single values for the heats of reaction: 110.2, 118.1, and 126.2 kcal/mol for Reactions 5, 6, and 7, respectively. The value of 118.1 kcal/mol does not agree with the values reported by Ackermann et al.⁷ (127.2 kcal/mol) and Phipps et al.⁵ (127.7 kcal/mol), who assumed that volatilization proceeded according to Reaction 6. The cause for this large discrepancy is not apparent at this time.

The partial pressures of Pu(g) , PuO(g) , and $\text{PuO}_2(\text{g})$

TABLE III-2. HEATS OF REACTION TO PRODUCE GASEOUS Pu , PuO , AND PuO_2 FROM TWO-PHASE ($\text{Pu}_2\text{O}_3 + \text{PuO}_{1.61}$)

Run No.	Cell Material	Temperature Range (°K)	Composition of Solid Material O/Pu	Heat of Reaction ^a (kcal/mol)		
				Pu	PuO	PuO ₂
PW-5A	W	1704–2145	1.55	108.3 ± 1.5	116.4 ± 0.9	—
PR-5A	Re	1797–2134	1.60 ^b	111.9 ± 1.6	114.4 ± 0.8	—
PR-6A	Re	1685–2147	1.56	111.2 ± 1.3	120.9 ± 1.1	—
PR-6C	Re	1657–2148	1.54	111.5 ± 2.8	119.1 ± 0.7	—
PR-6D	Re	1735–2147	1.56	109.9 ± 1.8	118.8 ± 0.6	126.2 ± 4.9

^a The errors listed are standard deviations; an ionizing electron energy of 11 eV was used for measurements of Pu^+ and PuO^+ , and 15 eV for measurements of PuO_2^+ .

^b Analysis is believed to be incorrect.

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FIG. III-4. Temperature Dependence of the Partial Pressures of PuO(g) , Pu(g) and $\text{PuO}_2(\text{g})$ in Equilibrium with Condensed ($\text{Pu}_2\text{O}_3 + \text{PuO}_{1.61}$).

over ($\text{Pu}_2\text{O}_3 + \text{PuO}_{1.61}$) as a function of temperature were determined by the procedure outlined above (Eq. 2) and are represented by the equations

$$\log P_{\text{Pu}} (\text{atm}) = - \frac{(24,090 \pm 340)}{T} + (5.270 \pm 0.170) \quad (8)$$

$$\log P_{\text{PuO}} (\text{atm}) = - \frac{(25,806 \pm 550)}{T} + (7.100 \pm 0.270) \quad (9)$$

$$\log P_{\text{PuO}_2} (\text{atm}) = - \frac{(27,575 \pm 1060)}{T} + (5.690 \pm 0.520) \quad (10)$$

The partial pressures as a function of temperature are shown in Fig. III-4. The indicated datum point, 2.27×10^{-6} atm at 2018°K, was determined from the average of three measurements of the rate of effusion assuming the vapor to be entirely PuO(g) . The vapor pressure data of Ackermann et al.,⁷ calculated assuming the vapor to be entirely PuO(g) , are included in Fig.

TABLE III-3. COMPARISON OF VAPOR PRESSURE DATA IN THE PLUTONIUM-OXYGEN SYSTEM AT 2132°K

	O/Pu Atom Ratio	Total Vapor Pressure (atm)
PuO _{1.83} :		
This study	1.83	6.76×10^{-7}
Ackermann et al ^a	1.83	5.970×10^{-7}
Ohse and Ciani ^b	1.84	1.65×10^{-6}
Pu ₂ O ₃ + PuO _{1.61} :		
This study	1.54	1.08×10^{-6}
Ackermann et al ^a	1.52	1.13×10^{-5}
Ohse and Ciani ^b	—	1.55×10^{-5}

^a Reference 7.^b Reference 11.

III-4 for comparison. The datum point obtained at 2018°K is in excellent agreement with the data of Ackermann et al.

Our vapor pressure data are compared with those of Ackermann et al⁷ and of Ohse and Ciani¹¹ in Table III-3 for hypostoichiometric plutonia (PuO_{1.83}) and the two-phase (Pu₂O₃ + PuO_{1.61}) solid mixture. For comparison with the literature, the vapor pressures reported in Table III-3 were determined considering the vapor phase to be entirely PuO₂(g) over PuO_{1.83}(s) and PuO(g) over the (Pu₂O₃ + PuO_{1.61}) solid mixture. The agreement among the three sets of data is good.

(2) Plutonium-Carbon System

Measurements of the partial pressures of vapor species over Pu-C and U-Pu-C have also been initiated. In the Pu-C system, there are, at particular temperatures above 640°C, four thermodynamically invariant two-phase fields consisting of solids only: PuC-Pu₂C₃, Pu₂C₃-C, Pu₂C₃-PuC₂, and PuC₂-C.

Mass-spectrometric analysis of the vapor phase in equilibrium with the condensed systems Pu₂C₃ + C and Pu₂C₃ + PuC₂, in the temperature ranges from 1638 to 1932°K and from 1932 to 2300°K, respectively, showed only the presence of Pu(g). No evidence was found for PuC(g) or PuC₂(g), which indicated that their abundance in the vapor phase, if they were present at all, was less than 0.1% at the higher temperatures. [Olsen and Mulford¹² reported about 0.1% PuC₂(g) in the vapor phase over condensed Pu₂C₃ + C at 1990°K.] Our results, coupled with X-ray dif-

¹¹ R. W. Ohse, C. Ciani, "Evaporation Behavior and High-Temperature Thermal Analysis of Substoichiometric Plutonium Oxide for $1.51 < \text{O/Pu} < 2.00$," in *Thermodynamics of Nuclear Materials*, p. 545, IAEA, Vienna (1967).

¹² W. M. Olsen, R. N. R. Mulford, "Thermodynamics of the Plutonium Carbides," in *Thermodynamics of Nuclear Materials*, p. 467, IAEA, Vienna (1967).

fraction analysis of the sample residues, indicate that vaporization of Pu(g) from the condensed phases proceeds mainly according to the reactions

However, the composition limits of the two-phase regions, Pu₂C₃-C and Pu₂C₃-PuC₂ are unknown. Tungsten effusion cells were used in both the measurements of temperature dependency and rates of effusion without any apparent reaction with the samples.

The temperature dependence of Pu⁺(g) in equilibrium with the condensed phases has been determined in two series of measurements for Reaction 11 and four series of measurements for Reaction 12. The heats of reaction calculated from the slopes of the lines of log *IT* vs. 1/*T* are 98.1 ± 1.1 and 118.7 ± 2.3 kcal/mol Pu(g) for Reactions 11 and 12, respectively.

Vapor pressures for reactions 11 and 12, each at a selected temperature, were determined from measurements of the rate of mass effusion (weight-loss method). When these values of the vapor pressures and the slopes of the temperature-dependence data are used to evaluate the intercepts, the following equations for the vapor pressures as a function of temperature are derived for Reactions 11 and 12, respectively:

$$\log P(\text{atm}) = - \frac{(21,440 \pm 240)}{T} + (4.560 \pm 0.130) \quad (1638\text{--}1932^\circ\text{K}) \quad (13)$$

$$\log P(\text{atm}) = - \frac{(25,950 \pm 500)}{T} + (6.910 \pm 0.270) \quad (1932\text{--}2300^\circ\text{K}) \quad (14)$$

The errors indicated for the intercepts of Eqs. 13 and 14 are the standard deviations in the slopes combined with an estimated standard deviation of 7% in the measurement of the mass effusion rates. Equation 13 agrees reasonably well with that of Olsen and Mulford,¹² namely, $\log P(\text{atm}) = (4.39 \pm 0.08) - (20,330 \pm 140)/T$. The condensed Pu₂C₃ + PuC₂ system has not been previously studied.

Measurements of rates of effusion and temperature dependence are currently being conducted on the condensed PuC₂ + C system. Since Olsen and Mulford¹² as well as others have investigated the PuC-Pu₂C₃ system, our results for the PuC₂ + C system should complete the characterization of the high-temperature volatilization behavior of the Pu-C system from PuC to C.

b. Phase Diagram Studies of Plutonium Compounds (A. E. Martin, F. C. Mrazek)

(1) Equipment Development

During the year, a plutonium facility for phase studies at elevated temperatures (see ANL-7375, p. 110) has been developed and placed in successful operation. The facility is housed in a 3-module, 1½-tier Cenham glovebox equipped with 36 gloveports on three levels. Access into the glovebox is obtained by three different size entry ports. The major pieces of equipment in the glovebox are three furnaces of different types and capabilities.

Arc furnace. The arc furnace was patterned after one developed by Kruger and Armstrong¹³ and successfully used in the ANL Metallurgy Division for the melting of plutonium materials. This furnace, designed for operation within a glovebox, consists of a 4-in. dia copper water-cooled hearth and tungsten electrode contained in a 6-in. dia, 6-in. high Pyrex tube surrounded by a light shield. The furnace is normally operated with a helium-argon atmosphere, which is admitted after evacuation. This arc furnace has the capability of melting uranium-plutonium oxide and carbide charges of an extremely wide composition range without appreciable contamination, since the only contact of the melts is with the water-cooled copper hearth and the gettered helium-argon atmosphere. Accordingly, the furnace will be used principally as a sample-preparation furnace. While some products from the arc melting may be examined directly to disclose useful phase diagram information, it is anticipated that the products usually will be reheated in the other furnaces where equilibration experiments can be carried out in essentially isothermal zones.

Tungsten resistance furnace. The most versatile furnace in the glovebox is a front-opening tungsten mesh resistance furnace¹⁴ with a heating zone 2½ in. in diameter and 6½ in. high. When the materials charged to this water-cooled furnace are contained in sealed crucibles, the furnace will be operated in vacuum; at other times, helium may be used to minimize vapor losses from the charges.

The furnace can be operated to about 3000°C in vacuum or about 2800°C in helium. The actual operating temperatures will be dictated by the system being investigated. For the uranium-plutonium-oxygen system, most of the experiments are likely to be in the temperature range from 1500 to 2500°C.

The temperature of a charge in the furnace will be

¹³ O. L. Kruger, J. L. Armstrong, *Rev. Sci. Instrum.* **35**, 156 (1964).

¹⁴ A modified Model 1064C furnace of the Richard Brew Co., Concord, New Hampshire.

measured with an optical pyrometer, located outside of the glovebox, by utilizing a prism above a quartz window in the top of the furnace and a hole through the upper heat-shield pack. The furnace shell has also been provided with suitable openings for thermocouple wires. The front-opening, double-hinged door of the furnace permits accurate positioning of regular and differential thermocouples in the furnace, and the minimum disturbance of the thermocouples when changing charges in the furnace.

A flange-connected quenching attachment is provided at the bottom of the furnace. In those experiments in which quenching will be carried out, the crucible containing the charge will be suspended from the upper heat shield pack. At the desired time, the lower heat shield pack can be swung aside and the crucible dropped into a V-shaped metal block in the quenching attachment.

The tungsten resistance furnace will be used for equilibration experiments and for thermal analysis. Products from the furnace will be examined by X-ray diffraction, chemical analysis, electron probe, and metallography to provide phase-diagram information.

Platinum resistance furnace. A horizontal-tube Marshall furnace capable of operation to about 1425°C is also located within the glovebox. This platinum resistance furnace is equipped with an impervious alumina tube and a quench attachment. The furnace shell is water-cooled to minimize the dissipation of heat to the glovebox. Various gases, including helium, 20% oxygen-80% helium, and 94% helium-6% hydrogen, can be passed over a sample contained in a refractory boat in the furnace. After equilibration, the boat and its sample can be pushed to the end of the furnace and dropped into a quenching liquid. The furnace temperature is maintained constant by means of a Honeywell controller actuated by a platinum/platinum-rhodium thermocouple.

The use of an impervious refractory tube in the platinum furnace will permit heating charges in oxidizing, neutral, or reducing atmospheres. Thus, studies on hypostoichiometric, stoichiometric, and hyperstoichiometric (U,Pu)O_{2±x} can be conducted in this furnace.

Other equipment. In addition to the three furnaces, the glovebox contains a Carver laboratory press (for compressing powders preparatory to arc melting and for forming crucibles), an analytical balance, a triple-beam balance, a low-speed cut-off wheel, a small ball mill, and miscellaneous tools.

The glovebox atmosphere will usually be helium maintained at a negative pressure (0.4 to 0.8 in. H₂O) relative to the surrounding room atmosphere. Because the helium repurification train is not yet operational,

the initial operations of the facility are being carried out in an atmosphere of nitrogen, which is passed through the glovebox continuously.

(2) U-Pu-O System

In ANL-7425, p. 96, for convenience of discussion, the U-Pu-O system was divided into hypostoichiometric and hyperstoichiometric composition regions depending upon whether the O/M ratios were less than or greater than 2.00, respectively. Additional ternary data has since been reported¹⁵ for both composition regions for temperatures up to 800°C. However, there is still need for higher temperature experimentation in both of these regions of the phase diagram along the general lines mentioned in ANL-7425.

In the hypostoichiometric region of the U-O phase diagram, a liquid miscibility gap was found¹⁶ above a temperature of 2470°C. The existence of this gap was later confirmed in another laboratory.¹⁷ It was obvious that this miscibility gap would extend into the U-Pu-O ternary system. Indeed, it seemed possible that the gap might extend completely across the system to the Pu-PuO₂ binary side, although no indication of this possibility was shown by existing Pu-PuO₂ phase diagrams. A check on the possible existence of such a liquid miscibility gap in the Pu-PuO₂ system was chosen as the first step in the study of the U-Pu-O ternary system. Some simple arc melting experiments were undertaken to establish whether or not the gap exists. It was felt that the experience gained by arc melting Pu-PuO₂ compositions, coupled with our prior arc melting experience with U-UO₂ compositions, would also indicate the compositional limitations of arc melting as a method of preparing ternary oxide compositions.

The charges for arc melting were mixtures of 1/8-in. dia plutonium rods and plutonium dioxide pellets. The pellets were made by compressing PuO₂ powder in a 3/8-in. die with a Carver laboratory press. Several charges with O/Pu ratios of 0.29, 0.38, 0.57, and 0.85 were arc melted; the products consisted of both metallic- and oxidic-appearing portions. On the other hand, arc melting a charge with an O/Pu ratio of 0.99 produced only an oxidic-appearing material. Metallographic examinations of the two-portion products showed that each of the metallic portions had a similar structure, namely, plutonium with some oxide inclu-

sions, and that each of the oxidic portions also had a similar structure, namely, a monotectic with plutonium as a finely dispersed phase in a matrix phase of oxide. Some of the larger oxide inclusions in the metallic portions were globular with a monotectic structure, whereas some of the larger inclusions in the oxidic portions were globules of plutonium. Figure III-5 shows the metallographic structures of the metallic and oxidic portions of the 0.57 O/Pu preparation. The obvious conclusion from these tests is that a rather wide liquid miscibility gap exists in the Pu-PuO₂ system at the arc melting temperature (~2500°C).

The products of the 0.29 and 0.85 O/Pu preparations were separated roughly into their oxidic and metallic portions. The metallic portions amounted to 79 and 8.5 wt %, respectively, for the two preparations. Material-balance calculations indicated that the compositions of the metallic and oxidic components of the products were 0.1 and 0.9 in O/Pu units, respectively. After applying a rough correction for selective volatilization losses from the 0.85 O/Pu preparations, which had encountered a 7.6% weight loss during melting, the O/Pu ratios of the metallic and oxidic liquids at the arc-melt preparation temperature were 0.1 ± 0.05 and 1.0 ± 0.1 , respectively. In view of the relatively small amount of metallic globules of appreciable size in the oxidic portions, it is likely that the monotectic in the system is also at about O/Pu = 1.0. (The 0.99 O/Pu preparation, which lost 22.7 wt % by volatilization during melting to yield a 1.11 O/Pu product by analysis, was probably very close to the monotectic composition.)

Of the well established plutonium oxide phases, the one with the least amount of oxygen is hexagonal Pu₂O₃. Hence, one would expect it to be the oxide phase in the monotectic in the Pu-PuO₂ system. An X-ray diffraction examination¹⁸ was made of a sample of the oxidic portion of the 0.38 O/Pu arc preparation. Hexagonal Pu₂O₃ was the dominant phase present, with alpha plutonium as a "possible, very minor" constituent. Thus, the expectation that hexagonal Pu₂O₃ is the oxide phase present in the monotectic has been confirmed.

The melting point of hexagonal Pu₂O₃ has been reported¹⁹ to be 2085°C. Consequently, the monotectic temperature in the Pu-Pu₂O₃ system must be less than this value. To establish the monotectic temperature, metallic plutonium was melted in a Pu₂O₃ crucible for short periods at successively higher temperatures: when a temperature above the monotectic was reached,

¹⁵ T. L. Markin, R. S. Street, *J. Inorg. Nucl. Chem.* **29**, 2265 (1967).

¹⁶ R. K. Edwards, A. E. Martin, "Phase Relations in the Uranium-Uranium Dioxide System at High Temperatures," *Thermodynamics*, Vol. 2, p. 423, IAEA, Vienna (1966).

¹⁷ P. Guinet, H. Vaugoyeau, P. Blum, "Le Systeme Uranium-Dioxyde d'Uranium a Haute Temperature," CEA-R 3060, Grenoble, France (1966).

¹⁸ The X-ray diffraction examination was carried out by R. Schablaske, Chemical Engineering Division.

¹⁹ T. D. Chikalla, C. E. McNeilly, R. E. Skavdahl, *J. Nucl. Mater.* **12**, 131 (1964).

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FIG. III-5. Metallic (left) and Oxidic (right) Portions of an Arc Melted Plutonium-Oxygen Sample, O/Pu = 0.57.

the reaction of the plutonium with the crucible caused the charge to melt through the crucible. In this way, the monotectic temperature was indicated as being between 1778 and 1863°C. The monotectic temperature will be more accurately defined by similar experiments utilizing smaller temperature increments. (Melting tests of 50-mg portions of the oxidic portion of the 0.38 O/Pu arc-melt preparation in tungsten crucibles confirmed the approximate value of the monotectic temperature; a sample heated to 1850°C melted, whereas one heated to 1800°C did not.)

The results of these experiments have, to a degree, established the main features of the plutonium-rich portion of the Pu-PuO₂ system at elevated temperatures; these are shown in Fig. III-6. It should be noted that the phase PuO has not been indicated from these data as a stable high-temperature phase in this system.

Since the liquid miscibility gap was observed in both the U-UO₂ and the Pu-PuO₂ systems in about the same O/M composition range, it seemed likely that a liquid miscibility gap extends as a two-phase field across the ternary U-Pu-O system at about the same O/M values. One check for the existence of this two-phase field in the ternary system was made at the Pu/U section of 0.25. An alloy of 20% Pu-80% U, made by arc melting, was in turn arc melted with 20% PuO₂-80% UO₂ oxide in proportions so that the over-

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FIG. III-6. Preliminary Phase Diagram of the Plutonium-Rich Portion of the Pu-PuO₂ System at High Temperatures.

all O/M composition was 0.5, which was well within the expected two-phase field. The metallographic examination of the product showed that there was a mis-

cibility gap in the ternary U-Pu-O system at this Pu/U section.

c. Transpiration Studies of the Uranium-Carbon System (*M. Tetenbaum, P. D. Hunt*)

An investigation of the vaporization behavior of the uranium-carbon system has been initiated. In addition to acquiring data on the U-C system, it is anticipated that the procedures used in this study will be applicable to later studies of the U-Pu-C system. For the U-C system, carbon activity and the total pressure of uranium binary species as functions of temperature and composition are measured by the transpiration technique. The transpiration equipment,²⁰ previously used to investigate the vaporization behavior of the uranium-oxygen system, has been modified for the uranium-carbon study. Hydrogen-methane mixtures are being used to fix the carbon activity in the carrier gases. The carrier gases are monitored for total carbon content with a Beckman hydrocarbon analyzer. From the measured carbon content in the exit gas and the equilibrium constants²¹ for the principal gaseous species in equilibrium with graphite at the temperature under investigation, the activity of carbon in the gas phase can be calculated. The total pressure of uranium binary species is obtained by collecting the vapor in a condenser tube and assaying the sublimate for uranium.

Emphasis has been placed initially on measuring carbon activities. Activity measurements over a wide range of temperatures and with well-defined compositions are needed to establish reliable partial thermodynamic quantities, as well as to define phase-boundary compositions. Storms²² at Los Alamos derived carbon activities from mass-spectrometric measurements of the ion intensity ratios of $UC_2(g)$ to $U(g)$ as functions of composition at 2100 and 2300°K. Virtually all of his measurements were with hyperstoichiometric compositions (UC_{1+x}). At General Electric,²³ gas-solid studies were made with hypostoichiometric compositions (UC_{1-x}) at 1773 and 1873°K with H_2 - CH_4 mixtures. However, the carbide specimens used in these measurements were highly contaminated with oxygen, e.g., ~6300 ppm. The total pressures of uranium binary

species were not measured by the G. E. investigators because the specimens were encapsulated in rhenium, which served as a membrane permeable to carbon. Sample compositions were obtained from lattice parameter measurements. Reaction of the specimens with the rhenium container was also observed.²⁴

The uranium carbide²⁵ used in our studies consisted of a coarse (-8+12 mesh) powder with the following composition: 4.55 wt % carbon, ~150 ppm oxygen, ~350 ppm nitrogen, and <200 ppm total metallic impurities. The results of the measurements of carbon activity as a function of UC_x composition at 2255, 2355, and 2455°K are shown in Fig. III-7. The shape of the isotherms is consistent with expectations, namely, a sharp decrease in carbon activity as the composition of the condensed phase is reduced towards the lower phase boundary [$U(l) + UC$] in the hypostoichiometric region. The plateaus of the 2255 and 2355°K isotherms are consistent with the miscibility gap $UC + \beta UC_2$ shown by the phase diagram of the uranium-carbon system.²⁶ Our measurements indicate that the composition at the lower phase boundary of the $UC + \beta UC_2$ diphasic region is $C/U \simeq 1.15$ at 2255°K, which is in good agreement with the composition $C/U \simeq 1.14$ estimated from the phase diagram. Our measurements indicate values of $C/U \simeq 1.2$ and 1.8, respectively, for initial and terminal compositions of the $UC + \beta UC_2$ diphasic region at 2355°K. The values obtained from the phase diagram at this temperature are $C/U \simeq 1.2$ and 1.35, respectively. Over the composition investigated at 2455°K, the shape of the carbon activity curve is typical of bivariant behavior, and is consistent with the phase diagram, which shows a single-phase region above the miscibility gap with a critical temperature of ~2100°C at $C/U \simeq 1.3$. Calculated carbon activity values at 2255°K are also shown in Fig. III-7; these are based on temperature coefficients derived by Storms²² from mass-spectrometric measurements at 2100 and 2300°K. Our results at 2255°K are in fair agreement with the calculated values.

Limited measurements for the total pressure of uranium-bearing species at 2255°K obtained by the transpiration method are shown in Fig. III-8. The general trend of these results also appears to be consistent with expectations, namely, a sharp increase in total pressure of uranium-bearing species as the com-

²⁰ M. Tetenbaum, P. D. Hunt, *J. Chem. Phys.* **49**(11), 4739 (1968).

²¹ B. J. McBride, S. Hermel, J. G. Ehlers, G. Sanford, "Thermodynamic Properties to 6000°K for 210 Substances Involving the First 18 Elements," NASA-SP-3001 (1963).

²² E. K. Storms, "A Mass Spectrometric Study of the Vapour Pressure of $U(g)$ and $UC_2(g)$ over Various Compositions in the Uranium-Carbon System," *Thermodynamics*, Vol. 1, p. 309, IAEA, Vienna (1966).

²³ "AEC Fuels and Materials Development Program Progress Report No. 69," GEMP-69 (Sept. 29, 1967), pp. 128-133.

²⁴ High Temperature Materials Programs, Part A. Annual Report No. 6, January 31, 1966-January 31, 1967," GEMP-475A (Mar. 31, 1967), pp. 280-283.

²⁵ Manufactured by Vitro Laboratories, West Orange, Jersey.

²⁶ E. K. Storms, *The Refractory Carbides*, Chap. XI, pp. 205-213, Academic Press, New York (1967).

FIG. III-7. Activity of Carbon as a Function of Composition and Temperature.

position of the condensed phase approaches the lower phase boundary [U(l) + UC]. For comparison, pressures derived from the mass-spectrometric measurements of Storms²² are also shown in Fig. III-8. Our results at 2255°K are in reasonable agreement with the measurements of Storms.

An estimate of the free energy of formation of UC_x compositions at 2255, 2355, and 2455°K can be made from our carbon activity values and Storms' extensive uranium vapor pressure values. These latter values, which were obtained from mass-spectrometric measurements, have been adjusted upward by 8% so as to average all of the absolute measurements from both collection and Langmuir studies, according to a recent reassessment of the data.²⁶ The estimated values of the free energies (using 126.5 kcal/mol as the heat of vaporization of uranium)²⁷ are given in Table III-4.

The calculated free energies of formation for UC_{1.00} are $-\Delta G_f^\circ \simeq 23.3$, 23.8, and 25.3 kcal/mol at 2255, 2355, and 2455°K, respectively. For comparison, the thermodynamic assessment of Holley and Storms²⁸

yields $-\Delta G_f^\circ = 25.2 \pm 2$ kcal at all of these temperatures. The values of the free energy of formation of UC_x shown in Table III-4 should be considered tentative.

Future work will be directed toward extending the measurements of the vaporization behavior of UC_x over a wider range of temperatures and compositions.

d. Transpiration Studies of Plutonium Compounds (J. W. Reishus, S. F. Banaszek)

A high-temperature transpiration system is being assembled to study total pressures and oxygen potentials in the Pu-O and U-Pu-O systems. The equipment consists of a gas-handling and monitoring system, balance chamber, pumping system, transpiration tubes, and resistance furnace. Except for the latter two items, the apparatus is contained in a glovebox mounted above the resistance furnace.

During the transpiration experiments, a H₂O-H₂ gas mixture is recirculated over the Pu-O or U-Pu-O sample until the mixture reaches a fixed composition in equilibrium with the sample. The H₂O/H₂ ratio establishes the oxygen potential for the sample. For higher oxygen pressures, mixtures of inert gas and oxygen will be recirculated over the sample, and oxygen potentials will be monitored by an oxygen concentration cell. Continued gas circulation transpires plu-

²⁷ R. J. Ackermann, E. G. Rauh, "The Vapor Pressure of Liquid Uranium, Effects of Dissolved Tantalum, Phosphorus, Arsenic, Carbon and Oxygen", *J. Phys. Chem.* (in press).

²⁸ C. E. Holley, E. K. Storms, "Actinide Carbides. A Review of Thermodynamic Properties," *Thermodynamics of Nuclear Materials*, 1967, p. 397, IAEA, Vienna (1968).

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FIG. III-8. Total Pressure of Uranium-Bearing Species as a Function of Composition (2255°K).

TABLE III-4. FREE ENERGY OF FORMATION OF UC_x

2255°K		2355°K		2455°K	
C/U	$-\Delta G_f^\circ$ (kcal/mol)	C/U	$-\Delta G_f^\circ$ (kcal/mol)	C/U	$-\Delta G_f^\circ$ (kcal/mol)
0.97	22.2	0.97	23.6	0.97	24.4
1.00	23.3	1.00	23.8	1.00	25.3
1.02	23.2	1.01	23.4	1.04	24.5
1.05	23.4	1.05	23.2	1.06	24.6
1.09	24.3	1.06	23.5	1.09	25.6
1.10	24.9	1.14	26.9	1.16	26.2
1.16	25.6	1.84	28.8	1.33	27.6
1.78	28.2			1.42	27.8
1.81	28.6			1.70	30.3

tonium oxide or uranium-plutonium oxide vapor. The rate of transpiration is monitored with a Cahn electrobalance which measures weight changes of the oxide sample. Alternatively, the overall rate of transpiration

is obtained at the conclusion of the experiment by chemically analyzing the condensed oxide vapor.

Assembly of the equipment is in its final stages. Before beginning a study of the Pu-O system, tests will be made in which O_2 and $UO_3(g)$ pressures will be measured over two-phase U_4O_9 - U_3O_8 . This system was chosen because oxygen levels and oxide pressures are expected to be comparable with those in the Pu-O and U-Pu-O systems.

e. Total Effusion of Pu-O and U-Pu-O (P. E. Blackburn, P. M. Danielson, S. F. Banaszek)

An effusion apparatus is being coupled to a glovebox (see ANL-7375, Fig. III-12, p. 112) to carry out effusion studies on the Pu-O and U-Pu-O systems. The effusion apparatus (previously used to determine the congruently vaporizing composition of urania) consists of an ultrahigh-vacuum furnace system and an induction heater. In addition, the apparatus is being modified for the installation of a quadrupole mass spectrometer and a microbalance within the furnace chamber. The mass spectrometer will allow analysis of vapors effusing from an induction-heated Knudsen cell. The microbalance will be positioned above the cell to collect a portion of the effusate on the weighing mechanism, thus permitting the determination of total effusion rates. The combination of the mass spectrometer and microbalance will be used for measuring relative ion cross sections. The glovebox, quadrupole mass spectrometer, and microbalance have been received. Modification of the effusion apparatus is under way and should be completed shortly.

The coupling arrangement of the furnace chamber to the glovebox is such that the flanges on the furnace chamber must be opened and closed within the glovebox. Suitable gasketing materials for these flanges (2¼-, 6-, 8-, and 12-in. OD) have been sought which would be amenable to glovebox operation. Tests of 12-in. OD polyimide²⁹ coated gaskets were unsuccessful, in that leak-tight seals could not be achieved, even though similar 6-in. OD gaskets earlier had proven satisfactory (see ANL-7425, p. 97). Another series of tests using 12-in. OD polytetrafluoroethylene (PTFE)³⁰ O-ring gaskets did prove to be successful. The PTFE gaskets provided a leak-tight seal that was almost as good as that attained with copper gaskets (10^{-10} Torr instead of 10^{-11} Torr). Since this difference in ultimate vacuum will not be detrimental to the proposed effusion studies, PTFE gaskets will be used.

²⁹ E. I. duPont de Nemours and Co. trademark "Pyralin".

³⁰ E. I. duPont de Nemours and Co. trademark "Teflon".

2. Enthalpy, Migration, and Other Physical Property Studies (M. G. Chasanov)

a. Enthalpies and Heat Capacities by Drop Calorimetry

(1) Resistance-Heated Calorimetric System (D. R. Fredrickson, R. Barnes³¹)

Enthalpies of materials of interest to the energy conversion program are being measured with the resistance-heated calorimetric system (ANL-7020, p. 172). To carry out these measurements, the system has been modified by installing new heating elements in the furnace and automating the copper-block calorimeter by installing a quartz crystal thermometer (see Fig. III-9). The work is focused on the determinations of enthalpies of Na_3Bi at about 850°C . However, enthalpies of UB_2 over the temperature range from 579 to 1486°K were carried out in conjunction with the studies employing the electron-beam-heated calorimetric system reported below. The enthalpy values of UB_2 over the temperature range studied can be represented by the equation

$$(H_T^\circ - H_{298}^\circ) = 19.0297T + 1.43535 \times 10^{-3}T^2 + 7.92523 \times 10^5/T - 8351.24 \quad (15)$$

(2) Electron-Beam-Heated Calorimetric System (D. R. Fredrickson)

The electron-beam-heated calorimetric system has been designed to measure high-temperature enthalpies relative to 25°C . A paper describing this system has been written.³² The furnace hot zone consists of a rotating tantalum target that is heated by electron bombardment. As reported in ANL-7425, p. 125, the wire method of supporting this target proved unsatisfactory at higher temperatures. An improved target design is now being used that utilizes a 1-in. dia tantalum tube, with a 2-mil wall thickness, for a target support. Because of heat flow, the primary concern is keeping the cross-sectional area of the supporting tube as small as possible, while retaining adequate strength. Tantalum discs are stacked inside the tube to reduce radiation to the rotating mechanism located above.

To minimize heat loss in a sample drop, the time required for the sample to drop from the furnace into the calorimeter must be made as short as possible. This was accomplished by attaching a rigid drop rod to the sample capsule, enabling a piston to accelerate the capsule downward. However, the rod protruded from

Based on 108-8345 Rev. 1

FIG. III-9. Resistance-Heated Drop Calorimetric System.

the calorimeter after the drop and caused an unpredictable heat loss. To circumvent this problem, provision has been made to separate the rod and capsule as the latter approaches the calorimeter. Figure III-10 shows the detail of this break-away capsule. View 1 shows the capsule with the rod attached. View 2 shows the capsule after separation from the rod. Separation takes place just above the open calorimeter shutter by abruptly stopping the drop mechanism, thus cutting the wire (F). The calorimeter shutter is closed after entrance of the capsule, and the capsule heat is then measured.

The calorimetric system has been tested over the temperature range from 1300 to 1900°K by obtaining enthalpy data for tungsten metal, a secondary calorimetric standard. The experimental data are presented in Table III-5 and may be represented by the following equation:

$$(H_T^\circ - H_{298}^\circ) = 998.48 + 2.0977T + 1.6150 \times 10^{-3}T^2 \quad (16)$$

³¹ Co-op Student from University of Missouri.

³² D. R. Fredrickson, R. Kleb, R. L. Nuttall, W. N. Hubbard, "A Drop Calorimeter with an Electron-Beam-Heated Furnace," *Rev. Sci. Instr.* (in press).

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FIG. III-10. Break-Away Capsule for use with Electron-Beam-Heated Calorimetric System (A. tungsten rod, B. break-away collet, C. pressure ring, D. capsule, E. cap, F. tantalum wire, G. sample, H. black body hole, I. holes for retaining wire).

TABLE III-5. ENTHALPY OF TUNGSTEN METAL

Temp. (°K)	$H_T^\circ - H_{298}^\circ$ (cal/mol)			Deviation (%)	
	This Work	Kirillin et al ^a	West ^b	From Kirillin	From West
1333	6668.48	6616.44	6609.81	+0.8	+0.9
1413	7177.28	7164.00	7163.36	+0.2	+0.2
1516	7896.86	7907.10	7884.52	-0.1	+0.1
1685	9117.03	9132.40	9091.84	-0.2	+0.3
1861	10,495.38	10,443.00	10,386.71	+0.5	+1.0

^a Reference 33.^b Reference 34.

Good agreement with data obtained in other laboratories,^{33, 34} also presented in Table III-5, is evident.

Work is currently under way on enthalpy measurements of UB_2 powder. Data at three temperatures overlapping the range of temperatures employed in the studies with the resistance-heated calorimetric system were in excellent agreement with those results. Extension of the measurements to higher temperatures is planned.

³³ V. A. Kirillin, A. E. Sheindlin, V. Ya Chekhovskoi, V. A. Petrov, *Russ. J. Phys. Chem.* **37**, 1212 (1963).

³⁴ E. D. West, National Bureau of Standards, private communication.

(3) Induction-Heated Calorimetric System; Enthalpy and Heat Capacity of Uranium Dioxide (L. Leibowitz, L. W. Mishler)

Work is continuing on the program to determine the heat capacity of liquid uranium dioxide, an important quantity in fast reactor safety calculations. Accurate values of the heat capacity and heat of fusion of molten UO_2 will facilitate estimation of the total energy released and the temperatures attained in the reactor core during destructive nuclear excursions. Although the techniques employed (induction heating in conjunction with a drop calorimeter) are conventional, they are being used to extend the measurements to temperatures that have not been previously explored.

Design of the calorimetric system was reported earlier (ANL-7325, p. 172) as was information on capsule design and calibration (ANL-7375, p. 153, ANL-7425, p. 158). In an experiment, a sample, sealed in a tungsten capsule, is suspended by tungsten wire in an induction coil and is heated to the desired temperature. For the temperature measurement, a disappearing filament-type optical pyrometer is sighted on a black-body cavity (length-to-diameter ratio of ten) extending into the capsule. When temperature equilibrium has been reached (~20 min), the suspension wire is vaporized by means of a condenser discharge and the hot capsule falls into a modified Parr adiabatic calorimeter. The temperature rise is measured with a quartz thermometer. The procedure is repeated with an empty capsule and the enthalpy of the sample found by difference.

As part of the initial testing of the system, measurements were made of the enthalpy of tungsten. Measurements had been made by Kirillin et al³³ up to 3093°K and by Hein and Flagella³⁵ up to 3248°K. Because of the capabilities of the present equipment, enthalpy measurements of tungsten were extended to 3594°K.³⁶ These results are presented in Fig. III-11. Most of the points shown were obtained with solid tungsten slugs, with corrections being made for radiative heat loss during the drop.³³ Two values for powder samples were obtained by measuring the difference in heat content between an empty tungsten capsule and one filled with tungsten powder. The values for the slug and powder samples are in good agreement. In the region of overlap with earlier work,^{33, 35} the data also agree well.

³⁵ R. A. Hein, P. N. Flagella, "Enthalpy Measurements of UO_2 and Tungsten to 3260°K," GEMP-578 (1968).

³⁶ L. Leibowitz, M. G. Chasanov, L. W. Mishler, "The Enthalpy of Solid Tungsten from 2800°K to its Melting Point," *Trans. Met. Soc. AIME* **245**, 981 (May 1969).

FIG. III-11. Enthalpy of Tungsten.

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Measurements of the enthalpy of uranium dioxide were, of course, the primary objective of this study and these have now been made from 2500 to 3300°K.³⁷ The data for temperatures below the melting point of UO₂ (3123°K) are presented in Fig. III-12. The equation

$$H_T^0 - H_{298}^0 = 1.0124 \times 10^3 + 3.0577T + 6.3963 \times 10^{-3}T^2 - 7.4317 \times 10^5/T \quad (17)$$

was fit to the data by the method of least squares, including the following two constraints:³⁸

- a) $H_T^0 - H_{298}^0 = 0$ when $T = 298$, and
- b) $\frac{d(H_T^0 - H_{298}^0)}{dT} = 15.2^{39}$ when $T = 298$.

The line based on this equation is included in Fig. III-12, along with the earlier data of Hein et al.^{35, 40, 41}

³⁷ L. Leibowitz, L. W. Mishler, M. G. Chasanov, "Enthalpy of Solid Uranium Dioxide from 2500°K to its Melting Point," *J. Nucl. Mater.* **29**, 356 (March 1969).

³⁸ T. G. Godfrey, J. M. Leitnaker, "A Computer Program to Calculate High-Temperature Thermodynamic Functions," USAEC report ORNL-TM-1599 (1966).

³⁹ "Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases", Technical Report Series No. 39, IAEA, Vienna (1965).

⁴⁰ R. A. Hein, C. H. Sjö Dahl, R. Szwarc, *J. Nucl. Mater.* **99** (1968).

⁴¹ R. A. Hein, P. N. Flagella, J. B. Conway, *J. Amer. Ceram. Soc.* **51**, 291 (1968).

Agreement between the present results for solid UO₂ and those of Hein and co-workers is excellent.

Two preliminary enthalpy values for liquid UO₂ (91,699 cal/mol at 3173°K and 96,277 cal/mol at 3329°K) have also been obtained. This latter temperature is about 70°K higher than previously attained during liquid UO₂ measurements by Hein et al.,⁴¹ but the data are in good agreement with their equation. The heat of fusion calculated from our preliminary results is approximately 18 kcal/mol, compared with the value 18.2 determined by Hein and co-workers.

Measurements of the enthalpy of liquid UO₂ are continuing to extend the temperature range of these data.

b. Other Physical Properties Studies (M. G. Chasanov, L. Leibowitz)

A serious difficulty in the analysis of fast reactor hazards is the lack of reliable data on physical properties of liquid uranium dioxide and other ceramic fast-reactor fuels. In addition to the heat capacities discussed above, data are needed on such properties as surface tension, viscosity, compressibility, expansion coefficients, and thermal conductivity.

This program was recently expanded to include those analytical and experimental studies of the high-temperature physical properties of fast reactor core materials that were previously reported as "Equation of State Studies" by the Reactor Physics Division.

Based on 308-1513 Rev. 1

FIG. III-12. Enthalpy of UO_2 .

Measurements of the vapor pressures of molten reactor fuels were chosen for initial effort in this area. After consideration was given to alternative methods of vapor pressure measurement, the transpiration technique was selected as the most promising. Construction and testing of suitable equipment have begun.

Concurrent analytical efforts have involved preliminary calculations of surface tension, compressibility, and volume expansivity of liquid UO_2 based on the scaled-particle theory.⁴² This theory has had out-

standing success when used in calculating properties of molten salts. Two input parameters are required: the density of the liquid (ρ) and the distance of closest approach of the ions (a). Some calculations for ρ and a were made using density estimates of Robbins⁴³ and the sum of ionic radii, respectively, assuming a corresponding-states behavior at higher temperatures. At 7000°K, these calculations yield a surface tension of 460 dyn/cm, a compressibility of $10^{-11} \text{ cm}^2/\text{dyn}$ and a volume expansivity of about $9 \times 10^{-5}/^\circ\text{K}$.

⁴² H. Reiss, "Scaled Particle Methods in the Statistical Thermodynamics of Fluids," *Advances in Chemical Physics* IX, p. 1, I. Prigogine (ed.), Interscience, New York (1965).

⁴³ E. J. Robbins, "Limits for the Equation of State of Uranium Dioxide," UK Atomic Energy Authority report TRG 1344(R) (1966).

These values seem reasonable for a first approximation and as appropriate experimental data become available, corrections and modifications will be made.

A computer program has been employed in conjunction with measurements of frozen UO_2 menisci (see ANL-7425, p. 158) to estimate the surface tension of liquid UO_2 at the melting point. A preliminary value obtained from examination of one meniscus is 420 dyn/cm.

c. Segregation in Ceramic Fuels: Fuel Migration Studies (*M. G. Chasanov, D. F. Fischer*)

Migration and segregation of fissile and fertile materials within a fast reactor fuel during its operational lifetime could have significant effects on the operational safety of the fuel. Redistribution of plutonium in $(\text{U,Pu})\text{O}_2$ fuels might change the chemical and physical properties of the affected regions enough to alter the neutronics of the system, affect fuel-cladding compatibility, and change the resultant fission product distribution. Investigation of the migration of plutonium and fission products in a thermal gradient is under way for mixed-oxide fuels. These experiments are being performed to evaluate the extent of migration and elucidate the mechanisms involved in the migration processes. Extension of the program to carbide fuels is planned.

Experiments are currently in progress with right-cylindrical pellets, $\frac{1}{2}$ in. high by $\frac{1}{2}$ in. in diameter, that were prepared from coprecipitated $\text{UO}_2\text{-PuO}_2$; the pellets are all nominally $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_{2.00}$. These are heated for the desired time period in the thermal-gradient furnace previously described (ANL-7425, p. 167).

A summary of the observations in this series of experiments is presented in Table III-6. The samples were analyzed for plutonium and uranium with an electron microprobe analyzer.

The two 100-hr experiments (P-1 and P-2) were reported earlier (see ANL-7425, p. 169). In Expt. P-3 ($T_{\text{top}} = 1980^\circ\text{C}$, $T_{\text{bottom}} = 1250^\circ\text{C}$), the pellet was heated for 500 hr in an inverted tungsten metal crucible which served as a barrier to loss of material by vaporization. In Expt. P-4 ($T_{\text{top}} = 2040^\circ\text{C}$, $T_{\text{bottom}} = 960^\circ\text{C}$), in which the pellet was heated for 504 hr, no such crucible was used. The thermal gradient obtained in Expt. P-3 was somewhat smaller because of conduction losses resulting from the use of the metal crucible.

An electron microprobe scan along the longitudinal axis of the pellet used in Expt. P-3 revealed no significant migration of plutonium, as was also the case for the corresponding 100-hr experiment, P-1. Electron microprobe analysis of the pellet used in Expt. P-4, seemed to indicate some enhancement in plutonium

TABLE III-6. SUMMARY OF THERMAL GRADIENT EXPERIMENTS WITH $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_2$

Expt. No.	Duration (hr)	Top Temp. ($^\circ\text{C}$)	Bottom Temp. ($^\circ\text{C}$)	Results of Electron Microprobe Analysis
P-1	100	1980	1280	No Pu redistribution
P-2	100	2070	975	No Pu redistribution
P-3	500	1980	1250	No Pu redistribution
P-4	504	2040	960	No significant Pu redistribution
P-5 ^a	1020	1970	1140	Apparent Pu increase at hot end
P-8 ^a	123	2340	1220	Apparent Pu increase at hot end

^a The sample was contained in an inverted metal crucible fabricated from 20-mil tungsten; this served as a barrier to loss of material by evaporation.

concentration in the hotter portion of the pellet (a concentration of 22 wt % PuO_2 in one area *vs.* a nominal average composition of 20 wt %). However, the single peak observed was not a part of a general trend in composition, and appeared to be most likely the result of an initial inhomogeneity.

In Expt. P-5, the pellet was heated in the thermal-gradient furnace for 1020 hr; the temperature was 1970°C at the pellet top and 1140°C at the pellet bottom. As in Expt. P-3, this specimen was heated in an inverted tungsten crucible. The results of an electron microprobe analysis along the longitudinal axis of the pellet after the heating had been completed are shown in Fig. III-13a. There seems to be clear evidence of an increase in plutonia concentration at the hotter end. The relative smoothness of this increase in concentration implies that it is probably not due to segregation originally present in the unheated pellet.

In Expt. P-8, the pellet was heated in a tungsten crucible for 123 hr; the top temperature was 2350°C (which was considerably higher than heretofore achieved) and the bottom temperature was 1220°C . The probe analysis along the longitudinal axis of this pellet is shown in Fig. III-13b. Although the variations in plutonia concentration along the pellet are greater than those for Pellet P-5, the increase in plutonia concentration at the hotter end of Pellet P-8 is quite evident.

Following the method used by Beisswenger et al.,⁴⁴ the redistribution of plutonium in the mixed oxide specimens can be described in terms of a thermal diffusion mechanism. Whether this approach reflects the important processes involved is not certain at this time; however, it does serve as a useful correlative technique.

⁴⁴ H. Beisswenger, M. Bober, G. Schumacher, *J. Nucl. Mater.* **21**, 38 (1967).

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FIG. III-13. PuO_2 Distribution in $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_2$ Pellets Heated in a Thermal Gradient. (a) Pellet P-5 (in tungsten crucible); $T_{\text{top}} = 1970^\circ\text{C}$, $T_{\text{bottom}} = 1140^\circ\text{C}$; 1020 hr. (b) Pellet P-8 (in tungsten crucible); $T_{\text{top}} = 2340^\circ\text{C}$, $T_{\text{bottom}} = 1220^\circ\text{C}$; 123 hr.

Oxygen analyses were performed on samples cut from several of the heated pellets. These showed the expected trend, a marked decrease in oxygen content in the hotter portions of the pellets. In addition, there was an overall loss of oxygen from the pellets, the losses being larger for pellets that were heated for longer periods and held at high temperatures. A sample from the top fourth of the Pellet P-5 had an O/M ratio of 1.92, whereas one from the bottom fourth had an O/M ratio of 1.94 (the initial O/M ratio of the un-

heated pellets was 2.01). In the case of Pellet P-8, heated at much higher temperatures, the O/M ratio was 1.81 for the top region and 1.92 for the bottom region. The O/M ratios in the heated pellets appeared to vary smoothly from the top to the bottom of the pellet.

Future work with $(\text{U,Pu})\text{O}_2$ pellets will be directed toward achieving temperature gradients similar to those achieved in Expt. P-8, but maintaining them for longer periods of time.

B. CHEMISTRY OF IRRADIATED FAST-REACTOR FUELS AND MATERIALS (C. E. Crouthamel)

The study of the chemistry of irradiated fast reactor fuels and materials is continuing. The emphasis of this program is on obtaining and interpreting information which will increase the understanding of the chemical behavior of fast reactor fuels and materials. This basic knowledge is needed in selecting, fabricating, and utilizing fuel and reactor components that will meet the high-performance criteria required in future commercial liquid-metal fast breeder reactors. The current program is concerned primarily with establishing the properties of irradiated uranium-plutonium oxides clad in stainless steel (much of the past work was directed toward uranium oxide fuel). Although research and development work is still needed on the longer range uranium-plutonium carbide fuel, effort is being concentrated on the mixed oxides to assure their successful near-term application in the Fast Fuel Test Facility.

A helium-atmosphere, shielded fuel-evaluation facility (see ANL-7425, p. 100) has been completed, and operation of the facility with irradiated fuel specimens is expected to begin during the coming year. In the meantime, a limited number of irradiated mixed-oxide

samples are being prepared in the General Electric cave facilities at Vallecitos Atomic Laboratory.

The ANL helium-atmosphere cave is unique in its capability to handle irradiated fuel in an inert atmosphere of extremely high purity. This capability will provide the means for undertaking several important investigations, such as the examination of failed fuel, the interactions of sodium coolant with the cladding and fuel matrix, and, in the future, the possible examination of sodium-bonded fuel pins. In each case it is important, if meaningful data are to be obtained, that sample preparations be made without appreciably altering the chemical species of the fuel or sodium.

A major effort is continuing on setting up instrumentation and equipment for the irradiated-fuels studies; this work includes (1) installation of auxiliary equipment in the cave and initiation of cave operations, (2) the installation and calibration of a spark-source mass spectrometer-densitometer analyzer system, and (3) installation of a shielded electron microprobe and readout system.

1. Chemical Studies of Irradiated Ceramic Fuels (M. D. Adams, L. E. Ross, C. C. Honesty, H. S. Edwards)

a. Fuel-Evaluation Facility

An existing shielded cell in the Chemistry Division cave complex has been modified for studies of irradiated ceramic fuel. This facility has been described in previous reports (ANL-7325, p. 107; ANL-7375, p. 113; and ANL-7425, p. 100). Construction work on the helium-atmosphere cave facility is now complete, and installation of in-cell equipment has begun. Operations with irradiated fuel are expected to begin early in 1969. Meanwhile, development and testing of techniques of microsampling, sample preparation, and sample handling are continuing with irradiated UO_2 - PuO_2 fuel and reactor components by utilizing very small samples and long-cooled fuel and working in small, shielded inert-atmosphere boxes.

An analytical facility in the Chemical Engineering Division, to be used in conjunction with the cave, has also been completed and is now in use. This facility contains a spark-source mass spectrometer, a single-focusing surface-ion-emission mass spectrometer, a laser microsampling system, a partially shielded elec-

tron microprobe, and a shielded electron microprobe and auxiliary equipment. The readout systems for both the spark-source mass spectrometer and the shielded electron microprobe are expected to be received and installed during the first part of 1969. Installation of a pneumatic sample-transfer tube between the cave and the analytical complex is expected to be completed in early 1969.

b. Laser-Beam Microsampling System

A small ruby laser attached to a microscope has found considerable utility as a microsampling device (see ANL-7425, p. 101). The optical system and performance characteristics of the sampling device with various materials are described in a recently published paper¹ entitled "Laser-Microscope System as a Microsampling Device". The paper also describes the utilization of alpha and gamma spectrometry, neutron activation, and mass spectrometry for the analysis of

¹ M. D. Adams, S. C. Tong, *Anal. Chem.* **40**, 1762 (October 1968).

TABLE III-7. RELATIVE CONCENTRATIONS OF URANIUM ISOTOPES IN LASER-VAPORIZED SAMPLES OF IRRADIATED UO_2 FUEL PREPARED BY BLENDING HIGHLY ENRICHED AND DEPLETED UO_2 PARTICLES (13% AVERAGE ENRICHMENT, 6.8 AT. % BURNUP)

Mass No.	Isotopic Concentration (%)	
	Porous Area	Matrix
234	0.25	0.26
235	13.17	6.83
236	2.07	1.21
238	84.52	91.71

microsamples of irradiated UO_2 that were obtained with this device.

The laser sampling system has provided samples for the mass-spectrometric determination of the relative isotopic concentrations of uranium in two areas of a UO_2 fuel rod irradiated to 6.8 at. % burnup. The fuel material, which had an average enrichment of 13%, had been prepared by blending highly enriched and depleted UO_2 powders. Previous electron microprobe studies of other specimens of this fuel (ANL-7425, p. 107) showed that the outer regions of the fuel had not attained a high enough temperature during irradiation to achieve complete isotopic mixing of the two types of UO_2 ; small areas with a porous appearance were identified as high-burnup regions, apparently associated with highly enriched UO_2 particles.

The two samples taken by the laser technique, which weighed $\sim 10^{-9}$ g, were from (1) a porous area of high burnup and (2) the adjacent matrix material. The vaporized UO_2 was deposited on a cover glass, dissolved, and plated on a filament of a thermal ionization mass spectrometer. The relative concentrations of uranium isotopes in the two samples are given in Table III-7. The differences in uranium isotopic composition of the two areas confirm the findings of the electron microprobe study, namely, that complete isotopic exchange did not occur in the outer regions of the fuel.

The capability of the laser sampling system was tested further in a study of sodium penetration in stainless steels. Specimens of steel with known exposures to sodium were mounted and then ground and polished using nonaqueous grinding, polishing, and etching procedures, which removed superficial sodium but did not remove any sodium that had penetrated the stainless steel. Grinding and polishing were carried out in a helium atmosphere, whereas the cathodic etching procedure was carried out under vacuum.

To prepare samples suitable for flame-photometric sodium analysis, one to five laser shots were made in an area of interest and all the vaporized material was deposited on a single cover plate. The individual craters produced by this method were of reasonably uni-

form size, having an average diameter of about 55 μm and a depth of about 10 μm ; this size corresponds to an estimated sample weight of about 70 ng for each laser shot. Because of the extremely small amounts of sodium involved, great care had to be taken during sampling and analysis to avoid cross-contamination. The fact that no sodium was found in blank specimens verified that no cross-contamination had occurred.

In a sample of type 304 stainless steel² that had been exposed to sodium of low oxygen concentration (<12 ppm), a trace of sodium was found in only one location. The area around this location was sampled further but no additional sodium was found. Other samples of type 304 stainless steel³ were also examined; in the exposure of these samples to sodium no attempt had been made to minimize the oxygen content of the sodium. Analyses showed that, in general, traces of sodium were found only at cracks or spots that showed some sign of attack; however, in one sample of this group, a different type of behavior was found. This sample was a tube having a 0.020-in. wall that had been machined to 0.005 in. in one segment. The tube had been filled with sodium, sealed, and heated to $\sim 600^\circ\text{C}$. Laser samples were taken from both the 0.020- and 0.005-in. portions of the tubing. In the 0.005-in. segment, sodium was found on the inner and outer polished surfaces of the tubing and within the tubing wall. In the 0.020-in. segment, sodium was found on both surfaces, but not within the tubing wall. Sodium concentrations, based on an estimation of sample weights, ranged from 0.3 to 1.5 wt %.

Further experiments are planned to investigate the nature of the interaction of sodium with stainless steel. Samples of stainless steel will be exposed to sodium under carefully controlled conditions, and an attempt will be made to correlate any evidence of interaction with conditions of exposure.

c. Determination of Thermodynamic Oxidizing Potential in Irradiated Oxide Fuel (H. S. Edwards)

A study has recently been undertaken to develop a reliable method for measuring the thermodynamic oxidizing potential of high-burnup oxide fuels, primarily uranium-plutonium oxides. This quantity is an important parameter in fuel-development studies, because it strongly affects such properties as thermal conductivity of the fuel and fuel-cladding compatibility.

In unirradiated uranium oxide and uranium-plutonium oxide fuels, the oxygen-to-metal (O/M) ratio is a good measure of the oxidizing potential, and a n

² Sample supplied by W. E. Ruther of the Metallurgy Division.

³ Samples supplied by F. A. Smith of the Reactor Engineering Division.

Several methods have been devised to determine O/M ratios in unirradiated fuels. An extensive literature survey has shown that four methods, or variations thereof, are in general use:

1) Determination of weight gain or loss in bringing the sample to a reproducible composition in a controlled atmosphere

2) Determination of the total oxygen in the sample

3) Measurement of the oxygen potential by an emf method in a high temperature galvanic cell

4) X-ray diffraction measurement of lattice parameter variations with O/M ratio

None of these methods, however, have been applied to the analysis of high-burnup fuels. In addition, it has not been established whether the O/M ratio of a fuel of even moderate burnup will provide a useful measure of the oxidizing potential.

The interpretation of data obtained from measurement of O/M ratios in irradiated fuels will be complicated by the following factors: (1) reaction of oxygen in the fuel with some of the fission products to produce a metal-oxygen system that is much more complex than the initial uranium-plutonium-oxygen ternary system, (2) reaction of oxygen in the fuel with the cladding and with impurities introduced into the fuel during fabrication, (3) the known mobility of oxygen in the fuel matrix, and (4) the large thermal gradients in the fuel during irradiation and consequent uncertainties in the temperatures attained in various regions of the fuel.

In our work and in the studies of other investigators, very distinct differences have been observed in the physical and chemical properties of irradiated fuels of

different initial stoichiometries. Some of the effects of initial stoichiometry on the behavior of fuel constituents are summarized in Fig. III-14. It should be emphasized that, although these effects are well established, the O/M ratios at which the changes occur are, at best, approximations based on sparse and often conflicting data. A correlation of effects such as these with changes in O/M ratio or oxidizing potential during irradiation should prove valuable in predicting the overall performance of a fuel in a reactor.

As a first step in this study, possible methods for determining oxidizing potentials will be evaluated and means for overcoming the difficulties associated with analysis of irradiated fuels will be investigated.

d. Spark-Source Mass Spectrometry (*P. K. Hon, N. Stahca*)

Installation of a spark-source mass spectrometer (Associated Electronics Industries Model MS-7) has been completed. The instrument has been checked and modified for high-vacuum sealing, alignment of the slit system, and focusing of the ion beam. It has now been calibrated and is in satisfactory operating condition.

Some preliminary calibration analyses were performed with a scandium sample, which was also analyzed by Oak Ridge National Laboratory. For most of the elements, results agreed reasonably well with those obtained at ORNL, however, for some impurities, the results varied widely. It is believed that these differences were caused by sample inhomogeneity. This is not considered unusual, since the sample used in the analysis was only a few micrograms.

In further work, a reference plate made from a series of graded exposures of a pure tin sample has proved practical as an intensity standard for visual comparison. Since tin has ten stable isotopes with a wide range of concentrations, the intensity of any impurity line in an analytical plate can be closely matched with that of a tin isotope line in the reference plate. By placing one plate over the other and comparing the two lines side by side, a small difference in intensity can be readily detected, and the variation of background of different lines can largely be compensated for. A random check of a few impurity lines in the scandium sample plate described above gave results that were reproducible within 20%. This method is considered to be a great improvement over the conventional method of visually estimating the impurity line intensity with a matrix line in the same plate. The latter method would normally give results with a reliability factor of 2 to 3.

Although the method of visual estimation of line in-

tensities gives improved precision, it is very time-consuming. The volume of work for the spark-source mass spectrometer is anticipated to be large enough in the future to warrant a densitometer evaluation of line intensity, and a Grant (series 800) microphotometer is being procured for this purpose. This instrument handles photoplates and evaluates line intensities automatically and thus minimizes operator attention.

In the immediate future, the mass spectrometer will be used for the analysis of metallic sodium samples from EBR-II (see Section III.B.3.a) as well as for radioactive fuel samples. A portable inert-atmosphere glovebox has been designed and is being constructed for transferring both types of samples into and out of the source chamber. After the source window is closed, the glovebox can be removed; hence, no inconvenience will be encountered with electrode manipulation. Some of the source parts, such as the heat-sink copper braid and electrode holder, have been modified for easy operation inside the glovebox.

2. Electron Microprobe Analysis of Irradiated Oxide Fuel Pins (*N. R. Stalica, C. A. Seils*)

The electron microprobe, which accomplishes micro-sampling and analysis directly, is being used to provide information on the distribution of fission products and fuel constituents, as well as on fuel-cladding interactions in irradiated oxide fuels. The instrument used in these studies, an Applied Research Laboratories EMX electron probe microanalyzer, provides adequate shielding for handling specimens having gamma-activity levels as great as 1 R/hr at 1 ft. This is possible because the magnetic objective lens, which focuses the electron beam on the area to be analyzed, completely surrounds the specimen. Complete cross sections of EBR-II fuel pins having gamma-activity levels below 1 R/hr at 1 ft have been prepared by carefully grinding the fuel specimens to thicknesses of about 1 mil.

Two types of oxide fuel pins have been examined: uranium oxide and mixed uranium-plutonium oxide. The studies of 13% enriched UO_2 fuel pins that were irradiated in MTR were reported previously (ANL-7325, pp. 116-118 and ANL-7425, pp. 104-113). Results of a detailed study of a cross section of a UO_2 -20 wt % PuO_2 fuel pin irradiated in EBR-II are described below.

The fuel pin (SOV-6), from which the cross-sectional sample was obtained, was fabricated by vibratory compaction of fully enriched UO_2 -20 wt % PuO_2 in type 304 stainless steel cladding. Prior to fabrication

of the fuel pin, the blended UO_2 - PuO_2 oxide mixture was pneumatically compacted (Dynapac process) to achieve a high density and was then ground. The effective density of the vibratorily compacted fuel was 83.5% of theoretical.

The cladding of the 11 $\frac{3}{4}$ -in. long pin had an inner diameter of 0.254 in. and a thickness of 21 mils. The irradiation history of the mixed-oxide fuel pin has been described in detail by F. L. Brown, et al.⁴ The fuel was irradiated in EBR-II for 119 days at 45 MW to a burnup of 2.7 at. % (5.6×10^{20} fissions/cm³). After irradiation, the specimen had an axial center void of 0.07 to 0.08 in. The maximum linear heating rate was about 19 kW/ft, and temperatures attained during irradiation were estimated to be 2670°C at the center void surface and 1065°C at the outer surface of the fuel. The maximum cladding temperature was estimated to be 605°C.

A complete transverse cross section, shown in Fig. III-15, was taken 3 in. from the top of the fuel pin. Prior to electron microprobe analysis, the specimen was reduced in thickness to 0.001-0.003 in. by grinding. The gamma-activity level of the sample was 1 R/hr at 1 ft and the beta-gamma level was 10 R/hr at 1 ft.

⁴ F. L. Brown, L. A. Neimark, B. J. Kaprowski, J. E. Ayres, J. H. Kittel, "Performance of Vibratorily-Compacted Mixed Oxide Fuel Rods under Fast Reactor Conditions," *Trans. Amer. Nucl. Soc.* **10**(1), 101 (1967).

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FIG. III-15. Transverse Cross Section of UO_2 -20 wt % PuO_2 Fuel Pin Irradiated in EBR-II (0.236-in. dia; 2.7 at. % burnup).

a. Distribution of Plutonium and Uranium

Plutonium and uranium concentrations as a function of radial position were obtained for several different radial segments of the fuel cross section. The distribution and homogeneity of the uranium and plutonium oxides were directly associated with concentric microstructural regions that are typical of the temperatures attained in these regions during irradiation. A photomicrograph of one of these segments is shown in Fig. III-16 along with a corresponding plot of the radial distribution of uranium and plutonium (uppermost plot). The concentrations of both plutonium and uranium are combined in the plot as wt % $(\text{PuO}_2)/(\text{PuO}_2 + \text{UO}_2)$. The points in the plot are average

values for contiguous areas $90 \mu\text{m}$ square and approximately $1 \mu\text{m}$ deep along a radius near the center of the micrograph.

The innermost zone, which reached the highest temperature during irradiation, contained long and short columnar grains. The concentration profiles of uranium and plutonium in the long columnar grains (A to B in Fig. III-16) were similar for each columnar grain examined. The grains were grouped in clusters of three or four having identical uranium and plutonium concentration profiles (within 0.1 wt % for any given radial position). However, a shift along the concentration axis occurred for adjacent clusters of grains. The maximum difference observed between groups of grains

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FIG. III-16. Radial Distributions of Plutonium, Uranium, Molybdenum, and Ruthenium in a UO_2 -20 wt % PuO_2 Fuel Pin (27 at. % burnup).

for identical radial positions was 2 wt %. In the long columnar grain region, the uranium and plutonium oxides formed a homogeneous solution on a micron scale. Distribution curves obtained by analyzing areas of 1, 100, or 8,100 μm^2 were identical.

Homogeneity was almost complete in the band of short columnar grains (B to C in Fig. III-16). Throughout this region, plutonium or uranium analyses of one-square-micrometer areas differed at most by 6 wt %; analyses of areas 0.1 mm apart differed at most by 2 wt %. The radial distribution curves in this region were not identical in shape; peaks and valleys occurred at different radial positions from curve to curve. The peaks in the distribution curves for plutonium or uranium were attributed to the presence of original particles of the respective oxides in the as-blended material.

Although some formation of solid solution was observed in the transition zone of equiaxed grains (C to D in Fig. III-16), many plutonium-free UO_2 particles exceeding 50 μm in cross section and smaller uranium-free PuO_2 particles were also observed. The distribution curves in this region, which attained intermediate temperatures during irradiation, varied markedly from one radial position to another. The peaks and valleys were much more extreme than in the region of short columnar grains.

Little, if any, solid solution occurred in the outer zone of the fuel (D to E in Fig. III-16), which attained the lowest temperature. The fuel in this region consisted of discrete particles of UO_2 and PuO_2 . Although particles of UO_2 as large as 200–300 μm in cross section were observed, most particles were less than 50 μm in cross section. Particles of PuO_2 did not exceed 50 μm in cross section. The presence of these discrete particles of UO_2 and PuO_2 caused the extreme variations in plutonium and uranium concentrations observed during microprobe analysis.

b. Distribution of Noble Metal Fission Products

Metallic inclusions found in the columnar grain region contained only the fission products molybdenum, ruthenium, technetium, and rhodium. As in the case of the 13% enriched UO_2 pins reported previously (ANL-7425, p. 106), these inclusions varied in composition as a function of radial position and were free of uranium and plutonium. Complete radial distributions of molybdenum and ruthenium were obtained, and their concentrations are plotted separately in Fig. III-16. In each case, the concentrations are average values for contiguous areas 90 μm square and approximately 1 μm deep along a radius near the center of the micrograph. The distributions shown along this radius are typical of all radii analyzed. The shapes of these dis-

tribution profiles were influenced mainly by the distribution of micron-sized metallic inclusions of these fission products.

No molybdenum or ruthenium was detectable in the columnar-grain region of the oxide matrix (other areas of the matrix were not analyzed for ruthenium and molybdenum). The absence of molybdenum in the matrix of the mixed-oxide fuel is in contrast to the behavior of molybdenum observed in the 13% enriched UO_2 fuel pins (ANL-7425, p. 113). In those pins, half of the molybdenum formed in fission was uniformly distributed throughout the columnar-grain region of the matrix. This variance is attributed to the difference in the stoichiometry of the fuels. The UO_2 - PuO_2 fuel was slightly hypostoichiometric with respect to oxygen, whereas the enriched UO_2 fuel was hyperstoichiometric (O/U, 2.02). Apparently, molybdenum can exist in either the oxide or the metal phase, with its thermodynamic stability dependent upon the amount of excess oxygen present in the fuel. Ruthenium was not found in the matrix of either pin; this was expected from thermodynamic considerations.

The metallic inclusions of ruthenium, technetium, molybdenum, and rhodium appeared to have migrated out of the columnar-grain region to cooler regions of the mixed-oxide fuel (this was also observed in the enriched UO_2 pins). These inclusions were concentrated at the juncture of the long and short columnar grains (B in Fig. III-16). The relative heights of the peaks at points B and C on the curve differed from one radial traverse to another, and were dependent upon the number of inclusions present per unit of analyzing area.

The increase in molybdenum concentration between C and D in Fig. III-16 is due to a large number of irregularly shaped, essentially pure molybdenum inclusions in this area. In addition, a band of a metallic iron-molybdenum eutectic phase was found in the region of point D. The reasons for the presence of molybdenum and iron in these areas is being investigated.

Palladium was found only in the coolest portion of the fuel (the region D to E) and was associated with metals such as tin and tellurium in the form of low-melting alloys.

c. Fuel Matrix

X-ray spectral profiles were obtained for the wavelength region covering the major lines of all the fission products at various locations across the radius of the fuel. The areas analyzed were approximately 10 μm square and were free of metallic inclusions. The fuel matrix contained the following fission product oxides: zirconium, cesium, barium, lanthanum, cerium, praseo-

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FIG. III-17. Radial Distribution of Neodymium in a UO_2 -20 wt % PuO_2 Fuel Pin (2.7 at. % burnup).

dymium, neodymium, and samarium. There was no detectable migration or selective relocation of the fission products zirconium, lanthanum, cerium, praseodymium, neodymium, and samarium. The distribution of neodymium as a function of radial position is shown in Fig. III-17. The ordinate of Fig. III-17 is expressed in three ways, namely, counts/sec neodymium, wt % neodymium, and equivalent burnup of total uranium and plutonium based on theoretical fission yields. The distributions of zirconium, lanthanum, cerium, praseodymium, and samarium as a function of radial position were similar to that of neodymium. The observed concentrations of these elements agree quite well with the expected values based on theoretical fission yields.

No cesium was detected in the columnar grain-growth region, but large amounts were found in the cooler (unsintered) region of the fuel, primarily adjacent to the cladding. Smaller amounts were found in the cooler portion of the equiaxed grain-growth region. The amount of barium in the matrix varied with radial position; it was barely detectable in the columnar-grain region, but was found in larger amounts in the cooler region.

d. Oxide Inclusions

Barium oxide was found not only in the UO_2 - PuO_2 matrix but also in oxide inclusions distributed throughout the equiaxed region. These inclusions, which varied in composition with radial position, resulted from the interaction of barium with an Al_2O_3 impurity introduced into the fuel during a ball-milling operation.

Molten Al_2O_3 that was in the columnar-grain region was not soluble in the UO_2 - PuO_2 matrix and migrated to the cooler equiaxed region, where it solidified. The molten alumina acted as a getter for barium oxide and other oxides. In the equiaxed region near the columnar grains, the inclusions were primarily $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$ (mp $\sim 1900^\circ\text{C}$) with trace amounts of chromium oxide ($<1\%$); in the cooler portion of the equiaxed region near the unsintered zone, the inclusions were either aluminum oxide or aluminum oxide with small amounts of barium oxide, chromium oxide, and, sometimes, strontium and cesium oxides.

A ternary oxide phase (iron-plutonium-uranium oxides) was also found at the same radial position as the molybdenum-iron eutectic phase (D in Fig. III-16).

e. Cladding-Fuel Matrix Interface

Examination of the optical image of the unetched specimen indicated a possible intergranular attack of the 0.021-in. type 304 stainless steel cladding to a depth of 0.003 in. Electron microprobe analyses of sixteen different areas of the fuel-cladding interface verified that intergranular attack of the cladding had occurred; the mechanism of attack was shown to be interaction with cesium in the fuel. All the analyses showed a depletion of iron and chromium, and an enhancement of nickel in the cladding grain boundaries. Cesium was found in the grain boundaries, associated with chromium on the fuel side of the cladding-fuel interface and unassociated with uranium, plutonium or fission products in voids and fissures near the cladding.

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FIG. III-18. Electron Microprobe Scanning Images of Fuel-Cladding Interface of Irradiated UO_2 -20 wt % PuO_2 Fuel Pin. (a) Specimen Current; (b) Chromium $\text{K}\alpha$ X-ray Image; (c) Iron $\text{K}\alpha$ X-ray Image; (d) Cesium $\text{L}\alpha$ X-ray Image; and (e) Nickel $\text{K}\alpha$ X-ray Image. (Each image corresponds to an area that is $50\text{ }\mu\text{m}$ square.)

Electron microprobe scanning images of one of these areas is shown in Fig. III-18. The brightness in the specimen current image (Fig. III-18a) is inversely proportional to the mean atomic number of the elements present: voids appear white; stainless steel, gray; and elements of higher atomic number, black. The iron, nickel, and chromium X-ray images are biased to show the enhancement of nickel and the depletion of chromium and iron at the grain boundaries. The depletion of iron and chromium in the grain boundaries can be seen in Figs. III-18b and c. The enhanced concentration of chromium at the fuel side of the cladding

was found in each of the areas analyzed and was always associated with cesium (Fig. III-18d).

The fuel-cladding interfaces of the 13% enriched UO_2 fuel pins irradiated from 0.7 to 7 at. % burnup in MTR were also analyzed. No interaction between cesium and the type 304 stainless steel cladding was detectable. It is believed that the differences exhibited by the two types of fuels may have resulted from temperature differences during irradiation. The inner cladding temperature of the UO_2 - PuO_2 fuel irradiated in EBR-II was about 600°C , whereas that of the UO_2 fuel irradiated in MTR was only about 180°C .

3. Feasibility Study of Fuel-Failure Detection

The development of methods for identifying the position of failed fuel in an operating fast reactor such as EBR-II is important to the overall fast reactor program. A program has been undertaken to investigate the feasibility of tagging each fuel element in a particular subassembly with a unique radiochemical or isotopic tag. In the event of a fuel failure, the tag would be released to the primary sodium coolant, and detection of the tag in the sodium would identify the subassembly containing the failed fuel. This method of tagging is intended for use in EBR-II with sodium-bonded fuel or encapsulated fuel having sodium in the annulus between the cladding and the capsule.

The goals of the program are (1) to select appropriate elements or isotopes as tags; (2) to evaluate their detection sensitivity in sodium (the concentrations of the tags will be a few nanograms per gram of sodium); (3) to develop techniques for placing the tags within the fuel elements so that they remain available for dispersion into the primary sodium; and (4) to evaluate the chemical stability of selected tags in flowing sodium.

A complementary technique, namely, the tagging of each fuel element in a subassembly with a unique isotopic mixture of xenon, has also been devised. This method is intended primarily for use with unencapsulated, gas-bonded fuel. The application of the xenon-tagging method to EBR-II is being carried out in a separate program (see Section III.C.).

a. Analytical Techniques for Determining Trace Elements in Sodium (*C. E. Johnson, L. E. Ross*)

Identification of failed fuel elements in EBR-II by means of sodium-soluble tags requires that the type and concentration of impurities already present in EBR-II sodium be known. Spark-source mass spectrometry, gamma-spectrometry, and neutron activation analysis are being evaluated as analytical techniques for determining the impurity content of EBR-II primary sodium. These techniques possess the advantages of high sensitivity and rapid multielement analysis. The spark-source mass spectrometer for this program was received, assembled, and put into operation during the past year.

A preliminary mass-spectrometric examination of "as-received" EBR-II sodium samples indicated traces of Al, Si, Ca, Cr, Fe, Ni, Mo, Pd, Sn, Bi, Ag and some rare earths. However, positive identification of the lines in the spectra was complicated by the presence of sodium oxide and complex sodium polymers. Further work on sodium samples awaits the installation of an inert-atmosphere box at the sample entrance port

of the spark-source mass spectrometer (see Section III.B.1.d, above). The more rigorous protection of the sample and sample chamber from oxygen should minimize oxide contamination. Techniques for removing the sodium from the trace elements by distillation will also be investigated; the distillation procedure will serve to concentrate impurities and reduce the problem of sodium handling.

The EBR-II sodium samples described above were also examined by gamma spectrometry. The spectra showed the presence of ^{134}Cs , ^{137}Cs , $^{113\text{m}}\text{In}$, $^{110\text{m}}\text{Ag}$ and ^{22}Na ; however, the detection sensitivity for impurities with low gamma energies was considerably reduced by the large Compton scattering of ^{22}Na . For this reason, effort was concentrated on developing techniques for the separation of the trace impurities from the bulk sodium.

Preliminary experiments indicated that impurities could be separated from the sodium by ion-exchange procedures using Dowex-1 and Chelex-100. Gamma spectra of the two resins showed the presence of trace amounts of ^{125}Sb , $^{117\text{m}}\text{Sn}$, ^{113}Sn , and $^{113\text{m}}\text{In}$ on the Dowex-1 and $^{110\text{m}}\text{Ag}$ on the Chelex-100.

Two samples of EBR-II primary sodium, taken on July 19, 1968 (Sample A) and July 22, 1968 (Sample B), were also examined. Each sample was divided mechanically into two approximately equal parts, an inner core and an outer shell. This separation was made to determine whether impurities other than cesium segregate in the outer region of the sample (segregation of cesium in the primary sodium has been demonstrated at EBR-II). Each portion of the two samples was dissolved in methanol and acidified with hydrochloric acid.

Cesium carrier was added to both fractions of Sample B and each solution was passed through a Dowex 1×10 column in 4.3 *M* HCl and then through a Chelex-100 column at pH 9. Each eluate from the Chelex-100 column was acidified with hydrochloric acid, and solid potassium cobaltiferrocyanate (KCFC) was added to adsorb cesium.

A ferric hydroxide scavenger was performed on each fraction of Sample A to precipitate other impurities. After separation of the precipitate, each filtrate was acidified with hydrochloric acid, and KCFC was added to adsorb cesium.

The KCFC-cesium, ferric hydroxide, and resin fractions were then assayed for gamma activity with a Ge(Li) multichannel analyzer. The spectra showed the presence of ^{125}Sb , $^{117\text{m}}\text{Sn}$, ^{113}Sn , $^{113\text{m}}\text{In}$, ^{54}Mn , $^{110\text{m}}\text{Ag}$, ^{134}Cs and ^{137}Cs . Cesium-137 and ^{125}Sb are fission products and their presence (as well as that of ^{134}Cs , an

TABLE III-8. GAMMA SPECTROMETRIC ANALYSIS OF EBR-II SODIUM SAMPLES

Isotope	Activity ($\mu\text{Ci/g}$ sodium)					
	Sample A			Sample B		
	Inner Core	Outer Shell	Total	Inner Core	Outer Shell	Total
$^{117\text{m}}\text{Sn}$	1.7×10^{-4}	1.3×10^{-4}	1.5×10^{-4}	3.7×10^{-4}	4.5×10^{-4}	4.1×10^{-4}
^{113}Sn	4.7×10^{-3}	2.8×10^{-3}	3.7×10^{-3}	2.9×10^{-3}	3.9×10^{-3}	3.5×10^{-3}
$^{113\text{m}}\text{In}$	2.9×10^{-3}	2.2×10^{-3}	2.5×10^{-3}	2.2×10^{-3}	3.3×10^{-3}	2.8×10^{-3}
^{125}Sb	2.0×10^{-4}	1.6×10^{-4}	1.8×10^{-4}	1.5×10^{-4}	2.9×10^{-4}	2.2×10^{-4}
$^{110\text{m}}\text{Ag}$	2.0×10^{-4}	2.5×10^{-4}	2.3×10^{-4}	8×10^{-5}	6×10^{-5}	7×10^{-5}
^{54}Mn	ND ^a	2.9×10^{-4}	1.0×10^{-4}	ND ^a	2.6×10^{-4}	1.4×10^{-4}
^{137}Cs	8.4×10^{-4}	2.57×10^{-2}	1.43×10^{-2}	1.6×10^{-3}	2.86×10^{-2}	1.61×10^{-2}
^{134}Cs	2.2×10^{-5}	4.5×10^{-4}	1.9×10^{-4}	2.5×10^{-5}	5.2×10^{-4}	2.3×10^{-4}

^a ND = not detected.

activation product of the fission product ^{133}Cs) could be due to a previous fuel pin rupture or to the fissioning of tramp uranium.⁵ The presence of radioactive tin isotopes was expected, since a portion of the reactor seal, a Sn-Bi alloy, had previously been lost to the primary sodium. Indium-113m is the daughter of $^{113\text{m}}\text{Sn}$. A summary of the gamma spectrometric data is given in Table III-8.

The total amount of cesium found in Sample B agrees very well with an independent determination of the cesium content of EBR-II sodium by Ebersole,⁶ namely, $1.65 \times 10^{-2} \mu\text{Ci/g Na}$. The lesser amount found in Sample A may be attributed to the fact that no cesium carrier was added to the sample. It was omitted to avoid interference with subsequent neutron irradiation of the sample.

The differences between the activities found in the inner and outer fractions suggest that segregation of other impurities may be occurring, but further refinement in methods of sectioning the samples is necessary before a definite conclusion can be reached. It is of interest that ^{54}Mn appears only in the outer fraction. The lesser amounts of silver and manganese found in Sample B may be the result of losses by adsorption onto container walls during the Chelex-100 ion-exchange step.

Present effort is being concentrated on neutron activation analysis to detect impurities with short-lived activation products. The ferric hydroxide precipitates described above were reirradiated in CP-5; subsequent reexamination by gamma spectrometry revealed that the spectra were highly complex. It is believed that analysis can be greatly simplified by computer treatment of the data. Accordingly, an existing computer program is being adapted for this purpose and a li-

⁵ Small amounts of fuel inadvertently introduced into the sodium coolant.

⁶ E. R. Ebersole, Idaho Division, private communication.

brary of data on gamma energies of activation products and fission products is being compiled.

b. Sodium Loop—Tag Confirmation Study (N. R. Chellew, G. W. Redding)

The feasibility of distinctively tagging fast-reactor fuel elements with isotopic tracers is under investigation. By monitoring the sodium coolant of an operating reactor for the release of these tags, the subassembly containing a ruptured fuel element could be identified, and remedial action could be taken with a considerable saving of reactor down-time. Potential tags must be tested with respect to their stability in circulating sodium, since their concentrations could be reduced below limits of detection owing to sorption on surfaces and cold-trapping. For this purpose, a small-scale experimental loop has been designed with the features described in the preceding report (ANL-7425, p. 197). Construction of this loop is under way, with completion expected in mid-1969.

c. Xenon Isotopic Tagging (C. E. Crouthamel)

EBR-II is currently being used for irradiation of experimental fuel for fast reactors. Until recently, such experimental fuel was clad into fuel elements and the clad elements placed in a secondary capsule to minimize the possibility of releasing fission products or fuel material into the sodium coolant. Irradiation of unencapsulated experimental fuel elements has begun recently, and it is expected that these fuel elements will soon occupy most of the EBR-II irradiation positions. During the early stages of EBR-II operation, essentially all of the fuel elements in the reactor were driver fuel elements, and, as a result of the very conservative limits of linear power and burnup imposed on these fuel elements, cladding failures did not occur. This situation changed when appreciable numbers of encapsulated experimental fuel elements were installed in

the reactor. Because the operating conditions for these fuel elements were selected to be representative of future fast reactors, the degree of conservatism was less than that previously used for EBR-II driver fuel, and fuel-cladding (and encapsulation) failures occurred. When encapsulated LMFBR experimental fuel elements are irradiated, it is possible that the incidence of cladding failures will increase, particularly if the reactor is operated at the high linear power which will be necessary in commercial fast reactors.

Although EBR-II is adequately instrumented to detect fuel-element failures, identification of the subassembly in which the failure occurred can be accomplished, at present, only by shuffling subassemblies in and out of the reactor. Because of the urgent need to provide a working method for detecting failures of experimental fuels, the use of tags consisting of mixtures of the light isotopes of xenon was recommended for early implementation. The method involves tagging each element in a subassembly with 1 ml of xenon of a unique isotopic composition. If a cladding failure is detected by the existing detection instruments, a sample of the reactor cover gas will be analyzed mass-spectrometrically to determine the isotopic composition of the released xenon. These data will indicate the xenon-tag mixture released and will identify the subassembly containing the failed fuel. The xenon tags are not, however, proposed as a panacea for all failure-identification problems, but as a complement to the sodium-soluble tags. The xenon-tagging method is intended primarily for use with unencapsulated gas-bonded fuel elements.

The initial evaluations of xenon-isotope tagging as a failed-fuel identification method showed that such a

system had a combination of many unusually favorable features:

1) Several isotopic mixtures of xenon that are highly enriched in the light isotopes, ^{124}Xe , ^{126}Xe , ^{128}Xe , and ^{129}Xe , are commercially available. By combining these light-isotope mixtures in various proportions with either natural xenon or pure ^{129}Xe (prepared by thermal irradiation of ^{127}I), a large number of unique tags can be prepared.

2) Since none of the light xenon isotopes are produced in fission in significant yields, contamination of a tag with fission product xenon is not expected to interfere with tag identification.

3) Transformation cross sections of the light xenon isotopes in a fast-neutron flux are expected to be relatively small; therefore, no significant changes in isotopic ratios of the tags are expected during irradiation.

4) Xenon is relatively inert and will have no strong chemical interactions with the sodium coolant.

5) In past incidents of fission-product xenon release in EBR-II, xenon has appeared promptly and almost quantitatively in the argon gas blanket. Solubility, surface-adsorption, or other disengagement problems were not evident.

6) Large samples (1 to 100 ft³) of the argon gas blanket can be quickly processed through Molecular Sieves to adsorb the xenon selectively. In addition, relatively pure samples of xenon can be prepared for mass-spectrometric analysis by gas-chromatographic techniques.

The application of the xenon-tagging method to EBR-II is being investigated in a separate program, which is discussed in the following section of this report (Section III.C.).

C. XENON TAGGING OF FUEL ELEMENTS IN EBR-II (*L. F. Coleman, G. J. Bernstein, T. R. Johnson, E. R. Ebersole,¹ P. B. Henault,² W. J. Larson,² R. R. Smith²*)

A program is under way to determine the feasibility of applying mixtures of xenon isotopes as tags for the identification of fuel elements that fail in a nuclear reactor (see Section III.B.3.c). The work will be carried out in EBR-II with experimental fuel elements, and will entail the development of the identification procedure, the production of suitable mixtures of xenon tags, and the design and construction of the

necessary equipment. Emphasis will be placed on the application of the xenon-tag method to the identification of unencapsulated, gas-bonded fuel elements, most of which will contain $\text{UO}_2\text{-PuO}_2$.

The EBR-II reactor is adequately instrumented to detect fuel-cladding failures. Direct exposure of the fuel material to the sodium coolant can be detected on-line monitoring the delayed neutrons in the coolant using the fuel failure rupture detector (FERD). Escape of bond sodium containing recoil-released

¹ Idaho Division.

² EBR-II Project, Idaho.

radiohalides can be detected by the on-line charged-wire fission gas monitor (FGM), which measures the radioactive particulate daughters of short-lived krypton and xenon daughters in the reactor cover gas. Gas escape from a fuel element can be detected in the cover gas by on-line monitoring of ^{133}Xe and ^{135}Xe with the reactor cover gas monitor (RCGM). Although detection of a cladding failure is thorough, identification of the subassembly in which failure occurred is difficult and time consuming; at present, it can be accomplished only by shuffling subassemblies in and out of the core and cautiously operating the reactor to detect a repetition of the failure indication. Implementation of the xenon tagging system in EBR-II would permit rapid identification of the failed fuel subassembly and would thus significantly increase the plant factor.

1. Preparation of Tag Mixtures

Because xenon isotopes with mass numbers 131 through 136 are abundantly produced by fission, xenon tag mixtures for failed fuel identification must contain significant concentrations of the lower mass numbers 124 through 129. Mound Laboratory³ is currently producing several different mixtures of xenon isotopes in which the lighter isotopes have been enriched by thermal diffusion. Table III-9 shows the isotopic compositions of natural xenon and of three available enriched isotopic mixtures.

Initially, tag mixtures will be prepared by blending each of the three Mound Laboratory mixtures with natural xenon in preselected proportions. In the resultant tag mixtures, designated as Series A, the $^{129}\text{Xe}/^{124}\text{Xe}$ isotopic ratio will be normally stepped so that each ratio is 1.2 times the previous ratio. The $^{129}\text{Xe}/^{124}\text{Xe}$ ratios in the Series A tag mixtures will range from 4.9 to 73 (the ratio in natural xenon is 275). Released tags from Series A tag mixtures will normally be identified by the $^{129}\text{Xe}/^{124}\text{Xe}$ isotopic ratio.

Because of the conservatism in the magnitude of the isotopic-ratio stepping factor and the allowable range of ratios, not all the EBR-II tagging needs can be provided by Series A tag mixtures. Therefore, additional tag mixtures having varying $^{128}\text{Xe}/^{124}\text{Xe}$ isotopic ratios will be prepared by blending Mound Laboratory enriched mixtures with pure ^{128}Xe prepared by neutron irradiation of natural iodine⁴ in a thermal reactor; these tag mixtures will be designated

In the proposed xenon-tagging system, each fuel element in a subassembly will be tagged with 1 ml of a mixture of xenon isotopes that is unique for a particular subassembly. If a cladding failure is indicated by one of the failure-detection instruments, a sample of the reactor cover gas will be analyzed mass spectrometrically to determine the ratios of xenon isotopes present. These ratios will provide an indication of the tagging mixture that had been released; positive identification will then be made by analyzing a master sample of the indicated mixture and comparing the two results. Positive identification of the released xenon mixture will permit identification of the affected subassembly and its location in the reactor. It is anticipated that identification can be accomplished within the 4-hr period required to prepare for removal of a subassembly.

Series B. The stepping factor for the $^{128}\text{Xe}/^{124}\text{Xe}$ isotopic ratios will vary from 1.2 to 1.4 in these Series B tag mixtures. The $^{128}\text{Xe}/^{124}\text{Xe}$ isotopic ratio in the Series B tag mixtures is presently planned to extend from 2.0 to 9.3 (the ratio in natural xenon is 20.0). The range may eventually be extended depending upon procurement costs of ^{128}Xe . Released tags from Series B mixtures will normally be identified by the $^{128}\text{Xe}/^{124}\text{Xe}$ isotopic ratio.

If a series of tagging mixtures are prepared by blending a component of one isotopic composition with one of another composition, the interrelationships between the isotopic ratios can be shown on straight-line arithmetic plots by using a common reference isotope for the ordinate and abscissa. The interrelation-

TABLE III-9. ISOTOPIC COMPOSITION OF NATURAL XENON AND THREE ENRICHED MIXTURES FROM MOUND LABORATORY

Xenon Isotope Mass Number	Total Xenon ^a (mol %)			
	Mound Mixture			Natural Xenon
	No. 1	No. 2	No. 3	
124	12.0	5.7	1.3	0.096
126	4.5	1.9	0.8	0.090
128	17.4	10.1	8.1	1.92
129	59.0	63.8	64.3	26.44
130	2.4	4.2	5.1	4.08
131	2.8	9.1	12.8	21.18
132	1.4	4.8	7.1	26.89
134	0.3	0.3	0.5	10.44
136	0.2	0.1	0.1	8.87

^a Xenon purity $\geq 99.0\%$.

³ Mound Laboratory, Miamisburg, Ohio; operated by the Monsanto Research Corporation for the USAEC.

⁴ Natural iodine is 100% ^{127}I ; ^{128}Xe is formed by the reactions $^{127}\text{I}(n,\gamma)^{128}\text{I} \xrightarrow{\beta^-} ^{128}\text{Xe}$.

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FIG. III-19. Isotopic Relationships of Xenon Tags.

ship between the four isotopes of interest (^{124}Xe , ^{126}Xe , ^{128}Xe , ^{129}Xe) requires six plots for completeness, but the most important interrelationship is shown in Fig. III-19. Each line represents a planned sub-series and each point an individual tagging mixture (see Table III-9 for the compositions of the Mound light-isotope mixtures).

Use of a plot of the type shown in Fig. III-19, or its algebraic equivalent, may prove especially valuable if xenon contamination of the reactor cover gas eventually proves to be a problem (this is not anticipated in EBR-II as presently operated). In this case, identification of a released tag can be determined from the coordinates (isotopic ratios) of the contaminant and the tag-contaminant mixture by the straight line function

$$y_t = y_m - \left(\frac{y_m - y_c}{x_m - x_c} \right) x_m + \left(\frac{y_m - y_c}{x_m - x_c} \right) x_t$$

where y is ordinate value
 x is abscissa value

subscript t refers to released tag

subscript c refers to contaminant

subscript m refers to tag-contaminant mixture.

Most of the xenon-tagged fuel elements will be irradiated in 37-element subassemblies. To tag all the elements in a subassembly, an experimenter will require 37 ml of the specific tag mixture plus an allowance for unavoidable wastage. Because of these considerations and the desire to minimize the effect of accidental loss of container contents, each tag mixture will normally be packaged in four 30-ml tag transfer containers and one 10-ml master sample container (the master sample will be used to provide positive identification of a mixture released to the cover gas). The containers will be maintained in a repository at EBR-II and two tag transfer containers will be sent to the experimenter when he is ready to prepare tagged fuel elements. A greater number of 30-ml tag transfer containers or larger containers will be prepared for the few cases when 61- and 91-element subassemblies are to be tagged.

2. Addition of a Tag to a Fuel Element

Gas-bonded fuel elements which are irradiated in EBR-II consist of a fuel region and a gas plenum to contain released fission gases. The inside diameter of the cladding is about $\frac{1}{4}$ in., the fuel length is about 14 in. and the gas plenum length is generally greater than 8 in. The method of transferring 1 ml of a xenon tag from the ANL-supplied 30-ml tag transfer container must be the responsibility of the experimenter as part

of his overall responsibility for the performance of the finished element and subassembly. However, a tag addition procedure has been devised and will be suggested to each experimenter.

A tag can be added to the bottom of the fuel element gas plenum using a syringe and long hypodermic needle. This addition would be made after fuel insertion and immediately prior to final closure of the

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FIG. III-20. Xenon Diffusion Experiments (1 ml Xe charged to 0.18-in. ID tube).

fuel element. This operation would be performed in a conventional helium-filled glovebox used for fuel-element closure and would require essentially no change in the conventional closure procedure. The hypodermic syringe would be successively loaded from the 30-ml tag transfer container using a mercury piston, which is basically a Toepler pump. The pump would be manually operated to remove tag gas at negative pressure from the transfer container and supply it to a needle-loading rubber septum at a slightly positive pressure. Ideally, the tag transfer container and pump would be outside the glovebox and the septum inside. The hypodermic needle would have a modified tip to minimize (1) coring of fragments from the rubber septum and (2) deposition of the rubber fragments into the fuel element.

Two experiments were performed⁵ to determine (1) whether the diffusional loss of xenon from a fuel element plenum before final closure would be excessive and (2) whether the presence of a diametral gap would increase the diffusional loss due to gas mixing at the bottom of the plenum. In the first experiment, 0.18-in. ID, 7.2-in. long tubes were used to simulate fuel-element plenums. In the second, longer tubes containing 14-in. lengths of 5/32-in. drill rod were used to simulate gas-bonded fuel elements having 7.2-in. long plenums and oversized fuel-to-cladding diametral gaps (24 mils instead of the usual 10 mils or less). In each experiment, the tubes were charged slowly (in 5 to 10 sec) with 1 ml of natural xenon, allowed to remain open to a helium atmosphere for a predetermined interval of time, and then capped with a septum. The xenon and helium in the tubes were then mixed, sampled, and analyzed with a gas chromatograph.

A comparison of the results of the two experiments (see Fig. III-20) showed that the rate of diffusion of

xenon was not increased by the presence of a diametral gap. In both experiments, approximately 90% of the charge remained after 110 sec. Since the estimated time required for insertion of a snug closure fitting in a fuel element is ~1 min, it is concluded that diffusional losses will not be significant during this time. After insertion of the end fitting, the rate of diffusion will be greatly reduced, but final closure by welding should be done within a few minutes. Losses of 10 to 20% of a tag during fuel element closure would not impair identification of a released tag because identification depends only on the determination of the isotopic ratios.

The experimental data on rates of loss of xenon by diffusion were also compared with calculated values obtained by the use of simplified diffusion equations⁶ in which the plenum is assumed to be a part of a semi-infinite tube:

$$f = 1 - \frac{1}{h} \int_{\ell}^{\infty} C \, dx$$

$$C = \frac{1}{2} \left(\operatorname{erf} \frac{h-x}{2\sqrt{Dt}} + \operatorname{erf} \frac{h+x}{2\sqrt{Dt}} \right)$$

f = fraction of xenon remaining in plenum

x = distance from bottom of plenum

h = length of plenum initially filled with pure Xe

ℓ = total length of plenum

D = Xe-He diffusion coefficient

t = diffusion interval

This comparison is illustrated in Fig. III-20. The experimental and calculated values were in good agreement up to losses of ~10%. This correlation will allow estimation of xenon diffusion rates for fuel elements of different sizes and geometries, and will thereby provide a guide for limiting losses to acceptable levels during closure.

⁵ Performed by A. Panek and M. Barsky, Analytical Group, Chemical Engineering Division.

⁶ J. Crank, *The Mathematics of Diffusion*, p. 13, Clarendon Press, Oxford (1964).

3. Possible Detrimental Effects of Xenon Tagging

Consideration was given to possible detrimental effects that might arise from the presence of a xenon tag in gas-bonded fuel elements. Only one such effect appeared possible, namely, a decrease in the thermal conductance of the fuel-to-cladding gap. The long-term gap conductance of ceramic fuels would not be affected by the addition of a 1-ml xenon tag because at the goal burnup of 100,000 MWd/metric ton, the volume of released fission xenon in the fuel-element plenum would be approximately 100 times the volume of the tag. Consideration had to be given, however, to the effect of the 1-ml xenon tag on the gap conductance during early irradiations.

Extensive experimentation with thermal irradiation of pelletized uranium oxide fuel elements had shown⁷ that, for low gap-to-diameter ratios, the gap conductance was relatively insensitive to the gas composition, and was primarily a function of the gap-to-diameter ratio and the characteristics of the fuel and the cladding. Experiments with representative FBR mixed-oxide fuels^{8, 9} having argon-bonded elements and

cladding temperatures of about 1000°F showed that these fuels exhibit conductance vs. gap-to-diameter ratio curves which are similar to the curves developed for thermal UO₂ fuels. The experiments with argon-bonded elements were operated at 20 kW/ft and gave gap conductances of 2000, 1400, and 600 Btu/(hr)-(ft²)(°F) for diametral gaps of 2, 4 and 10 mils, respectively. At 520°C (968°F), a He-75% Xe gas mixture is equivalent in thermal conductivity to pure argon.¹⁰ From these data, it was concluded that the gap conductance of conventional helium-bonded elements probably will not be affected significantly by the expected xenon contamination (7 to 20% for oxide elements) and certainly will not be decreased to a value lower than that determined for the argon-bonded elements.

presented at Nucl. Met. Symp. AIME, Oct. 4-6, 1967, Phoenix, Arizona.

⁹ W. E. Baily, C. N. Craig, E. L. Zebroski, "Effect of Diametral Gap Size on the In-Pile Performance of Fast Ceramic Reactor Mixed-Oxide Fuel," *Trans. Amer. Nucl. Soc.* **9**(1), 40 (1966).

¹⁰ H. von Vbisch, S. Hall, R. Skrivastav, "Thermal Conductivities of Mixtures of Fission Product Gases with Helium and with Argon," *Proc. U.N. Int. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 1958*, **7**, 697-700 (1958).

⁷ J. Belle, *Uranium Dioxide: Properties and Nuclear Applications*, pp. 585-609, U.S. Government Printing Office, Washington (1961).

⁸ W. E. Baily, E. A. Aitken, R. R. Asamoto, C. N. Craig, "Thermal Conductance of Uranium-Plutonium Oxide Fuels,"

4. Identification of a Released Xenon Tag

If any of the EBR-II on-line monitors indicate that a cladding failure has occurred, a sample of the reactor cover gas will be analyzed for the presence and identity of a xenon tag. Three percent of the cover gas will be passed over a sorbent at -78°C to sorb the xenon. This xenon will be further concentrated in a chromatographic column and passed into a mass spectrometer specifically selected for xenon isotopic analysis. The relationship between cover-gas sample size and spectrometer sensitivity is extremely conservative and experience may permit a significant reduction in sample size.

The factors that could create difficulties in identifying a released tag are as follows: (1) contamination of the tag by light xenon isotopes in either the fuel-element gas plenum or the reactor cover gas, (2) significant neutron transformations of the tag isotopes within the fuel element, and (3) delay or prevention of transport of the tag to the reactor cover gas by solubility effects in the bulk sodium.

Contamination of the tag by light xenon isotopes from cumulative fission yields will not be significant

because the isotopes of primary interest are shielded by stable ¹²⁴Te and ¹²⁸Te and by 1.6×10^7 -yr ¹²⁹I. Under assumed operating conditions,¹¹ approximately 0.02 ml of ¹²⁸Xe can result from neutron capture by fission product ¹²⁷I. This could result in a contamination of 0.02% in the 1-ml tag if all the ¹²⁸Xe is released from the fuel matrix. In the Series B tags, which are primarily identified by the ¹²⁸Xe/¹²⁴Xe ratio, the ¹²⁸Xe concentrations were selected so that there was at least a 0.04% ¹²⁸Xe difference between tag mixtures; thus, the presence of 0.02% of ¹²⁸Xe contaminant would not prevent identification.

The xenon isotopes in a tag will undergo neutron transformations. If the transformation cross sections for the two isotopes in an isotopic ratio are large and differ greatly, neutron transformation could prevent identification of a released tag. Direct analysis of this problem is difficult because transformation cross sections for the pertinent isotopes are not available for

¹¹ Mixed-oxide fuel element (72 g) irradiated at 15 kW/ft to 100,000 MWd/metric ton burnup near center of 50-MW EBR-II.

EBR-II neutron spectra. However, under the assumed operating conditions,¹¹ if the ^{124}Xe cross section were zero, the ^{128}Xe cross section would have to be >0.50 b and the ^{129}Xe cross section would have to be >0.24 b before tag identification would be impaired. It is doubtful that the effective cross sections would be this high in the hard (95% of the neutrons >0.07 MeV) EBR-II flux.

The solubility of xenon in the 370°C bulk sodium will not impair tag transfer from a damaged fuel element to the reactor cover gas; the solubility at 370°C is estimated¹² to be $\sim 5 \times 10^{-12}$ atoms Xe/atom Na at 1 atm xenon gas pressure. From this solubility and from Henry's Law, it was estimated that 1 ml of a particular xenon isotope present in the cover gas would be in equilibrium with 1.3×10^{-7} ml of the isotope in the bulk sodium. If tag gas is released from a cladding defect as microbubbles, conceivably these bubbles might remain in the bulk sodium for an appreciable time before disengagement. Sorption of xenon on internal surfaces might also delay transit of a released tag to the cover gas. However, results of more than 15 accidental fission-gas releases in EBR-II have shown that neither the pseudo-solubility nor the surface-sorption effect occurs.

Other possible sources of xenon contamination of the reactor cover gas are the following: (1) natural xenon introduced either with air during fuel-handling operations or with make-up argon, (2) fission xenon resulting from tramp fuel¹³ or previous fuel-cladding failures, and (3) previously released xenon tags. A three-stage experiment was performed¹⁴ to determine whether contamination from air, argon, tramp fuel, and previous cladding failures would hinder identification. The reactor cover gas was sampled and analyzed on a mass spectrometer at the NRTS Central Facilities. A 0.7-ml tag (first tag mixture in A2 subseries; 100% Mound Mixture 2, no natural xenon) was then injected into the cover gas and samples of the cover gas were taken after 24- and 48-hr intervals

¹² E. Veleckis, Argonne National Laboratory, private communication (1968).

¹³ Small amounts of fuel inadvertently introduced into the sodium coolant.

¹⁴ These tests were performed by the ANL Idaho Division under the direction of E. Ebersole.

TABLE III-10. CONCENTRATIONS OF XENON ISOTOPES IN EBR-II COVER GAS SAMPLES

Xenon Isotope	Isotopic Concentration (mol %)			
	Xenon Back-ground in Cover Gas	Tag + Bkgd (24 hr)	Tag + Bkgd (48 hr)	Tag ^a
124		5.31	5.40	5.58
126		1.83	1.80	1.92
127	0.2			
128	0.9	9.73	9.90	10.32
129	10.3	60.33	61.06	63.02
130	1.6	4.16	4.25	4.32
131	17.3	9.83	9.85	9.43
132	22.8	6.05	5.77	5.03
134	25.3	1.64	1.14	0.34
136	21.5	1.12	0.73	0.026
129/124 Ratio		11.36	11.31	11.29

^a First tag mixture in A2 subseries: 100% Mound Mixture 2, no natural xenon. The minor variations between this analysis and the Mound Laboratory analysis of Mixture 2 (see Table III-9) are the result of the use of different mass spectrometers.

and analyzed on the same mass spectrometer. The results are shown in Table III-10. Calculations showed that after addition of the tag, the background xenon in the cover gas from all contaminant sources was only 3 to 5% of the total xenon. The Series A tag would normally be identified by the $^{129}\text{Xe}/^{128}\text{Xe}$ isotopic ratio. The contaminants in the cover gas changed this ratio from 11.29 to 11.36. A comparison of this value with the ratio of the next tag in Series A (13.5) shows that contamination of the cover gas by the means discussed above will not impair tag identification.

The xenon tagging system was thoroughly discussed at a joint meeting of EBR-II operators and experimenters, and the system is considered feasible and desirable. The special mass spectrometer needed for tag identification has been ordered. Series A tag mixtures are being procured and contract negotiations are under way for procurement of the ^{128}Xe necessary for the Series B tag mixtures.

The first tag mixture has been provided to an experimenter, and in the near future all unencapsulated gas-bonded fuel elements entering EBR-II, except in rare cases, should be xenon-tagged.

D. CALORIMETRY (*W. N. Hubbard, H. M. Feder, M. Ader*)

The calorimetry program is directed toward the experimental, empirical, or theoretical determination of thermodynamic properties of substances that are of interest in high-temperature chemistry and nuclear technology. Room-temperature enthalpies of formation (ΔH_f°) are being measured; complementary experimental determinations of high-temperature enthalpy increments ($\Delta H_T - \Delta H_{298}$), previously reported in this section, are now reported in Section III.A.2.a.

The method of fluorine bomb calorimetry was developed for substances not amenable to more conventional calorimetry and has been used to determine

the enthalpies of formation of 35 elemental fluorides and 18 binary compounds. Where appropriate, oxygen bomb calorimetry is also employed. The acquisition of a commercial solution calorimeter and the development of a rocking solution calorimeter, now in the testing stages, considerably widen the scope of calorimetric reactions that can be studied.

The data and results presented in this report are to be considered preliminary; when published in their final form in a journal article, they may be slightly different owing to refinements in the calculations.

1. Thermochemistry of Uranium Compounds (*P. A. G. O'Hara, J. L. Settle*)

a. Enthalpy of Formation of Uranium Diboride

As part of a continuing program to provide accurate thermochemical data for uranium compounds, the standard enthalpy of formation of uranium diboride was determined by fluorine bomb calorimetry. The only other value for $\Delta H_f^\circ(\text{UB}_2)$ in the literature is Rand and Kubaschewski's estimate¹ of $-35.3 \pm 3 \text{ kcal mol}^{-1}$ based on Alcock and Grievson's measurements² of uranium activities in $\text{UB}_2\text{-UB}_4$ mixtures.

Uranium diboride was synthesized³ by repeated arc melting of a mixture of high-purity boron and uranium. Metallographic examination showed the diboride product to be single phase. X-ray diffraction analysis yielded the following cell parameters: $a = 3.1309 \text{ \AA}$, $c = 3.9837 \text{ \AA}$, and $c/a = 1.2724$ (literature value, 1.2728⁴). Chemical and spark-source mass spectrometric analyses indicated a total impurity content of about 0.05%. The boron and uranium contents of the sample were found to be $8.24 \pm 0.02\%$ and $91.69 \pm 0.04\%$, respectively. In calculating the B/U atomic ratio, 1.979 ± 0.006 , all metallic impurities were considered to be incorporated on the uranium sublattice, and all non-metallic impurities on the nonmetal sublattice.

The fluorine combustion technique used was similar to that described for uranium monophosphide⁵ except

¹ M. H. Rand, O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, Interscience Publishers, New York, N. Y. (1963).

² C. B. Alcock, P. Grievson, "Study of Uranium Borides and Carbides by Means of the Knudsen Effusion Technique," in *Thermodynamics of Nuclear Materials*, p. 563, International Atomic Energy Agency, Vienna (1962).

³ By A. E. Martin and F. C. Mrazek of the High-Temperature Thermodynamics and Physical Property Studies Group.

⁴ B. W. Howlett, *J. Inst. Metals* **88**, 91 (1959).

⁵ ANL-7375, p. 126.

for the use of a higher fluorine pressure (in a new two-compartment reaction vessel⁶) and powdered sulfur as an ignition aid. Samples of diboride ranging from 0.8 to 1.8 g were burned. The gaseous combustion products were identified by infrared spectroscopy as UF_6 and BF_3 . A gray, solid residue weighing 5–50 mg remained in the crucible after each combustion. It was identified by X-ray powder diffraction and chemical analyses as a mixture of UB_2 and UF_5 .

The standard enthalpy of the reaction

at 298°K was calculated from eight acceptable calorimetric experiments to be $-1021.2 \pm 2.2^7 \text{ kcal mol}^{-1}$. This value, when combined with $\Delta H_f^\circ(\text{UF}_6, \text{c}) = -522.6 \pm 0.4 \text{ kcal mol}^{-1}$ ⁸ and $\Delta H_f^\circ(\text{BF}_3, \text{g}) = -271.7 \pm 0.2 \text{ kcal mol}^{-1}$ ⁹, yields $\Delta H_f^\circ(\text{UB}_{1.979}, \text{c}) = -39.1 \pm 2.6^7 \text{ kcal mol}^{-1}$ for the reaction

This ΔH_f° value for uranium diboride is about 4 kcal mol⁻¹ more negative than Rand and Kubaschewski's estimate. The corresponding value for $\Delta G_f^\circ(\text{UB}_{1.979}, \text{c})$ is calculated to be $-38.6 \pm 2.6^7 \text{ kcal mol}^{-1}$, based on S_{298}° values (cal deg⁻¹ mol⁻¹) of 12.00,¹ 1.403,¹⁰ and

⁶ J. L. Settle, E. Greenberg, W. N. Hubbard, *Rev. Sci. Instrum.* **38**, 1805 (1967).

⁷ Uncertainty = 2σ (twice the combined standard deviations from all known sources).

⁸ J. L. Settle, H. M. Feder, W. N. Hubbard, *J. Phys. Chem.* **67**, 1892 (1963).

⁹ G. K. Johnson, H. M. Feder, W. N. Hubbard, *ibid.*, **70**, 1 (1966).

¹⁰ *JANAF Thermochemical Tables*, Dow Chemical Co., Midland, Mich. (December 1964).

13.17¹¹ for U(α), B(β -rhomb), and UB_{1.979}(hex), respectively.

b. Enthalpy of Formation of β -Uranium Disulfide

The energy of combustion of orthorhombic uranium disulfide (β -US₂) in fluorine was measured by essentially the same technique as that used for uranium diboride. The specimen was prepared at Stanford Research Institute by heating uranium metal with sulfur

¹¹ H. E. Flotow, D. W. Osborne, Argonne National Laboratory, private communication.

in a sealed quartz bulb. It was supplied as a fine powder, which was analyzed and found to have the following characteristics: single phase; cell parameters $a = 7.115$ Å, $b = 4.122$ Å, and $c = 8.480$ Å; impurity content $\sim 0.09\%$; and anion-to-cation ratio = 2.000 ± 0.002 . The enthalpy of the fluorination of β -US₂ was combined with the enthalpies of formation of UF₆⁸ and SF₆¹² to give $\Delta H_f^\circ(\text{US}_2, \beta) = -124.2 \pm 2.1^7$ kcal mol⁻¹. Rand and Kubaschewski¹ had estimated this value as -120 ± 10 kcal mol⁻¹.

¹² P. A. G. O'Hare, J. L. Settle, W. N. Hubbard, *Trans. Faraday Soc.* **62**, 558 (1966).

2. Thermochemistry of Plutonium Compounds (G K. Johnson, E. H. Van Deventer)

The technique of oxygen bomb calorimetry was selected for determining the enthalpies of formation of PuN and PuC; it will probably be used for lower oxides of plutonium, such as Pu₂O₃. Glovebox experience with calorimetric techniques was gained by measuring the enthalpy of combustion of plutonium metal in oxygen, for which a reliable calorimetric value already existed. These techniques have since been applied to combustions of PuN and PuC.

a. Enthalpies of Formation of PuO₂ and PuN

Calorimetric measurements of the enthalpies of combustion of plutonium and PuN in oxygen have been completed. The work is described in a paper to be published under the title, "The Enthalpies of Formation of Plutonium Dioxide and Plutonium Mononitride."¹³ The abstract is as follows:

The energies of combustion in oxygen of α -plutonium metal and plutonium mononitride were

¹³ G. K. Johnson, E. H. Van Deventer, O. L. Kruger, W. N. Hubbard, *J. Chem. Thermodyn.*, **1**, 89 (1969).

measured in a bomb calorimeter. The standard enthalpies of formation, $\Delta H_f^\circ(298.15^\circ\text{K})$, of PuO₂(c) and PuN(c) were calculated to be -1055.85 ± 0.72 kJ mol⁻¹ (-252.35 ± 0.17 kcal mol⁻¹) and -299.2 ± 2.6 kJ mol⁻¹ (-71.51 ± 0.62 kcal mol⁻¹), respectively.

The value obtained for $\Delta H_f^\circ(\text{PuO}_2)^7$ is in good agreement with previous calorimetric determinations; the value for $\Delta H_f^\circ(\text{PuN})^7$ differs from previously reported values but is believed to be the most reliable obtained thus far.

b. Enthalpy of Formation of Plutonium Monocarbide

Plutonium monocarbide, like PuO₂ and PuN, has received considerable attention as a potential reactor fuel. Unfortunately, there is no reliable calorimetrically determined enthalpy of formation for this compound. A specimen of arc-melted PuC_{0.85} has been obtained and trial experiments to determine the best oxygen bomb calorimetric procedure are under way.

3. Enthalpy of Formation of Liquid Hydrogen Fluoride (E. Greenberg)

The importance of hydrogen fluoride as a key thermochemical compound requires that its enthalpy of formation be well established. Accordingly, $\Delta H_f^\circ(\text{HF}, \text{l})$ was determined by measuring the energy evolved on reaction of fluorine with hydrogen in a bomb calorimeter whose combustion chamber had been presaturated with gaseous HF (by addition of liquid HF). With this technique, the only product of combustion was liquid HF, and the uncertain correction for the nonideality of HF(g) was avoided.

A new two-compartment, high-pressure bomb (Ni-8) was fabricated for this work. Fluorine was charged to

the inner (combustion) compartment, which was gold plated for protection against HF corrosion; excess hydrogen was charged to the outer (tank) compartment. The results of auxiliary experiments had shown that no significant quantity of fluorine remained in the bomb after combustion. Thus, the amount of the reaction in the calorimetric measurements could be based on the weight of fluorine charged. In one combustion experiment, more than 99% of the HF produced was recovered, which gives further assurance that the hydrogen-fluorine reaction proceeded quantitatively according to Eq. 3:

A series of calorimetric combustions of hydrogen in

fluorine has been completed, yielding the preliminary value $\Delta H_{f298}^\circ(\text{HF}, \text{l}) = -71.8 \pm 0.2^7 \text{ kcal mol}^{-1}$.

4. Enthalpies of Formation of IF_5 and IF_7 (J. L. Settle, J. H. E. Jeffes,¹⁴ P. A. G. O'Hare)

The thermochemistry of metallic iodides, particularly thermally decomposable iodides used in purification and vapor plating of metals (van Arkel-de Boer technique), is of interest. Preliminary experimentation¹⁵ showed that iodides, e.g., ZrI_4 , can be studied by fluorine bomb calorimetry. This technique yields $\text{IF}_5(\text{l})$ and $\text{IF}_7(\text{g})$ as reaction products (in addition to metallic fluorides). Thus, the auxiliary data $\Delta H_f^\circ(\text{IF}_5, \text{l})$ and $\Delta H_f^\circ(\text{IF}_7, \text{g})$ are needed to supplement calorimetric measurements of iodine-fluorine reactions. Because the literature information on both these quantities was inadequate for our purposes, calorimetric combustions of iodine in fluorine were undertaken.

Iodine and fluorine reacted spontaneously on contact, giving a mixture of IF_5 and IF_7 . By varying the excess of fluorine, the yield of IF_7 could be made as small as a few tenths of a percent or as large as 80%. The relative amounts¹⁶ of IF_5 and IF_7 produced in each combustion were determined by hydrolysis of the combustion product, followed by a differential titration¹⁷ for iodate and periodate. A linear relationship was derived between the mole percent of IF_7 produced and the internal energy change per gram of iodine reacted. Extrapolation

of this line to 100% IF_5 gave a value of $-1648.2 \pm 2.7 \text{ cal g}^{-1}$ for the energy of combustion of iodine in fluorine to yield $\text{IF}_5(\text{l})$. Extrapolation of the line to 100% IF_7 gave a value of $-1780 \pm 10 \text{ cal g}^{-1}$ for the energy of combustion of iodine in fluorine to yield $\text{IF}_7(\text{g})$. Conversion to molar quantities and combination with appropriate other data gives -209.2 , -210.6 , and -186.4 (all $\pm 0.5^7$) kcal mol^{-1} , respectively, for the standard energy, enthalpy, and Gibbs energy of formation of $\text{IF}_5(\text{l})$ at 298.15°K . The corresponding values for the formation of $\text{IF}_7(\text{g})$ are -225.9 , -227.4 , and -198.4 (all $\pm 1.4^7$) kcal mol^{-1} .

The value $\Delta H_{f298}^\circ(\text{IF}_5, \text{l}) = -210.6 \pm 0.5 \text{ kcal mol}^{-1}$ disagrees with that reported by Woolf,^{18a} $-204.7 \text{ kcal mol}^{-1}$, which is based on his measurements of the enthalpy of solution of $\text{IF}_5(\text{l})$. However, Woolf recently revised this value to $\Delta H_{f298}^\circ(\text{IF}_5, \text{l}) = -211.5 \pm 0.5 \text{ kcal mol}^{-1}$,^{18b} and thus the two most recent determinations of $\Delta H_f^\circ(\text{IF}_5, \text{l})$ are in accord.

The enthalpy difference $\Delta H_f^\circ(\text{IF}_7, \text{g}) - \Delta H_f^\circ(\text{IF}_5, \text{l}) = -16.8 \pm 1.6 \text{ kcal mol}^{-1}$ compares favorably with the corresponding value of $-19 \pm 2 \text{ kcal mol}^{-1}$ obtained by combining the enthalpy of the thermal decomposition $\text{IF}_7(\text{g}) \rightarrow \text{IF}_5(\text{g}) + \text{F}_2(\text{g})$ [$\Delta H = 28.5 \pm 2.0 \text{ kcal mol}^{-1}$ ¹⁹] with the enthalpy of vaporization of $\text{IF}_5(\text{l})$ [$\Delta H = 9.6 \text{ kcal mol}^{-1}$ ²⁰]. There is no reported value of $\Delta H_f^\circ(\text{IF}_7)$ with which to compare the present experimental value.

¹⁴ Resident Research Associate, Imperial College, London.

¹⁵ ANL-7425, p. 120.

¹⁶ A previously reported analytical scheme¹⁵ was based on the widely different vapor pressures of IF_5 and IF_7 and the assumption of ideal solution behavior. This scheme was abandoned after finding invalid the assumption of ideal solution. In fact, the solubility of $\text{IF}_7(\text{g})$ in $\text{IF}_5(\text{l})$ was found to be negligible.

¹⁷ *Standard Methods of Chemical Analysis*, 6th ed., Vol. 1, p. 522, N. H. Furman (ed.), D. Van Nostrand Co., Inc., Princeton, N. J. (1962).

¹⁸ (a) A. A. Woolf, *J. Chem. Soc.*, 231 (1951);

(b) A. A. Woolf, private communication.

¹⁹ R. B. Bernstein, J. J. Katz, *J. Phys. Chem.* **56**, 885 (1952).

²⁰ D. W. Osborne, F. Schreiner, H. Selig, *J. Chem. Phys.* (in press).

5. Enthalpy of Formation of GeF_4 (P. A. G. O'Hare, B. Klemecki^{21a}, M. Mulvihill^{21b}, J. Johnson^{21c})

Exploratory calorimetric combustions made about two years ago showed that 0.5 to 1.5 g of germanium could be burned completely in fluorine to yield $\text{GeF}_4(\text{g})$ as the only product. However, the determination of $\Delta H_f^\circ(\text{GeF}_4)$ was not pursued further as it subsequently became known to us that this datum was being determined by Gross and his coworkers at Fulmer Research

Institute and also by Margrave's group at Rice University. It was anticipated that both groups would arrive at concordant results. The investigation by Gross, Hayman, and Bingham²² yielded $\Delta H_{f298}^\circ(\text{GeF}_4, \text{g}) = -284.37 \pm 0.15 \text{ kcal mol}^{-1}$; the investigation by Charlú and Margrave²³ yielded $\Delta H_{f298}^\circ(\text{GeF}_4, \text{g}) = -274.13 \pm 0.13 \text{ kcal mol}^{-1}$. As there was

²¹ Summer Engineering Practice School student from (a) University of Illinois, (b) Michigan State University, (c) University of Arizona.

²² P. Gross, C. Hayman, J. T. Bingham, *Trans. Faraday Soc.* **62**, 2388 (1966).

²³ T. V. Charlú, J. L. Margrave, private communication.

no apparent reason for such a large discrepancy between the two values, it was decided to determine $\Delta H_f^\circ(\text{GeF}_4, \text{g})$ at this laboratory.

A series of ten calorimetric combustions of germanium in fluorine was carried out. The results are described in a paper accepted for publication in the *Journal of Chemical Thermodynamics*. The abstract of the paper is as follows:

6. Enthalpies of Formation and Solution of Boric Oxides (G. K. Johnson)

A previous report²⁴ gave our results for the enthalpies of formation of crystalline and amorphous B_2O_3 as determined by fluorine bomb calorimetry. As noted then, the value obtained for $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{amorph})$, $-299.52 \pm 0.51 \text{ kcal mol}^{-1}$, agreed with the literature values obtained by solution calorimetry; however, the values obtained for $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{c})$, $-303.02 \pm 0.51 \text{ kcal mol}^{-1}$, and for the enthalpy of transition, $3.50 \pm 0.33 \text{ kcal mol}^{-1}$, disagreed with those in the literature. Because a significant error in one or both of our combustion results was possible, additional calorimetric combustions of crystalline B_2O_3 in fluorine were made, and the enthalpies of solution in water of both forms of B_2O_3 were determined. For these measurements, a new specimen of crystalline boric oxide was prepared as previously described.²⁴ The impurities found in the specimen were (in ppm) C (63), H (270), Fe (100), Si (50), and Mg (5). The amorphous B_2O_3 was prepared by melting and quenching a portion of the crystalline preparation.

The solution measurements were performed with an LKB-8700 Precision Calorimetric System.²⁵ Samples of B_2O_3 ($\sim 0.55 \text{ g}$) sealed in glass ampoules were dissolved by breaking the ampoules under 100 ml of water. The calorimetric reaction was

where $\text{B}_2\text{O}_3(\text{s})$ is either crystalline or amorphous. The enthalpy at 298°K obtained for Reaction 4 was $-3.54 \pm 0.04^7 \text{ kcal mol}^{-1}$ with $\text{B}_2\text{O}_3(\text{c})$ and $-7.98 \pm 0.06^7 \text{ kcal mol}^{-1}$ with $\text{B}_2\text{O}_3(\text{amorph})$. Therefore, the enthalpy of transition is $4.44 \pm 0.07^7 \text{ kcal mol}^{-1}$, which is in accord with the literature values 4.36 ± 0.02^{26} and

The energy of fluorination of germanium to GeF_4 was measured in a bomb calorimeter, and the standard enthalpy of formation $\Delta H_f^\circ(\text{GeF}_4, \text{g})$, was determined to be $-284.5_8 \pm 0.2_1 \text{ kcal mol}^{-1}$. This result⁷ is in excellent agreement with that of Gross, Hayman, and Bingham and, taken together with other evidence, points to an error in the result of Charlu and Margrave.

$4.33 \pm 0.06^{27} \text{ kcal mol}^{-1}$. It should be noted that the hydrogen impurity in the specimen (assumed present as HBO_2) made it necessary to add a relatively large correction to the solution data. This correction by itself can account for the difference between our result and those in the literature, for which no hydrogen correction was applied.

The combustions of crystalline B_2O_3 in fluorine were carried out in the same manner as before²⁴ and yielded $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{c}) = -304.50 \pm 0.59^7 \text{ kcal mol}^{-1}$. This value is $1.48 \text{ kcal mol}^{-1}$ more negative than the earlier result and clearly points to some (as yet unknown) error in the earlier work. Only two combustions of the amorphous specimen were made, yielding a value of $-300.1 \text{ kcal mol}^{-1}$ for $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{amorph})$. No uncertainty has been assigned to this value because of the limited number of experiments, but it does agree with the earlier result well within any realistic assessment of the uncertainties. The enthalpy of transition computed from the present combustion data, $4.4 \text{ kcal mol}^{-1}$, is in excellent agreement with that obtained for the same specimens by solution calorimetry.

The following conclusions can now be made: (1) The enthalpy of transition (298°K) between crystalline and amorphous boric oxide is $4.44 \pm 0.07 \text{ kcal mol}^{-1}$; (2) the value obtained for $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{c})$ in our earlier work is in substantial error, and the correct value is better represented by the new data reported herein; and (3) although there is no reason to reject the earlier result for $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{amorph})$, we choose to combine our new value for $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{c})$, $-304.50 \pm 0.59 \text{ kcal mol}^{-1}$, with our value for the enthalpy of transition, $4.44 \pm 0.07 \text{ kcal mol}^{-1}$, to obtain $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{amorph}) = -300.1 \pm 0.6^7 \text{ kcal mol}^{-1}$.

²⁴ ANL-7225, p. 147.

²⁵ LKB Instruments, Inc., Rockville, Maryland.

²⁶ J. C. Southard, *J. Amer. Chem. Soc.* **63**, 3147 (1941).

²⁷ L. G. Fasolino, *J. Chem. Eng. Data* **10**, 373 (1965).

7. Correlation of the Enthalpies of Formation of the Rare Earth Trifluorides (E. Rudzitis)

The experimentally determined enthalpies of formation of the trifluorides of Sc, Y, La, Nd, Gd, Ho, and Er were listed in the preceding report.²⁸ This report also gave the results of an attempt to estimate the enthalpies of formation of all the rare earth trifluorides by use of the Born-Haber cycle. Due to the lack of sufficient input data for the Born-Haber cycle, the lattice energies for the isostructural trifluorides of Ce, Pr, Nd, and Pm were based on the lattice energy calculated for LaF₃ from the experimental value for $\Delta H_f^\circ(\text{LaF}_3)$. If an error existed in $\Delta H_f^\circ(\text{LaF}_3)$, it would affect the calculated lattice energy for LaF₃ and, consequently, the estimated ΔH_f° values based on this lattice energy.

It was noted that the experimentally determined value for $\Delta H_f^\circ(\text{NdF}_3)$ was $\sim 22 \text{ kcal mol}^{-1}$ less nega-

tive than the calculated value, whereas the other experimental ΔH_f° values were in excellent agreement with the calculated values. This was taken as evidence that the experimental value for NdF₃ was erroneous, although it could equally well have indicated that a serious error of $\sim 15 \text{ kcal mol}^{-1}$ existed in the previously reported experimental value for $\Delta H_f^\circ(\text{LaF}_3)$. Some recently published calorimetric data²⁹ for the enthalpies of formation of the rare earth trifluorides point to the likelihood of the latter. Thus, it now appears that an error of $\sim 15 \text{ kcal mol}^{-1}$ exists in the previously reported experimental value for $\Delta H_f^\circ(\text{LaF}_3)$ as well as in the estimated ΔH_f° values for CeF₃, PrF₃, NdF₃ and PmF₃. This work is currently being reexamined in light of the new data.

²⁹ Yu. V. Kondratyev, "The Determination of the Heat of Formation of Some Rare Earth Elements," Thesis, Leningrad State University (1967).

²⁸ ANL-7425, p. 122.

8. Extended Hückel Molecular Orbital Calculations for the Chalcogen Hexafluorides (P. A. G. O'Hare)

Measurements¹² of ΔH_f° for the series SF₆(g), SeF₆(g), TeF₆(g) showed that the average bond energies varied nonmonotonically. Although qualitative rationalizations for this finding were advanced previously,³⁰ it would be desirable to put these rationalizations on a more quantitative basis. Therefore, extended Hückel molecular orbital (EHMO) calculations are being made, which should yield theoretical information on the nature of the bonding, charge transfer between atoms, and bond energies.

Valence-state ionization energies for the various possible electronic configurations of both the chalcogen and the fluorine atoms were deduced from atomic spectral data.³¹ The atomic wave functions were approximated by Slater-type orbitals.³² Screening parameters, which are a measure of the screening of the valence electrons from the nucleus by the inner electrons, were calculated by the method of Burns.³³ A computer program³⁴ was used to evaluate both chalcogen-fluorine and fluorine-fluorine overlap integrals, and resonance integrals were calculated for all 48 valence electrons

(7 on each fluorine and 6 on the chalcogen atom). A 33×33 secular determinant was solved to yield the orbital energy levels, the electronic configurations of the atoms, and the charge distributions within each molecule. The procedure was iterated until the input and output charge distributions were in accord.

The following charge distributions have been obtained for the three hexafluoride molecules:

These results indicate considerably more charge transfer in TeF₆ than in SF₆ or SeF₆; the Te-F bonds are more ionic than the S-F or Se-F bonds. This result is consistent with the original qualitative rationalizations and with other chemical evidence, such as the much greater ease of hydrolysis of TeF₆ in polar solvents.

No allowance for the effect of charge transfer on the valence-state ionization energies and the screening parameters was made in these calculations. Therefore, a new iteration is required before the results can be subjected to more detailed scrutiny of the energy levels, etc.

³⁰ ANL-7125, p. 136.

³¹ C. E. Moore, *Nat. Bur. Stand. (U.S.), Circ.* **467** (1964).

³² J. C. Slater, *Phys. Rev.* **26**, 57 (1930).

³³ G. Burns, *J. Chem. Phys.* **41**, 1521 (1964).

³⁴ Dr. Audrey Companion of Illinois Institute of Technology very kindly made much of this program available to us and has assisted in many other ways.

9. Thermodynamic Properties of Molecules in the Ideal Gas State (*P. A. G. O'Hare*)

A computer program has been set up to calculate by means of the rigid-rotator, harmonic-oscillator approximation the thermodynamic functions C_p° , S° , $-(G^\circ - H_0^\circ)/T$, and $(H^\circ - H_0^\circ)/T$ for molecules in the ideal gas state. The program also derives values for the functions $H^\circ - H_{298}^\circ$, ΔH_f , ΔG_f , and $\log K_f$. Tabulated values of these functions for the following molecules have been published in ANL topical reports: (a) 24 fluorides of oxygen, sulfur, selenium, and tellurium (0 to 2000°K);³⁵ (b) As_2 , As_4 , and AsF_n ,

³⁵ P. A. G. O'Hare, "The Thermodynamic Properties of Some Chalcogen Fluorides," USAEC Report ANL-7315 (July 1968).

where $n = 1, 2, 3, 4$, and 5 (0 to 2000°K);³⁶ (c) P_2 , P_4 , P_2F_4 , and PF_n , where $n = 1, 2, 3, 4$, and 5 (0 to 6000°K);³⁷ (d) Ge_2 , and GeF_n , where $n = 1, 2$, and 4 (0 to 6000°K).³⁸ One of the intended uses of these tables is to calculate the thermodynamic equilibria of high-temperature gaseous reactions.

³⁶ P. A. G. O'Hare, "The Thermodynamic Properties of As_2 , As_4 , and Some Arsenic Fluorides," USAEC Report ANL-7456 (November 1968).

³⁷ P. A. G. O'Hare, "The Thermodynamic Properties of P_2 , P_4 , and Some Phosphorus Fluorides," USAEC Report ANL-7459 (December 1968).

³⁸ P. A. G. O'Hare, "The Thermodynamic Properties of Gaseous Ge_2 , GeF_4 , GeF_2 , and GeF ," USAEC Report ANL-7523 (December 1968).

E. CHEMISTRY OF LIQUID METALS (*F. A. Cafasso, H. M. Feder, M. Ader*)

These studies are directed toward a better understanding of the chemistry of liquid metals in general and the particular chemistry of liquid sodium pertinent to its use as a reactor coolant. For the sake of

clarity, the discussion of these studies is divided into two sections: (1) fundamental studies and (2) liquid sodium coolant chemistry.

1. Fundamental Studies

In these studies, an attempt is being made to broaden and systematize knowledge of the nature of the liquid metallic state and of metallic solutions. Basic physicochemical data on simple metallic systems that lend themselves readily to theoretical treatment are being collected. In this connection, the thermodynamic activity of alkali metals in their liquid binary solutions and the attenuation of high-frequency sound in liquid metallic solutions are being measured. An effort is being made to derive statistically an empirical expression that relates the heat of mixing of equiatomic binary liquid alloys to selected physicochemical properties of the pure components.

a. Ultrasonic Measurements in Liquid Metallic Solutions (*F. A. Cafasso, R. Blomquist*)

Controversy concerning the existence or nonexistence of interatomic complexes in liquid metallic solutions is

long standing. Resolution of this controversy by optical spectroscopy, a common and convenient method for detecting complexes in liquids, has been hampered by the opacity of metals. However, because liquid alloys are not opaque to ultrasound, ultrasonic absorption spectrometry, which has been used to reveal or confirm complex formation in nonmetallic liquids, may offer an alternate approach to the problem. The existence or nonexistence of dissociable complexes in nonmetallic liquids can be correlated with the presence or absence of maxima in the absorption *vs.* frequency spectra. This same distinction is expected to hold for metallic liquids.

Accordingly, the ultrasonic absorption spectra of liquid metallic systems claimed to contain complex molecules are being determined. Three such systems that have been examined are Hg-50 at. % In,^{1,2} In-33

¹ N. Sundén, *Z. Elektrochem.* **57**, 100 (1953).

² E. W. Collings, *Advan. Phys.* **16**, 459 (1967).

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FIG. III-21. Absorption Coefficient per Wavelength vs. Frequency for Hg-Na, Hg-In, and In-Bi Alloys. (The magnitude of the errors for the mercury alloys is approximately the same as that shown for In-33 at. % Bi.)

at. % Bi,³ and Hg-18 at. % Na.⁴ Figure III-21 shows for each alloy the variation of the coefficient of absorption per wavelength ($\alpha\lambda$) with frequency between 45 and 165 MHz. Over this frequency range, no maxima are apparent and no support is given to the concept that complexes form in these systems. However, they are not precluded because of the possibility that $\alpha\lambda$ may peak at frequencies higher or lower than those studied. Hence in future measurements, as the search for complexes continues, a considerably broader range of frequencies will be employed, namely, 1 MHz to 1 GHz.

³ G. B. Styles, *Advan. Phys.* **16**, 275 (1967).

⁴ B. W. Mott, M. E. Downey, P. A. Cumming, UK Atomic Energy Authority report AERE-Bib 151 (September 1966).

b. Thermodynamics of Binary Alkali Metal Solutions: The Na-Cs System (F. A. Cafasso, R. Blomquist, M. Perin)

In recent years, the pseudopotential method⁵ has come into prominence for calculating the properties of liquid metallic systems. Although many properties may be so treated, provided that appropriate pseudopotentials are known, the thermodynamic properties of alloys have received only limited attention. Since reasonably accurate pseudopotentials are available for all the alkali metals, the thermodynamic properties of alkali metal alloys can be calculated and then compared with the measured values. The heats of mixing of binary alkali metal mixtures have been measured, but their excess free energies and entropies have not. Obtaining this missing information and using it to evaluate the pseudopotential method is the purpose of the present research. In this connection, the thermodynamic activities of sodium and potassium in liquid Na-K^{6,7} alloys and of sodium in Na-Rb⁸ alloys have already been measured; similar measurements for sodium and cesium in Na-Cs alloys are reported below.

Activities in the Na-Cs system are being measured by the technique of vapor-phase atomic absorption spectrophotometry. Resonance radiation characteristic of one of the alkali metals (the 5890-Å line of sodium, the 8521-Å line of cesium) is beamed through the vapor over the pure alkali metal and over the alloys. The absorption is a measure of the partial pressure of monomeric alkali metal in the vapor. Comparison of the absorption by the vapor over the alloy (p_i) with that by the vapor over the pure metal (p_i^0) yields the activity ($a_i = p_i/p_i^0$) of the metal in the alloy.

Sodium activities in several Na-Cs alloys were determined at $\sim 140^\circ\text{C}$. Figure III-22 shows the results and, for comparison, the similarly obtained data for Na-Rb and Na-K alloys. Significant positive departures from ideality are evident; however, the departures are smaller than those for the Na-Rb system but larger than those for the Na-K system. It is noteworthy that the heats of mixing for the three systems vary in the same way.⁹

The Gibbs-Duhem equation can be used to deduce the dependence of cesium activity on composition. The error inherent in such a calculation, however, is large; hence direct experimental determination of the cesium activity is being undertaken.

⁵ W. A. Harrison, *Pseudopotentials in the Theory of Metals*, W. A. Benjamin, Inc., New York (1966).

⁶ F. A. Cafasso, V. M. Khanna, H. M. Feder, *Advan. Phys.* **16**, 535 (1967).

⁷ ANL-7425, p. 126.

⁸ ANL-7375, p. 130.

⁹ T. Yokokawa, O. J. Kleppa, *J. Chem. Phys.* **40**, 46 (1964).

FIG. III-22. Variation of Sodium Activity with Composition of Liquid Alkali Metal Alloys at $\sim 140^\circ\text{C}$.

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c. Theoretical Studies (*H. Schnyders*)

The prediction of thermodynamic properties of liquid metallic solutions from physicochemical properties of the pure metals has long been a challenge. The concepts of size, valence, and electronegativity have been found to be of value in accounting for the qualitative behavior of simple systems such as the binary alkali metals. It has been recognized for some time that for more complex systems other factors must be important, yet little has been done to elucidate these factors. Therefore, an attempt to gain insight into this matter by statistical methods has been undertaken. Stepwise multiple regression analysis is being used to determine whether or not a significant correlation exists between selected properties of pure metals and the heats of mixing of binary liquid alloys at the equiatomic position (ΔH_{50}^M).

Of prime importance in a study of this kind is the form of the expression that relates the heat of mixing (dependent variable) and the properties (independent variables). With simple solution theory serving as a

guide, an expression of the following general form was selected:

$$\Delta H_{50}^M = \sum_{i=1} b_i X_i + \frac{1}{2} \sum_{i \neq j} b_{ij} (X_i X_j)^{1/2} \quad (1)$$

where b_i and b_{ij} are regression coefficients, and X_i or X_j represents the difference in magnitude of some physicochemical property of the two pure liquids forming the alloy. The ten X_i terms shown in Table III-11 were used.

Reliable heat-of-mixing data were available for 34 liquid binary systems. Thirty of these were included in the regression; the remaining four were used to test the predictive capability of the derived equation. The best regression equation obtained was

$$\Delta H_{50}^M = Y_7 + Y_{1.3} + Y_{1.6} + Y_{1.10} + Y_{2.6} + Y_{2.7} + Y_{4.6} + Y_{4.7} + Y_{5.6} + Y_{6.8} + Y_{7.10} + Y_{8.10} \quad (2)$$

where $Y_i = b_i X_i$ and $Y_{i \cdot j} = b_{ij} (X_i X_j)^{1/2}$. The equation

TABLE III-11. GLOSSARY OF TERMS USED IN REGRESSION ANALYSIS

Subscripts	
a and b refer to the pure component metals	
Parameters	
Z = valence; $Z_{<}$ = the lesser of Z_a or Z_b Ω = atomic volume; $\Omega_{<}$ = the lesser of Ω_a or Ω_b A = electronegativity (Gordy-Thomas scale) G = group number = 0 or 1, respectively, for Group A or B metals of periodic table $I = \sum_{i=1}^Z I_i$; I_i = i th ionization potential ΔH^V = heat of vaporization E^F = Fermi energy $\propto (Z/\Omega)^{2/3}$ r = Wigner-Seitz radius = $(3\Omega/4\pi Z)^{1/3}$ δ = Hildebrand solubility parameter = $(\Delta H^V/\Omega)^{1/2}$	
Functional Form of X_i	
$X_1 = [Z_{<}(A_a - A_b)^2]^{2/3}$	$X_6 = (G_a - G_b)^2$
$X_2 = E_a^F - E_b^F $	$X_7 = \Delta H_a^V - \Delta H_b^V $
$X_3 = (Z_a - Z_b)^2$	$X_8 = \left \log \left(\frac{r_a}{r_b} \right) \right $
$X_4 = Z_{<}(A_a - A_b)^2$	$X_9 = (\Omega_a + \Omega_b)(\delta_a - \delta_b)^2$
$X_5 = \left \frac{\Omega_a - \Omega_b}{\Omega_{<}} \right $	$X_{10} = I_a - I_b $

gives the correct sign and, within a factor of two, the magnitude of ΔH_{50}^M for all 30 systems and for three of the four test systems.

Examination reveals that of the nine parameters tested, eight appear in the regression equation. The Hildebrand solubility parameter, δ , is the only one with which a correlation was not found. Its absence is particularly notable since this parameter has been very useful in the correlation of the thermodynamic data for solutions of nonmetallic substances. Previous less extensive trials (e.g., B. W. Mott's¹⁰) of the solubility parameter for calculating the heats of mixing of binary liquid alloys have not been notably successful.

It is also noteworthy that, except in one case, the eight significant parameters appear in the best regression equation not as Y_i terms but as $Y_{i,j}$ terms. Most of the parameters are found more than once. The possibility that a change in the functional form of one of the terms containing a given parameter (e.g., electronegativity) may reduce the number of significant terms, while maintaining or improving the goodness of fit, is now being explored.

¹⁰ B. W. Mott, "Liquid Immiscibility in Metal Systems," UK Atomic Energy Authority report AERE-R-4388 (July 1963)

2. Liquid Sodium Coolant Chemistry

The chemical and physical properties of liquid sodium are being studied to provide basic data for understanding and possibly controlling the phenomena that lead to corrosion of structural materials and hence affect the use of sodium as a coolant in nuclear reactors. Structural materials in contact with sodium are known to undergo corrosion owing to transport of carbon, nitrogen, and oxygen, as well as to mass transfer. Of special interest then are the interactions of structural elements, such as iron, nickel, and chromium, and the elements which can enter metals interstitially, such as carbon, nitrogen, hydrogen, and oxygen, and which may arise from contaminants in sodium. The current research is centered on the elements carbon, nitrogen, iron, and copper. The immediate objectives are (1) to identify the mechanism(s) of carbon transport in sodium systems, (2) to determine the stabilities and solubilities of carbon- and nitrogen-bearing species in sodium, (3) to assess the importance of surface phenomena in the corrosion of solids in liquid sodium, and (4) to examine the distribution into liquid sodium of various constituents of stainless steel, particularly tramp copper.

a. Carburization and Decarburization of Steels in Liquid Sodium (C. Luner, J. Althoetmar)

(1) Mechanism of Carbon Transport in Liquid Sodium

Various mechanisms for carbon transport in liquid sodium systems have been proposed, but none has been generally accepted. Identification of the migrating carbon-bearing species could provide significant insight into this mechanism, and experiments with this aim have been undertaken. Materials labeled with beta-active ¹⁴C are being used to differentiate between the carbon that is transported and the carbon that exists as a contaminant of sodium, a distinction that has proven difficult to make in past studies.

It was shown previously¹¹ that the carbon from a capsule made of a ferritic ¹⁴C-labeled iron-carbon alloy migrated through liquid sodium at 650°C to an immersed austenitic coupon made of type 304 stainless steel. Detectable quantities of labeled carbon were found in the sodium after 165 hr at temperature. To prove

¹¹ ANL-7425, p. 128.

samples of sodium for the identification of this ^{14}C -labeled species, further experiments, both with and without transport, were made and are discussed below.

Experiments without transport. In a typical experiment, reactor-grade sodium was sealed in a crucible made of a ferritic iron-carbon alloy (0.030% C) labeled with carbon-14. The crucible was sealed in a secondary capsule and heated at 650°C for 120 hr. After being cooled to room temperature, the crucible was opened and the sodium was dissolved in deaerated water, which was subsequently acidified. The solution, it was found, contained very little labeled carbon; much larger amounts appeared in the off-gas and residue from the dissolution. The initial effort was concentrated on identifying the labeled species in the off-gas fraction. Results of radiogas chromatographic analyses¹² on a typical off-gas are given in Table III-12 under "Ferritic Alloy + Na."

Acetylene is the major ^{14}C -labeled gas. Its specific activity is in close agreement with that of the carbon in the ferritic iron-carbon alloy. The ethylene and ethane found in small amounts are believed to originate from hydrogenation of acetylene during dissolution. The similarity of their specific activities is consistent with this contention. The minor amount of CO_2 found and its very low specific activity indicate that it originated from a carbonate impurity that was originally present in the sodium or introduced during the experiment.

Experiments with transport. In these experiments, an austenitic type 316 stainless steel coupon was immersed in the sodium; otherwise, the experimental conditions were identical with those above. The results of a typical analysis of the off-gas from the sodium in these experiments are given in Table III-12 under "Ferritic Alloy + Na + 316 SS." The concentrations of acetylene and of ethylene plus ethane (and therefore of the acetylene precursor) are drastically reduced. This result is consistent with the frequent observation made here and elsewhere that austenitic steels in liquid sodium behave as sinks for carbon supplied by ferritic alloys. Note also that the specific activities of the hydrocarbons are about 30% lower than that of the source carbon in the ferritic crucible. Dilution by inactive carbon in this experiment is most likely due to the precursor of CO_2 , i.e., Na_2CO_3 . This is suggested by the fact that acetylene is one of the gases evolved on hydrolysis of sodium that has been contaminated with Na_2CO_3 and then heated above 450°C .

Separation of the precursor of the acetylene from sodium for identification by direct methods was im-

TABLE III-12. RADIOGAS CHROMATOGRAPHIC ANALYSIS OF GASES FROM AQUEOUS DISSOLUTION OF SODIUM

Gas	Ferritic Alloy ^a + Na		Ferritic Alloy ^a + Na + 316 SS	
	Ppm C in Na	Specific Activity (dpm/ μg C)	Ppm C in Na	Specific Activity (dpm/ μg C)
C_2H_2	18	2740	0.34	1910
C_2H_4 and C_2H_6	2.2	2600	0.19	1750
CH_4	trace	—	trace	—
CO_2	1.8	28	3.7	15

^a Specific activity 2650 ± 200 dpm/ μg C.

practical; hence its identity was deduced. Only acetylides (salts of C_2^{2-}) are known to react with water to give acetylene. Hence the most likely precursor of acetylene in these experiments is disodium acetylide (Na_2C_2). The possibility that CaC_2 (from calcium impurity in the sodium) was involved was ruled out in separate experiments that showed that acetylene production was independent of calcium concentration in sodium. Cementite, Fe_3C , from the ferritic crucible—which might have gotten into the sodium—was ruled out as a precursor of acetylene by showing that methane, but no acetylene, was formed by the hydrolysis of manganese-stabilized Fe_3C with aqueous NaOH .

The finding that considerably less acetylene was evolved from the sodium with the carbon sink than without strongly suggests that its precursor, Na_2C_2 , partook in the carbon transport. Insight into the mechanism of Na_2C_2 formation was gained from the mechanism postulated for Li_2C_2 formation in lithium-steel systems. Various workers¹³⁻¹⁵ have proposed that corrosion of carbon steels in lithium proceeds via the reaction of cementite, according to the following thermodynamically favored reaction:

The formation of Na_2C_2 in sodium-steel systems may proceed by an analogous reaction:

Flint in 1965 suggested that Na_2C_2 , formed according to Reaction 4, was involved in carbon transport. By assuming that the free energy and enthalpy of forma-

¹³ N. M. Beskorovainyi, V. K. Ivanov, M. T. Zuev, in *High-Purity Metals and Alloys*, V. S. Emel'yanov, A. I. Evstuyukhin (eds.), Consultants Bureau, New York (1967).

¹⁴ M. Beniere, M. Chemla, M. Aucouturier, P. LaCombe, C. Roques-Carnes, *Corrosion* **24**(4), 83 (1968).

¹⁵ E. F. Hoffman, USAEC report ORNL-2924 (1960).

¹² R. Wolfgang, F. S. Rowland, *Anal. Chem.* **30**, 903 (1958).

tion of Na_2C_2 were approximately equal, he estimated the free energy of Reaction 4 to be about -3 kcal/mol at 550°C , i.e., the reaction is thermodynamically possible. However, because of the tenuous nature of this conclusion, accurate measurements of the thermodynamic functions of Na_2C_2 are needed, and this work is now beginning.

(2) Cyanide-Steel Interaction in Liquid Sodium

It is noteworthy that the solubility found for sodium cyanide (see Part 2.c below) is the highest measured so far for any carbon- or nitrogen-containing compound in sodium. Consequently the tendency of cyanide to carburize and nitride steel was tested. Type 304 stainless steel tabs were immersed for about 8 days at 660°C in reactor-grade sodium (~ 8 ppm carbon, 20 ppm oxygen) to which had been added 0.15% NaCN. The reactants were contained in an alumina crucible, which was sealed inside a stainless steel capsule. Analysis of the tabs showed that the carbon and nitrogen concentrations, initially 0.07% and 0.03%, respectively, increased approximately threefold. It appears that cyanide in liquid sodium is quite effective in simultaneously carburizing and nitriding steel.

b. Formation and Stabilization of Carbon-Bearing Species in Sodium (*D. Vissers, R. Yonco*)

Considerable evidence has accumulated that strongly suggests that carbon-bearing particles, varying in size and nature, are dispersed in reactor-grade sodium. The tendency of sodium to act as a dispersion medium for particulates may, therefore, be as important in carburization phenomena as its tendency to act as a solvent. To assess the importance of dispersed carbon in carburization, stable and well-characterized dispersions of carbon in sodium will be needed. Attempts to prepare such dispersions are now in progress.

Ultrasonic dispersion, which has been used successfully with a wide variety of nonmetallic liquids, appeared to offer great promise for liquid sodium. Accordingly, attempts were made to disperse 90-Å carbon black¹⁶ in NaK eutectic by ultrasonic stimulation. The NaK eutectic was selected for the initial studies because it is, conveniently, a liquid at room temperature and is similar to the systems of interest. The ultrasonic unit consisted of a continuous-wave generator and magneto-strictive transducer probe and was capable of generating 1000 W at 20 kHz.

Preliminary experiments have yielded encouraging results; dispersions of up to 4 wt % carbon in NaK eutectic have been achieved. The stability of these dis-

persions appears to depend on (among other factors) the concentration of the dispersed carbon. Dispersions with 0.5 wt % carbon have broken within 24 hr. Moreover, the dispersions containing 1 wt % carbon were found to show a marked increase in viscosity and also to readily wet glass and stainless steel containers. The effects of time, temperature, and dilution on the stability of these ultrasonically produced dispersions are now under study. Efforts are also being made to generate carbon dispersions in liquid sodium with a heatable ultrasonic unit built especially for this purpose.

c. Solubility of NaCN in Liquid Sodium (*E. Veleckis, G. W. Redding, W. A. Kremsner*)

Carburization and nitridation of steels are corrosion phenomena frequently observed in liquid sodium systems. Cyanide, which has been found in experimental and reactor sodium loops, particularly in cold traps, is potentially both a carburizing and a nitriding agent. As a first step in the investigation of cyanide behavior, its stability and solubility in sodium were determined in the temperature range 400 – 650°C .

Cyanide solubilities were determined by equilibrating reactor-grade sodium with excess sodium cyanide at temperature, withdrawing a sample of the melt through a stainless steel filter into a tantalum pipette, dissolving the sodium from the pipette, and assaying the resulting aqueous solution for cyanide by a spectrophotometric method.¹⁷

The solubility data are shown in Fig. III-23 together with similar data obtained by Bredig et al.¹⁸ for NaCl, NaBr, and NaI. Solubilities were measured both below and above the monotectic temperature, which was found by thermal analysis to be $565 \pm 2^\circ\text{C}$. A monotectic in the Na-NaCN system had been anticipated because cyanide ion is a pseudohalide¹⁹ and monotectics had been observed with the Na-sodium halide systems. The reliability of each solubility value was established by multiple determinations. Data collected below the monotectic temperature were fitted by the method of least squares to the linear equation

$$(400\text{--}565^\circ\text{C}) \log S_{\text{CN}} = 13.5 - 9140 T^{-1}$$

where S_{CN} is the cyanide solubility in parts per million, and T is absolute temperature. The uncertainty of S_{CN} in this equation is $\pm 16\%$ at the 95% confidence level; the heat of solution is 42 ± 5 kcal/mol.

¹⁷ I. Nusbaum, P. Skupeko, *Metal Finishing* **49**(10), (1951).

¹⁸ M. A. Bredig, J. W. Johnson, W. T. Smith, Jr., *J. Amer. Chem. Soc.* **77**, 307 (1955).

¹⁹ T. Moeller, *Inorganic Chemistry*, p. 463, John Wiley and Sons, Inc., New York (1952).

¹⁶ Carbolac 1, produced by the Cabot Corporation, Boston, Mass.

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FIG. III-23. Solubilities (Mole Fraction) of Sodium Cyanide and Sodium Halides in Liquid Sodium.

d. Solubility of Nitrogen in Liquid Sodium (E. Veleckis, K. E. Anderson)

The solubility of nitrogen in liquid sodium has been measured in connection with its presence in the blanket gases of sodium-cooled nuclear reactors. The magnitude of this solubility may be important to the understanding and control of nitridation, a corrosion phenomenon known to occur in liquid sodium systems.

Nitrogen solubility, which is very small, was determined with the aid of ^{15}N -enriched nitrogen gas. The technique employed was adapted from a technique used by Grimes et al.²⁰ to measure the solubility of rare gases in eutectic mixtures of fused fluorides. In this study, liquid sodium was saturated at temperature with ^{15}N -enriched nitrogen, and the dissolved nitrogen was stripped from ~ 2 liters of the sodium with helium. The stripped nitrogen was trapped on liquid-nitrogen-cooled molecular sieves, thus separating it from most of the helium, and then transferred to a gas-sample bulb for analysis with a mass spectrometer. The use of nitrogen-15 enabled a distinction to be made between nitrogen that had dissolved in the sodium and nitrogen

²⁰ W. R. Grimes, N. V. Smith, G. M. Watson, *J. Phys. Chem.* **62**, 862 (1958).

TABLE III-13. SOLUBILITY OF NITROGEN IN LIQUID SODIUM^a

Temperature (°C)	Mean Solubility (g N_2 per 10^{12} g Na per atm pressure)
451	10 ± 8
502	17 ± 7
550	25 ± 8
600	44 ± 9

^a All solubilities were determined at ~ 10 atm pressure of nitrogen.

that was subsequently introduced as a contaminant during the stripping step.

The typical gas sample contained both dissolved and contaminant nitrogen and a small amount of helium. A natural distribution²¹ of nitrogen isotopes was assumed for the contaminant nitrogen, namely, 99.27 mol % $^{14}\text{N}_2$, 0.73 mol % $^{14}\text{N}^{15}\text{N}$, and 0.00134 mol % $^{15}\text{N}_2$. The concentration of the dissolved nitrogen in the gas sample, C , was calculated from the equation

$$C = \frac{\beta + 1}{\beta - \alpha} \left(C_{30} + \frac{1 - \alpha}{2} C_{29} - \alpha C_{28} \right) \quad (5)$$

where β is the $^{15}\text{N}/^{14}\text{N}$ atom ratio in the initial gas mixture, α is the $^{15}\text{N}/^{14}\text{N}$ atom ratio in atmospheric nitrogen, and C_{30} , C_{29} , and C_{28} are the relative concentrations of $^{15}\text{N}_2$, $^{15}\text{N}^{14}\text{N}$, and $^{14}\text{N}_2$ species in the gas sample as determined by mass spectrometric analysis. The value of C , in conjunction with the volume and pressure of the gas in the sample bulb, was used to calculate the amount of nitrogen dissolved per unit volume of sodium.

Solubilities were measured at 50-degree intervals between 450 and 600°C and at ~ 10 atm pressure of nitrogen. At least six measurements were made at each temperature, with the results shown in Table III-13. The weighted data were treated by the method of least squares to yield the linear equation

$$(450\text{--}600^\circ\text{C}) \log S_{\text{N}_2} = -7.18 - 2780 T^{-1}$$

where S_{N_2} is nitrogen solubility in grams of nitrogen per gram of sodium per atmosphere, and T is absolute temperature. The uncertainty of S_{N_2} in this equation is $\pm 16\%$ at the 95% confidence level; the heat of solution is 13 ± 3 kcal/mol.

An earlier attempt to measure the solubility of nitrogen in liquid sodium was brought to our attention by C. H. Lemke of du Pont's Niagara Falls Research Laboratory. In an unpublished report, dated 1958 and entitled "Nitrogen in Sodium Metal," by C. H. Lemke and W. C. Sharples, it was concluded that within the sensitivity of the experimental method, namely 5 ppm, nitrogen at 1 atm pressure was insoluble in sodium at

²¹ G. A. Junk, H. J. Svec, USAEC report ISC-1138 (1958).

100°C. This finding is consistent with the extraordinarily low solubility of nitrogen in sodium indicated by our results.

The use of nitrogen-15 tracer provided not only the requisite sensitivity for the solubility measurements but also an insight into the nature of the dissolution process. The sodium was saturated with isotopically unequilibrated nitrogen having the typical composition 27.4 mol % $^{15}\text{N}_2$, 49.6 mol % $^{14}\text{N}_2$, and 23.0 mol % $^{14}\text{N}^{15}\text{N}$. If this nitrogen dissolved monatomically, then random recombination of the atoms on exsolution would be expected to give the equilibrated composition 15.2 mol % $^{15}\text{N}_2$, 37.3 mol % $^{14}\text{N}_2$, and 47.5 mol % $^{14}\text{N}^{15}\text{N}$. However, mass-spectrometric analyses of the stripped gas revealed only a small change in isotopic composition to 25.7 mol % $^{15}\text{N}_2$, 46.1 mol % $^{14}\text{N}_2$, and 28.2 mol % $^{14}\text{N}^{15}\text{N}$, which is not consistent with purely monatomic dissolution. More likely, this change is due to catalytic reactions occurring at the hot steel surfaces of the apparatus. (Slow exchange between $^{15}\text{N}_2$ and $^{14}\text{N}_2$ over hot iron catalysts has been observed.²²) The results, therefore, appear to be consistent with the mechanism of diatomic dissolution of molecular nitrogen in sodium. Past studies have shown that diatomic gases dissolve or react monatomically in liquid metals; this is the first to show that molecular dissolution also occurs.

Having established the diatomicity of the dissolved nitrogen, its solubility in sodium was calculated according to the hard-sphere model of Reiss et al.²³ and Pierotti.²⁴ In this model, the calculated solubility is a sensitive function of the value selected for the hard-sphere diameter of sodium. The literature indicates that this diameter is 3.2 Å at 500°C,²⁵ for which the

²² J. T. Kummer, P. H. Emmett, *J. Chem. Phys.* **19**, 289 (1951).

²³ H. Reiss, H. L. Frisch, E. Helfand, H. L. Lebowitz, *J. Chem. Phys.* **32**, 119 (1960).

²⁴ R. A. Pierotti, *J. Phys. Chem.* **67**, 1840 (1963).

²⁵ N. W. Ashcroft, J. Lenker, *Phys. Rev.* **145**, 83 (1966).

model predicts a solubility about 10^5 times greater than that measured. On the other hand, much better agreement (within 15%) was obtained for a diameter of 3.72 Å, the interatomic Na-Na distance in crystalline sodium. An explanation for this better agreement is being sought.

e. Surface Diffusion in Liquid Sodium (*J. Eberhart*)

Surface diffusivity is a phenomenon known to be important in enhancing the corrosion of solids in some liquid media. Whether or not surface diffusivity plays a role in the mass transfer that occurs in liquid sodium systems has not been examined. So as not to overlook this possibly important corrosion mechanism, the surface behavior of iron and of type 304 stainless steel, immersed in sodium, is being studied by interferometric measurement of the rate of decay of grain-boundary grooves and surface scratches. The effect of the sodium will be determined by comparing these measurements with those obtained in a helium or vacuum environment at the same temperature. If enhanced surface mass transfer in sodium is demonstrated, a detailed study of the diffusion mechanism and rate will be undertaken.

f. Stainless Steel-Liquid Sodium Compatibility (*D. R. Vissers, R. Yonco*)

The partition of copper between type 304 stainless steel and liquid sodium is being examined. This information is of interest because type 304 stainless steel, a commonly used material of construction for liquid sodium systems, may contain up to 0.5% tramp copper.

Tantalum capsules, each loaded with enough sodium to completely immerse a type 304 stainless steel coil of large surface area, are being heated at 650°C for extended periods. The capsules will be opened periodically to analyze the sodium for copper. The results of these experiments will be used to decide the nature and direction of future studies in this area.

F. PREPARATION OF REACTOR MATERIALS: CERAMIC FUELS (*P. A. Nelson, R. K. Steunenberg, J. D. Arntzen*)

The preparation of ceramic fuels for nuclear reactors is being studied to develop processes that economically fit into appropriate fuel cycles. In the past year, efforts were directed toward procedures for preparing uranium carbide and uranium-plutonium carbide fuels. Two fluidized-bed processes were studied

for preparing monocarbides: (1) carburization of hydrided metal or alloy at 750 to 800°C with methane-hydrogen gas mixtures and (2) reaction of spherical particles consisting of a blended mixture of UO_2 and carbon bonded with an organic polymer.

The fluidized-bed process studies have been com-

pleted. However, work on the development of an advanced method for converting oxides to carbides,

namely, reaction of oxide-carbon mixtures in a plasma jet, is being continued.

1. Synthesis of Carbides by Metal-Methane Reaction

a. Preparation of Carbide Fuel Powder (*S. Vogler, P. W. Krause*)

A fluidized-bed process that had been developed previously (ANL-7325, p. 113; ANL-7375, p. 119; and ANL-7425, p. 114) was utilized for preparing (U, 15 wt % Pu)C powder containing fully enriched uranium. This material was to have been fabricated into pellets for irradiation testing, but the fabrication of the actual test specimens was postponed indefinitely as a result of de-emphasis of carbide fuel development.

In the powder-preparation runs, 400-g batches of ^{235}U -15 wt % Pu alloy ($\frac{3}{8}$ -in. dia by 1-in. long rods) were hydrided at 250°C in a H_2 -2 vol % CH_4 atmosphere and dehydrided by heating to about 500°C in the same atmosphere. This procedure was carried out twice to produce a fine powder. The powder was then reacted with a H_2 -6.2 vol % methane fluidizing gas at 800°C and two atmospheres pressure to produce the carbide.

The carbon content of the (U,Pu)C product leveled off at slightly above the stoichiometric value after 5 to 8 hr of uninterrupted carbiding as illustrated in Fig. III-24. The virtual cessation of reaction at this level, despite a methane concentration high enough to cause formation of the sesquicarbide [(U,Pu) $_2\text{C}_3$] at equilibrium, is probably due to the formation of a thin layer

of the sesquicarbide around the powder particles. The layer restricts further diffusion of carbon to the interior of the particle. The thin (U,Pu) $_2\text{C}_3$ layer can be removed by reacting the powder with pure hydrogen at 800°C after carbiding has been completed, as shown in Fig. III-24 (Exp. 23). The hydrogen treatment reduces the carbon content from about 5.0 wt % to the stoichiometric monocarbide level of 4.8 wt %. Recent experiments in which newly prepared batches of carbide powder were purged with helium have established that the excess carbon is not present as adsorbed methane.

Several batches of (U, 20 wt % Pu)C and one batch of UC were also prepared using the above procedure. The results were similar to those with (U, 15 wt % Pu)C. However, the data show that the rate of reaction increases with increasing plutonium concentration.

Both the carbon and the oxygen contents of the products of recent (U,Pu)C runs have been controlled to within acceptable tolerances (see Table III-14). However, the nitrogen analyses for these runs indicate a higher nitrogen content than the 0.02% that had been obtained previously (ANL-7325, p. 113). Much of the nitrogen and oxygen content in the product is due to impurities present in the original alloy (see Table III-14).

FIG. III-24. Reaction of Methane with Finely Divided Uranium and U-15 wt % Pu Alloy to Form Monocarbide.

TABLE III-14. CHEMICAL ANALYSIS OF UC AND (U,Pu)C POWDER PREPARED BY THE FLUIDIZED-BED TECHNIQUE

Conditions of Preparation

Temperature: 800°C
 Pressure: 2 atm
 Gas composition: 6.2 vol % CH₄-93.8 vol % H₂
 Gas velocity: 12 cm/sec
 Feed material: $\frac{3}{8}$ -in. dia by 1-in. long rods hydrided and dehydrided twice in the fluidized bed

Run No.	Starting Alloy	Product Impurities (figures in parentheses are levels in starting alloy)			
		Carbon (wt %)	Hydrogen (ppm)	Oxygen (ppm)	Nitrogen (ppm)
20	U-15 wt % Pu	4.92	—	340 (170)	1700 (1270)
21	U-15 wt % Pu	5.00	50	270 (170)	830 (1270)
22	U ^e -15 wt % Pu	4.92	180	190 (110)	540 (810)
23	U ^e -15 wt % Pu	4.77	250	320 (110)	270 (810)
24	U ^e -15 wt % Pu	4.75	250	270 (110)	900 (810)
25	U-15 wt % Pu	5.03	80	520 (170)	520 (1270)
26	U	4.76	10	220 (170)	2800 (1280)
27	U	4.79	0.8	130 —	2500 —
30	U-15 wt % Pu	5.05	90	700 (170)	290 (1270)
32	U-15 wt % Pu	4.81	220	680 (320)	450 (20)
33	U ^e -20 wt % Pu	4.75	260	660 (680)	420 (10)

* Indicates enriched uranium.

The volume median particle diameter for the (U, 15 wt % Pu)C produced in the recent runs was determined by sieve analysis to be about 30 to 40 μ m. A recently prepared sample of UC had a volume median diameter of approximately 30 μ m. However, (U, 20 wt % Pu)C containing fully enriched uranium that was prepared in a recent run was much coarser, with a volume median particle diameter of approximately 80 μ m.

Five size fractions of (U, 15 wt % Pu)C with a composite analysis of 5.00 wt % carbon were analyzed individually for carbon content. The analyses of these fractions varied between 4.97 and 5.05 wt %, and there was no significant correlation with the size fraction. This uniformity of carbon content with size distribution is another indication that the extent of carbiding in the fluidized bed is self-limiting at a carbon content slightly above the stoichiometric monocarbide value of 4.80 wt %.

The bulk density of several batches of (U, 15 wt % Pu)C powder varied between 4.4 and 5.0 g/cm³. The bulk and tap densities for (U, 20 wt % Pu)C were about 4.4 and 5.1 g/cm³, respectively, while the corresponding values for UC were 2.5 and 3.8 g/cm³, respectively.

Preparation of plutonium carbide. A single "scouting" run was carried out in which PuC was pre-

pared by reacting methane with plutonium metal. The preparation of powder from bulk feed material was found to be more difficult for plutonium feed material than for either uranium or U-Pu alloy feed material. Since PuH₂ decomposes at a hydrogen pressure of 4 Torr and a temperature of 600°C, which is near the melting point of plutonium, an attempt was made to powder the plutonium by cycling it between PuH₂ and PuH₃ (by adjusting the temperature and pressure) rather than by hydriding and complete decomposition to form the metal. This procedure did not produce the desired results.

The PuH₂ product was ground with a mortar and pestle, and the resulting powder was reacted with H₂-6.2 vol % CH₄. The rate of reaction was low. Analysis of samples of the product indicated an uneven distribution of carbon in the product. X-ray diffraction data indicated that the product was Pu₂C₃ and PuH₂. Some of this material was pressed into a pellet at 75,000 psi and then sintered at 1650°C for 0.5 hr under an argon pressure of 25 Torr. The resulting pellet had a shiny silver appearance and a density of 11.6 g/cm³. The carbon content was 5.59 wt %, which would indicate a mixture of plutonium monocarbide and plutonium sesquicarbide.

b. Pellet Fabrication (D. E. Grosvenor, N. P. Quattronani)

The high-purity UC and (U, 15 wt % Pu)C powders prepared by the metal-methane process were pressed and sintered into pellets to determine the appropriate fabricating techniques for preparing irradiation test specimens. The pellets were pressed directly from the fluidized-bed products to avoid contamination from milling or the addition of binders. Binders have been shown to increase both the oxygen and carbon content of (U,Pu)C pellets.¹ Although the powder prepared in the fluidized bed is judged to be sufficiently free flowing for automatic press feeding, manual feeding was used in these experiments.

The following are typical requirements for the irradiation test pellets that were to be prepared in this program: diameter, 0.255 $\pm$ 0.001 in.; length, 0.3 in.; density, 11.6 $\pm$ 0.4 g/cm³ (85 $\pm$ 3% of theoretical). After determining the approximate fabrication conditions required to meet these specifications, a series of eight (U,Pu)C pellet preparation runs was carried out to define the optimum conditions more exactly and to determine the reproducibility of the pellet character-

¹ J. M. Horspool, N. F. Rose, M. B. Finlayson, "The Fabrication of Uranium-Plutonium Monocarbide Ceramics," *Proceedings of the British Ceramic Society* 7, 23-40, Stoke-on-Trent (February 1967).

FIG. III-25. Effect of Sintering Temperature on (U, 15 wt % Pu)C Pellet Density.

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istics. A single batch of powder was used for the entire series of runs, and ten pellets were prepared in each run.

The pellets were produced at 75,000 psi in a double-acting hydraulic press constructed from components made by Enerpac Test Systems.² The density of the (U,Pu)C pellets was 8.0 ± 0.1 g/cm³. The green pellets produced had satisfactory strength and could be measured and weighed easily without damage. The green pellet diameters were 0.001 to 0.002 in. greater than the corresponding die bore diameter (0.288 in.). Many pellet-pressing operations depend on a binder in the feed material to lubricate the die. However, since no binder was used in these runs, the die was lubricated by pressing a stearic acid pellet after each carbide pellet pressing.

The green pellets were sintered in a high-temperature, high-vacuum furnace³ heated with a graphite resistance element. The pellets were contained in tight-fitting tantalum trays about 2 in. in diameter by $\frac{3}{4}$ in. high during the sintering operation. The bottoms of the trays were covered with thin UC wafers to avoid reaction between the pellets and the tantalum. The sintering procedure involved heating to the sintering tem-

perature in 1 hr, holding at temperature for 30 min, and cooling to near room temperature in 1 hr. This rapid cycle kept plutonium vaporization losses to about 0.2%. The pellets produced by this procedure were silver-gray and had a bright metallic luster.

The effect of sintering temperature on the sintered density of (U,Pu)C pellets shown in Fig. III-25 indicates that a temperature of about 2100°C is required to obtain the desired density of 11.6 g/cm³. The small slope of the density-temperature curve facilitates accurate control of the density. The average density for each of five batches of ten pellets that were sintered at 2115°C varied by only 0.07 g/cm³ from the average of all of the pellets sintered at that temperature. This is a much higher temperature than that used by other experimenters⁴⁻⁶ who found that ~1500°C was suffi-

⁴ L. E. Russell, J. H. Harrison, "The Sintering of UC and (U,Pu)C," in *New Nuclear Materials Including Non-Metallic Fuels*, Vol. 1, p. 543, International Atomic Energy Agency, Vienna (1963).

⁵ R. Ainsley et al, "Carbides as Reactor Fuels: Preparations from Oxides and Sintering Characteristics," in *New Nuclear Materials Including Non-Metallic Fuels*, Vol. 1, p. 349, International Atomic Energy Agency, Vienna (1963).

⁶ J. C. Anderson, A. A. Strosser, "A Reproducible Process for the Preparation of High-Density Uranium-Plutonium-Carbide Pellets," *Chem. Eng. Progr. Symp. Ser.* **63**(80), 76 (1967).

² Enerpac Test Systems, Butler, Wisconsin.

³ Centorr Associates, Inc., Suncook, New Hampshire.

TABLE III-15. FABRICATION OF (U, 15 WT % Pu)C PELLETS
 Pressing conditions: 0.288-in. dia die, 75,000 psi pressure
 Sintering conditions: 1 hr heatup, $\frac{1}{2}$ hr holding, 1 hr cool-down, 25 Torr argon pressure
 Grinding conditions: minimum grinding for uniform diameter within entire batch

Sintering Temperature (°C)	Sintered Density ^a (g/cm ³)	Ground dia (in.)	Weight Change (%)		Pellet Analysis		
			Sintering	Grinding	C (wt %)	O (ppm)	N (ppm)
1800	10.83	0.255	+0.3	-2.5	5.04	465	490
1900	10.97	0.255	-0.2	-2.1	6.03	663	290
2115	11.47	0.251	+0.2	-2.7	4.97	293	340
2115	11.48	0.251	+0.1	-2.7	4.99	530	412
2115	11.54	0.250	-0.1	-2.9	4.97	892	349
2115	11.54	0.2495	-0.2	-3.1	4.93	660	282
2115	11.60	0.2485	-0.2	-3.3	4.96	843	427
2215	11.95	0.246	+0.3	-2.9	4.79	850	443

^a After grinding pellets.

cient for sintering (U,Pu)C produced by other techniques.

The (U,Pu)C produced in a fluidized bed requires a high sintering temperature because of certain characteristics of the feed material such as its coarseness and, perhaps, its high purity. However, the high sintering temperature is not considered to be a disadvantage because of the low plutonium loss inferred from the small weight changes occurring during sintering shown in Table III-15; the short sintering cycle and the argon pressure (25 Torr) are important factors in reducing this weight loss. It is hoped that the high sintering temperature will yield pellets that are dimensionally stable at high irradiation temperatures.

Because of their low green density, the (U,Pu)C pellets shrank 11 to 12% in diameter and about 10%

in length during the sintering process. The pellet shrinkage for a given batch of powder was fairly uniform for the same sintering temperature as shown by the uniform sintered densities at 2115°C in Table III-15. Because of the large and slightly irregular shrinkage during these runs, the pellets varied from the predicted diameter by ± 0.002 in., rather than the desired tolerance of ± 0.001 in. In addition, the pellets were slightly hourglass shaped. This was apparently caused by slight variations in pressure within the pellets during pressing.

A small centerless grinder for grinding the pellets to a uniform diameter was constructed and installed in a helium-atmosphere glovebox. Tests showed that 0.002 in. can be removed from UC and (U,Pu)C pellets in a single pass without using a lubricant and that the finished pellets are of uniform and predictable diameter within the limits of accuracy for measurements that can be made in the glovebox (± 0.0005 in.).

Several batches of UC pellets were also fabricated. The UC pellets met the 11.6-g/cm³ density requirement and the diametral specification of 0.255 ± 0.001 in. when sintered at 1710°C for 2 to 3 hr. The achievement of satisfactory density at a lower temperature than is required for (U,Pu)C pellets may be due to a higher oxygen content in the UC powder.

Analyses of two (U,Pu)C pellets from each sintering run are shown in Table III-15. The nitrogen content is about the same as that of the metal alloy feed material and the oxygen content is about twice that of the alloy. Preparation of high-purity (U,Pu)C pellets from high-purity feed material should be attainable on a routine basis, since the preparation and handling of high-purity powder without introducing contaminants has been demonstrated.

2. Synthesis of Carbides by Conversion from Oxides (J. T. Holmes, J. R. Pavlik)

A fluidized-bed process was studied for converting UO₂ to UC. The process involved making composite particles to UO₂ and graphite and reacting them at 1450 to 1800°C in a 2-in. dia fluidized-bed reactor using an inert gas (helium or argon) for fluidization. A schematic of the reactor is shown in Fig. III-26. The rate of reaction was relatively high in all of the twelve runs made in the study. Projections to plant scale indicate that at least 30 kg per day of UC could be produced in a 12-in. dia fluidized-bed reactor. However, two significant problems were encountered in these runs: sintering of the product and high oxygen content.

Some or all of the particles sintered together in each of the runs. When the reaction neared completion, some of the particles would stick to the graphite reactor walls or to the molybdenum thermocouple well. Other particles would then sinter to the previously immobilized particles until part or all of the bed was completely immobilized. Bed sintering prevents rapid removal of the product and, therefore, in its present state of development, this fluidized-bed process is no more attractive than existing batch or semicontinuous processes. The run having the least sintering was carried out at 1450°C (the lowest temperature in the se-

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FIG. III-26. Fluidized-Bed Reactor Used for UO_2 -Carbon Reaction Study.

ries) with the largest particles, 1.41 to 2.00 mm in diameter. Only a few dozen particles were stuck to the reactor wall at the end of the run. It is possible that many similar runs could be carried out before it would be necessary to cool the bed to room temperature and remove the sintered material. However, the residual oxygen content after a long reaction time of 450 min was an unacceptably high 0.78 wt %. Difficulties experienced in sintering mixed uranium-plutonium carbides into fuel pellets suggest that bed sintering might not be a problem if mixed uranium-plutonium oxides were used as the starting material, rather than UO_2 alone. However, testing this possibility is beyond the scope of this study.

The lowest residual oxygen content obtained in any of the runs, 0.22 wt %, was achieved in a run at 1550°C where a small amount of nickel was added to the particles. The lowest oxygen content for the runs without the nickel additive, 0.38 wt %, was achieved in a run at 1550 to 1650°C where a large excess of carbon was available from an intermittent methane gas treatment. The residual oxygen content in the product carbide compares quite well with the oxygen content of carbides obtained from other carbothermic reduction processes. The carbon stoichiometry of the fluidized-bed reaction product is close to that expected, based on complete reaction of the starting materials and allowing for the unreacted oxygen in the product.

Although the fluidized-bed process is capable of high production rates and gives a product of acceptable purity, bed sintering has not been eliminated at temperature levels where low oxygen content can be attained ($>1550^\circ\text{C}$), and rapid removal of all of the reaction products from the fluidized-bed reactor has not been achieved. Work on the fluidized-bed process has been suspended because of these difficulties and to allow the effort to be directed toward development of the plasma-torch process described below. The work is reported in detail in a topical report, ANL-7482.

Plasma-torch process. The use of a plasma-torch reactor for continuously converting uranium oxide to the monocarbide is being investigated. Small (100 mesh) composite particles of uranium oxide and carbon will be reacted in the flame of an inductively heated plasma torch. The carbide product will probably be in the form of small, free-flowing spheres. The CO reaction product will be removed from the reaction chamber with the inert plasma-forming gas. Equipment construction is under way, and the initial runs are being planned.

IV

Reactor Safety¹

(*R. O. Ivins, A. D. Tevebaugh, J. D. Bingle*)

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

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 SPERT-1 and BORAX-1 destructive tests. In addition, the reaction of the cladding metal changes the character of the cladding (oxide formation), which can affect its physical behavior. Studies of these chemical reactions and physical interactions are being carried out so that realistic estimates can be made of their rates and extents during hypothetical reactor accidents.

The interactions with water of the reactor fuel materials of interest are being studied by experimental and calculational methods. Experimental studies include both in-pile and out-of-pile simulations of loss-of-coolant accidents, in-pile meltdown studies of excursion accidents, and studies of heat transfer and pressure generation resulting from the reaction of reactor materials with water. Correlations of experi-

mental results are used to develop methods for accident analysis.

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) high-temperature physical properties of fast reactor materials; (2) chemical and physical interactions of the fuel, cladding, and coolant; (3) transient heat transfer associated with the dispersal of fuel and cladding materials into liquid sodium; (4) in-pile meltdown of typical fast-reactor fuel materials; (5) reaction of sodium with air; and (6) fuel migration and segregation in mixed uranium-plutonium compounds. In addition, a study of the propagation of fast-reactor fuel element failure has been initiated in conjunction with other Argonne Divisions.

The results of the tasks on high-temperature physical properties and on fuel migration and segregation are described in Section III.A of this report. In September 1968, the remainder of the work on reactor safety (both thermal and fast) that had been the responsibility of the Chemical Engineering Division was transferred to the Reactor Engineering Division. Results of these studies are reported here only in summary form and are reported in more detail in an annual report describing all safety-oriented studies at Argonne National Laboratory.

¹ A summary of this section is given on pages 11 to 12.

A. THERMAL REACTOR SAFETY STUDIES

1. Studies Relating to the Analyses of Loss-of-Coolant Accidents

(*J. C. Hesson, K. Nishio*)

A loss-of-coolant accident, assumed to be caused by a break in a primary-system water pipe, has been taken to be the "maximum credible accident" or "de-

sign basis accident" for most of the power reactors built to date. The loss of water (moderator) following the pipe break causes the reactor to shut down (nu-

near) and leaves the core in contact with steam. In the absence of auxiliary cooling, decay of fission products in the core releases sufficient energy to cause the fuel cladding to be heated, within a few minutes, to temperatures at which metal-steam reactions can occur.

Analyses of the behavior of a reactor core during a loss-of-coolant accident in a water-cooled power reactor have continued. These studies have included analytical calculations and experimental laboratory simulations. The analytical calculations have resulted in the CHEMLOC-II computer program described in detail in a topical report.² This program covers the case of emergency coolant failure and describes the core heating and chemical reactions of cladding with steam from the end of blowdown through core heat-up,

² J. C. Hesson, J. L. Anderson, R. O. Ivins, "CHEMLOC-II: A Computer Program Describing the Core Heating and Cladding-Steam Reaction for a Water-Cooled Power Reactor following a Loss of Coolant," ANL-7361 (April 1968).

2. Studies Relating to the Analyses of Excursion Accidents (J. J. Barghusen, K. A. Varteressian, F. Testa, G. Rogers, L. Harrison³)

The general objective of the in-pile studies of excursion accidents is to contribute to the development of experimental and theoretical information needed for the analysis of accidents in water-cooled thermal reactors. The experiments have been designed to simulate an uncontrolled nuclear excursion that can cause an immersed fuel element to overheat, with possible melting or vaporization and reaction with water. Fuel-failure thresholds and mechanisms are examined. The energy release resulting from metal-water reactions may exceed that which would be expected from the nuclear energy release in an excursion. Molten fuel or cladding materials could be dispersed in water and result in a violent and destructive steam explosion. The hydrogen evolved from the chemical reaction with water can also react with the oxygen present in the containment building and release considerable energy.

Additional in-pile (TREAT facility) photographic experiments were conducted to study the high-temperature behavior of Zircaloy-2-clad fuel rods during a reactor transient. Five experiments using sintered UO₂ pellets and six experiments using vibrationally compacted UO₂ powder were conducted. The failures were found to follow two different patterns, which appear to be the result of different mechanisms:

(1) a prompt failure generally occurring during the power transient and manifested by a rapid pressurization in the cladding, a vigorous rupture of the clad-

ding, and injection of some of the fuel into the coolant, and

(2) a delayed failure occurring after the transient due to weakening of the cladding by excessive temperatures and reaction with water and UO₂ fuel.

Figure IV-1 shows the failure behavior pattern of the fuel rods as a function of total transient energy and reactor period. In the figure the nature of the residue is classified in four categories: complete destruction, broken into large sections, holes or blisters,

TABLE IV-1. FAILURE PATTERN OF SINGLE INDUCTIVELY HEATED SIMULATED FUEL RODS DURING OUT-OF-PILE LOSS-OF-COOLANT EXPERIMENTS

Quench Temperature (°C)	Power On After Quench Initiated		Power Off After Quench Initiated	
	Top Quench	Bottom Quench	Top Quench	Bottom Quench
1064	I ^a			
1182	I			
1462 to 1498	I	I		I
1534 to 1569	F ^b	I	I	
1646 to 1663	F	F	F	I
1798				F
1849 to 1868	F		F	F
2050 to 2110	FF			

^a I indicates that test rod remained intact.

^b F indicates that test rod failed.

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FIG. IV-1. Behavior of Zircaloy-Clad UO₂ Fuels in TREAT Photographic Tests.

and intact. Prompt failures generally result in the first two categories and delayed failures in the second and third categories. Computational studies have been continued. The studies have resulted in simple but valid

computational procedures which, utilizing available material property data, enable a reasonable definition and prediction of fuel rod failure thresholds consistent with the experimental observations.

3. Pressure Generation due to Particle-Water Energy Transfer (*D. R. Armstrong, D. Cho, J. C. Hesson, W. Gunther, J. Peck, M. Silverman, C. Stretch*)

To analyze adequately the consequences of an accident in a water-cooled thermal reactor in which hot fuel materials are injected and dispersed into the water coolant, a knowledge of the manner in which large amounts of energy are transferred from these particles to the liquid coolant is needed. Such a process can occur in either an excursion or loss-of-coolant accident and could result in an explosive generation of steam. A better understanding of the dispersal mechanisms and of the nature of steam vapor formation around the hot particles, as well as a knowledge of the pressures and forces generated due to the vapor formation, is needed.

Theoretical and experimental studies of pressure generation due to reactions of hot or molten core materials with water have continued. The studies have included (1) heat transfer rates from small hot spheres moving in water, (2) pressure pulses and forces generated during heat transfer from hot spheres and molten metals falling through a water column, and (3) investigation of steam explosions.

Laboratory experiments are being conducted by two different techniques. In the first of these, the boiling heat transfer occurring between small moving particles and water is being studied by the swinging-arm method. The second technique employs a pressure transducer to measure the forces produced, as a result of void formation, when small hot particles fall into a water column.

In the heat-transfer studies, 1/4- and 1/2-in. dia silver spheres and 1/2-in. dia stainless steel spheres have been used. Experimental conditions have included velocities from 2.5 to 25 ft/sec, water temperatures from 20 to 90°C, and sphere temperatures from 100 to 800°C. Due to the high thermal conductivity of silver, the temperatures throughout the silver spheres were fairly uniform during their passage through the water, and the heat-transfer rates were largely dependent upon the heat-transfer coefficient at the surface film. However, in the case of the stainless steel, which has a lower thermal conductivity, there were large temperature variations throughout the spheres. The heat-transfer

rates with stainless steel spheres were largely dependent upon heat conduction within the spheres and thus relatively independent of the heat-transfer coefficient at the surface film. These experiments confirm the theory that for transient heat transfer from the interior to the surface of a sphere, a small radius compensates for low thermal conductivity. Thus, small particles of material having a poor thermal conductivity, such as UO_2 , could transfer their heat as rapidly as much larger particles of a good conductor, such as silver.

In the pressure-pulse column studies, pressure pulses due to dropping stainless steel and silver spheres as well as molten bismuth into water columns have been measured. The dynamic pressures are inversely proportional to the cross-sectional area of the water column and directly proportional to the depth of the water over the spheres or bismuth, as predicted by

simple theory. In the model, the water is assumed to be noncompressible. The dynamic pressures are greatest at transition from quiet to violent boiling. The pulses were found to be greater for molten bismuth than for solid silver or stainless steel under similar conditions. This is caused by the dispersal of the bismuth into fine particles with a larger surface and thus a greater heat-transfer rate. High-speed motion pictures of the hot metals dropping into the water column were taken and screen size analyses of the fragmented bismuth were made.

In the investigations of steam explosions, the literature has been surveyed and several calculations have been performed. Small steam explosions have been produced by injecting small amounts ($\sim 1 \text{ cm}^3$) of water into molten tin and molten potassium iodide. High-speed motion pictures of these phenomena were taken.

B. FAST REACTOR SAFETY STUDIES

1. Interactions of Fuel, Cladding, and Coolant (*D. R. Armstrong, W. Gunther*)

An accident in a nuclear reactor can result in the contact of large quantities of molten fuel materials with the reactor coolant. If these materials break up into small droplets of high surface area, explosive pressures can be generated. This breakup or fragmentation could occur by any of several mechanisms: dynamically, because of the relative velocity of molten material and coolant; by Taylor instability owing to

acceleration forces; or by encapsulating portions of the coolant within the mass of molten material.

A survey study of the velocity and acceleration effects on fragmentation using the system water-tin has been conducted. These studies show that the extent of fragmentation is dependent upon the relative velocity of tin and water and that acceleration effects due to violent boiling on the surface of the tin enhance the fragmentation.

2. Pressure Generation due to Violent Meltdown (*D. R. Armstrong, K. A. Varteressian, J. J. Barghusen, J. C. Hesson, F. Testa, G. Rogers, J. Boland³*)

The study of forced-convection heat transfer from hot spheres in liquid sodium has continued. A series of experiments has been conducted to determine the heat transfer rates for a $\frac{1}{2}$ -in. dia sphere swinging through a sodium bath at temperatures of 500–650°C.

The first TREAT meltdown experiment in a sodium-filled piston autoclave has been conducted. The double-containment autoclave containing a cluster of five stainless steel-clad, UO_2 -core fuel rods and four dummy rods submerged in sodium was subjected to three transients (energies of 214, 330, and 340 cal/g UO_2).

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FIG. IV-2. Portion of Ruptured Fuel Rod Showing Failure.

³ Idaho Division.

After the third transient, the autoclave was disassembled and the fuel-rod cluster removed. The center rod of the cluster had failed, allowing approximately 60% of the UO_2 to escape. Figure IV-2 shows the split in the cladding located at the top of the fueled section of the rod. None of the others showed any signs of rupturing or crushing; however, all of the rods were warped.

One of the reactor accident situations that is being studied involves the generation of high-pressure waves by the rapid heating of liquid sodium under acoustic

constraint. In case of water, it has been shown that this situation can lead to "steam" explosions with the generation of high pressures in the system. A one-dimensional calculational model for "steam" explosions has been developed, employing conditions of acoustic constraint. A combined heat transfer-surface area generation rate of energy transfer is used as an input parameter. As an example of its use, this model has been applied to the SPERT-1D excursion test. Application of the model to the sodium system is being investigated.

3. Violently Sprayed Sodium-Air Reaction (*T. S. Krolkowski, L. Leibowitz, R. E. Wilson, J. Cassulo*)

Safety analyses of sodium-cooled nuclear reactors must consider the potential hazards associated with sodium-air reactions because of the significant release of energy which accompanies these reactions. The first

phase of a study of the reaction rate of molten sodium sprays with air and air depleted in oxygen has been completed.

A mathematical model was developed to predict the burning rate and burning temperature of a single spherical sodium particle moving through an oxygen-nitrogen atmosphere. The model was based on the assumption that the reaction rate is controlled by the diffusion of oxygen to a vapor-phase combustion zone surrounding the particle. Then, to correlate the reaction rates of the individual particles forming a spray with the burning rate of the spray itself, a quasi-steady state approach and an averaging technique were used. The pressure rise in the volume enclosing the spray was also calculated.

The apparatus used in the experimental portion of this work has been described previously (see ANL-7325, p. 177). Briefly, it consists of a pneumatically operated, piston spray-injector which discharges approximately 10 g of molten sodium through a set of orifices into a chamber of known volume. The orifice pattern has six holes equally spaced on a 0.25-in. dia circle, with a seventh hole located at the center of the circle. Two different orifice plates are available, one with 0.010-in. (0.0254-cm) and one with 0.030-in. (0.0762-cm) dia holes.

Pressure-rise rates due to the sprayed sodium-air reaction were measured as functions of the ambient oxygen concentration, orifice size, and spray velocity. The experimental data were compared on a reduced pressure-rise rate basis, $(\text{atm/sec}) / (\text{g Na/cm}^3)$. The pseudo-concentration factor, g Na/cm^3 , is the weight of "in-flight" burning sodium in the spray, at any time after the spray reaches the top of the chamber, divided by the volume of the chamber. This conversion serves

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FIG. IV-3. The Effect of Ambient Oxygen Concentration on the Experimental Pressure-Rise Rate.

to eliminate the restrictions of sodium mass flow rate and chamber geometry.

The experimental reduced pressure-rise rate for the two orifice sizes as a function of the initial oxygen concentration in the spray chamber is shown in Fig. IV-3; calculated curves are also shown.

A detailed topical report⁴ on both the experimental and calculational studies of the violently sprayed sodium-air reaction has been published.

⁴T. S. Krolkowski, "Violently Sprayed Sodium-Air Reaction in an Enclosed Volume," ANL-7472 (Sept. 1968).

4. Fuel Failure Propagation (*R. E. Wilson, R. O. Ivins, M. Deerwester*)

A program was initiated in cooperation with other Argonne Divisions to study the possibility and consequences of the propagation of fuel element failures to neighboring elements under near-normal reactor operating conditions. The goal of the program is to develop a predictive analytical description of fuel element failure propagation by using both experimental and analytical techniques. The experimental techniques consist of out-of-pile and in-pile tests to determine the important variables governing the modes of transport of fuel element failure from the initial element failure to failure of the neighboring fuel elements.

Prior to the transfer of this work to the Reactor Engineering Division, the Chemical Engineering Division efforts were in overall program planning and in

aiding with the out-of-pile experiments, which utilize both water and sodium loops to study the specific modes of failure transport. Some preliminary water-loop tests of fission-gas-release behavior from a breached fuel element were carried out.

Feasibility has now been established for the design, construction, installation, and operation of an in-pile dynamic sodium package loop in the Engineering Test Reactor. The package loop can simulate an LMFBR environment and can accommodate a fuel element bundle (7 or 19 fuel elements) for integrated failure propagation tests. A set of initial in-pile tests has been defined, which will form the basis for both the design of the in-pile loop and for the interaction of the analytical and experimental studies.

V

Energy Conversion¹

(E. J. Cairns, A. D. Tevebaugh, J. D. Bingle)

The use of electrochemical cells and systems for the conversion of thermal energy to electrical energy and for the storage of electrical energy continues to be an area of potential importance in the effective use of nuclear and radioisotopic energy. Thermal energy from nuclear reactors or radioisotopes can be converted into electricity in thermally regenerative galvanic cells at efficiencies approaching the Carnot-cycle efficiency. Reasonable temperatures for the heat source are 700–1300°C and for the heat sink, 270–680°C. The corresponding system efficiencies are expected to be 12 to 25%, depending on operating conditions. The cell portion of the thermally regenerative galvanic cell system can operate at high power densities and can be electrically recharged in less than fifteen minutes (ANL-7055, p. 226; ANL-7225, p. 221; ANL-7375, p. 165). These experimental results prompted the investigation of systems which showed promise as electrically rechargeable (secondary) cells for use as high-specific-power (W/lb), high-specific-energy (W-hr/lb) devices for energy storage (ANL-7425, pp. 182, 185).

The systems of possible interest for use in thermally regenerative cells and secondary cells have been selected using a set of guidelines based on electronegativity, equivalent weight, conductivity, exchange-current density, solubility, and (for thermally regenerative systems) vapor pressure.² The application of these guidelines resulted in the selection of lithium and sodium as the two most promising anode materials. Tin, lead, and bismuth appeared most promising as cathode materials for thermally regenerative cells, whereas tellurium, selenium, sulfur, and phosphorus were selected as cathode materials for secondary cells. The variety of systems and the range of requirements for the cells have made it necessary to carry out a broadly based research program to provide the required thermodynamic, electrochemical, and physicochemical data. The cells and the corresponding systems can be

divided into two groups: those having lithium anodes and those having sodium anodes.

Lithium is preferred as the anode material for thermally regenerative cells to be used with heat sources above 1000°C because its vapor pressure is lower than that of sodium. In addition, the cell portion of the system can be operated at lower temperatures because of the lower melting points (264–342°C) of lithium halide electrolytes, resulting in lower self-discharge rates. For secondary cells, lithium is the preferred anode material because of its low equivalent weight, low electronegativity, and low solubility in its halides, and because of the low melting points of lithium halide electrolytes.

Sodium, because of its higher vapor pressure, is the preferred anode material for thermally regenerative cells when the heat-source temperature is below about 1000°C. Secondary cells with sodium anodes may also find application in special circumstances—for example, a relatively high-temperature environment (above 550°C).

The research program of the energy conversion group for the period 1961–1966 was summarized in the topical report, ANL-7316. Subsequent work has been reported in ANL-7375, pp. 160–175, ANL-7425, pp. 172–189, and in the open literature.^{3–6}

³ V. A. Maroni, E. J. Cairns, "A Review of Raman Spectroscopy of Fused Salts and Studies of Some Halide-Containing Systems," Abstracts of Papers, 156th Amer. Chem. Soc. Mtg., Atlantic City, N. J., Sept. 8–13, 1968, ANAL-30.

⁴ H. Shimotake, G. L. Rogers, E. J. Cairns, "Secondary Cells with Lithium Anodes and Immobilized Fused-Salt Electrolytes," *Ind. Eng. Chem. Process Des. Develop.* **8**, 51 (1969).

⁵ H. Shimotake, E. J. Cairns, "A High Rate Lithium/Selenium Secondary Cell with a Fused-Salt Electrolyte," Comité Intern. de Thermodynamique et de Cinétique Electrochimiques, Intern. Union Pure and Appl. Chem., 19th Meeting, Detroit, Sept. 23–27, 1968. Extended Abstracts, pp. 254–255.

⁶ H. Shimotake, E. J. Cairns, "A Lithium/Tin Cell with an Immobilized Fused-Salt Electrolyte: Cell Performance and Thermal Regeneration Analysis," Intersoc. Energy Conversion Eng. Conf. 1968 Record, pp. 76–91, IEEE, New York (1968).

¹ A summary of this section is given on pages 13 and 14.

² E. J. Cairns, H. Shimotake, "High Temperature Batteries," *Science* (in press); also, ANL-7316, p. 33.

A. CELLS WITH LITHIUM ANODES

Thermally regenerative and secondary cells with lithium anodes continue to be attractive for a range of possible applications from topping units and off-peak energy storage devices to specialty power sources for space, military, industrial, and perhaps, ultimately,

consumer applications. The research program has continued to gather the needed thermodynamic and electrochemical information necessary for the choice of the best systems, designs, and operating conditions for these applications.

1. Thermodynamics of the Lithium-Tin System by the Vapor-Liquid Equilibrium Method (*A. K. Fischer, S. A. Johnson*)

The lithium-tin system is being investigated for application in a thermally regenerative galvanic cell. The rational design of a regenerator requires knowledge of the liquid-vapor equilibrium. Thus, the vapor pressures and vapor-phase compositions for the lithium-tin

system were determined for the full composition range at 1200°C (a likely regeneration temperature) and for selected compositions at lower temperatures (<1000°C). The data were collected mainly by transpiration techniques. Where the behavior of lithium-

FIG. V-1. Schematic Diagram of High-Temperature Transpiration Apparatus.

rich mixtures made the transpiration method impractical, a boiling-point method was used to obtain the total vapor pressure.

As discussed in ANL-7425, p. 175, the high-temperature transpiration apparatus was redesigned for use with the lithium-tin system. The redesigned apparatus is shown schematically in Fig. V-1. The liquid-metal sample is contained in a tall tantalum can (10), which rests inside a stainless steel furnace well (8) connected to a helium-atmosphere glovebox. Three openings penetrate the cover plate (5); two of these permit gastight positioning of the tantalum thermocouple well (11) and of the tantalum quench tube (7), whereas the third is the carrier-gas inlet (4). A quick-disconnect fitting (3) at the top of the quench tube allows gastight positioning of the collector tube (2), which has an orifice at the bottom (12).

To protect the stainless steel furnace well from oxidation by air at 1200°C, the well is surrounded by a tubular alumina enclosure (13) filled with argon. Tantalum heat shields (9) inside the tantalum can help to maintain the sample region at a uniform temperature. Heat is supplied by a platinum-wound resistance furnace.

At the beginning of an experiment, while thermal equilibrium is being established, argon carrier gas enters the collector tube at the top (2) and exits through the inlet tube (4). (This keeps the collector tube free of spurious vapor and condensate.) When sample collection is to begin, the gas flow is reversed so that argon enters at (4) and exits at (2). The sample is condensed in the upper part of the collector tube, and the gas volume is measured. To terminate an experiment, the gas is made to enter the quench tube at (1) and to

leave at (4) while the collector tube is raised quickly to bring the orifice inside the quench tube. By this means, the orifice is brought into a cool region while gas streams over it but not through it. The condensed lithium sample is subsequently dissolved out of the collector tube with water and hydrochloric acid and analyzed by flame photometry.

The data from the transpiration experiments at 1200°C are presented in Table V-1. Tin vapor pressures and the tin content of the vapor were calculated from the tin activity coefficients obtained by a Gibbs-Duhem integration. The pressure-composition diagram for the lithium-tin system is presented in Fig. V-2 and the activity coefficient curves are shown in Fig. V-3.

Useful information for regenerative cell design is available from Fig. V-2. For example, Fig. V-2 shows that at 1200°C a cathode alloy with 60 at. % lithium has a total vapor pressure of 18.8 Torr and a vapor composition of 2.52×10^{-3} at. % tin.

The low-temperature (635–880°C) series of transpiration experiments was performed by techniques that have been described previously (ANL-7055, p. 222). The objective of these experiments was to determine the critical pressure below which solid will deposit in the regenerator and interfere with cell operation (see ANL-7125, p. 220). The lithium-tin phase diagram indicates two compounds, Li_4Sn and Li_7Sn_2 , in the region of 80 at. % lithium. Transpiration measurements were, therefore, made at 79, 80, 81, 85.5, and 90 at. % lithium. The results of these measurements are shown in Fig. V-4. Three of the curves, for 79, 81, and 85.5 at. % lithium, represent measurements on compositions and temperatures such that the system contained solid as well as liquid and vapor. The 81 and 85.5 at. %

TABLE V-1. EXPERIMENTAL AND CALCULATED RESULTS OF TRANSPIRATION MEASUREMENTS OF THE LITHIUM-TIN SYSTEM AT 1200°C.

Atom Percent Lithium in Liquid	Total Lithium Vapor Pressure (Torr)	Monatomic Lithium Vapor Pressure ^a (Torr)	Activity of Lithium	Activity Coefficient of Lithium	Activity Coefficient of Tin ^b	Activity of Tin ^b	Vapor Pressure of Tin ^b (Torr)	Atom Percent Tin in Vapor
10.0	0.266	0.266	1.09×10^{-3}	0.0109	0.994	0.895	4.56×10^{-3}	1.69
20.0	0.705	0.705	2.89×10^{-3}	0.0144	0.947	0.758	3.86×10^{-3}	0.544
29.6	1.62	1.62	6.63×10^{-3}	0.0223	0.817	0.574	2.93×10^{-3}	0.181
30.0	2.41	2.41	9.87×10^{-3}	0.0328	0.695	0.486	2.48×10^{-3}	0.103
40.0	4.84	4.83	0.0198	0.0496	0.553	0.332	1.69×10^{-3}	0.0349
50.0	9.2	9.2	0.0377	0.0754	0.388	0.194	9.89×10^{-4}	0.0107
60.0	19.1	18.9	0.0775	0.129	0.195	0.0780	3.98×10^{-4}	2.08×10^{-3}
70.0	46.2	45.3	0.186	0.266	0.0517	0.0155	7.91×10^{-5}	1.71×10^{-4}
80.0	90	86.6	0.354	0.442	0.0108	2.16×10^{-3}	1.10×10^{-5}	1.22×10^{-5}
90.0	195	180	0.739	0.821	2.57×10^{-4}	2.57×10^{-5}	1.31×10^{-7}	6.71×10^{-8}

^a Calculated using the equilibrium constant for the reaction $\text{Li}_2(\text{g}) \rightleftharpoons 2\text{Li}(\text{g})$. Data for evaluation of this constant came from B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, *J. Amer. Chem. Soc.* **77**, 2144 (1955). The value of the constant was 2.887 at 1200°C for pressures in atmospheres.

^b These values were calculated from the Gibbs-Duhem integration.

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FIG. V-2. Pressure-Composition Phase Diagram for Lithium-Tin System at 1200°C.

308-1756

FIG. V-3. Activity Coefficients for Lithium-Tin System at 1200°C.

308-1793

FIG. V-4. Solid-Liquid-Vapor and Liquid-Vapor Equilibrium Curves for the Lithium-Tin System (based on low-temperature transpiration experiments).

lithium curves reflect the presence of one compound and have approximately the same slope. By determining the temperature of complete melting of these compositions from the phase diagram and then extrapolating the curves to the respective melting temperatures, the pressure that defines the limit between liquid-vapor and liquid-vapor-solid equilibrium is obtained. All curves have been extrapolated to this point, which is marked on the graph with a perpendicular bar that terminates the line. The 79 and 81 at. % curves both show this point at 0.41–0.42 Torr. For the lithium-richer systems, 85.5 and 90 at. % lithium, the point falls at considerably lower pressures.

It can be concluded from the above data that a lithium/tin thermally regenerative galvanic cell should be operated at pressures greater than 0.42 Torr. Because this is a rather low limiting pressure, there will be considerable latitude in the choice of operating pressures that optimize the throughput of the cell reactants and maximize the thermal efficiency of the system. A temperature-composition phase diagram will be constructed for the system, using these vapor-liquid equilibrium data. This diagram can then be used to determine the number of equilibrium stages (theoretical plates) needed in the regenerator if fractionation of the vapor is necessary.

2. Thermodynamics of the Lithium-Tellurium System by an Emf Method (M. S. Foster, G. H. Kucera)

The optimum operating conditions for a lithium/tellurium cell may be predicted by considering the thermodynamics of the lithium-tellurium system. Previously, the free energy of formation of $\text{Li}_2\text{Te(s)}$ at 798°K was determined by means of emf studies⁷ to be -77.9 kcal/mol. The first results of emf studies of lithium/tellurium cells were also reported (ANL-7425, p. 173). These studies have now been completed for several cathode alloy compositions over the temperature range 660 to 840°K .

The cell apparatus consisted of two porous BeO crucibles immersed in a common bath of electrolyte (LiF-LiCl-LiI eutectic). One crucible contained the liquid lithium anode, and the other contained the lithium-tellurium alloy cathode. To avoid the rapid exothermic reaction that occurs when liquid lithium is added di-

rectly to liquid tellurium, the cathode alloy was formed *in situ* in the following manner. A weighed quantity of tellurium was placed in the porous BeO crucible, a layer of molten electrolyte was added, and a weighed quantity of lithium was floated on the electrolyte. A tungsten rod was then lowered into the cup to form a shorted electrochemical cell. All of the lithium was thereby transferred electrochemically into the tellurium.

The open-circuit voltage of the cell was measured potentiometrically at various temperatures between 660 and 840°K , with cathode compositions of 8.6, 17.2, 26.3, 30.3, and 33.2 at. % lithium in tellurium. These cathode compositions were established by analysis of the cathode material after the experiment was completed. The temperature changes were made in random order to avoid possible systematic errors which could

⁷ M. S. Foster, C. C. Liu, *J. Phys. Chem.* **70**, 950 (1966).

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FIG. V-5. Emf-Temperature Characteristics of the Lithium/Tellurium Cell as a Function of Cathode Composition.

be caused by slow thermal equilibration. Under conditions corresponding to the formation of a solid phase in the cathode alloy, supercooling was prevented by vibrating the cathode alloy.

The emf of the experimental cells as a function of temperature is shown in Fig. V-5. Three regions of solid formation in the cathode alloy can be identified. For the cell with a cathode composition of 33.2 at. % lithium, a change in slope is noted near 720°K. Below this temperature, solid Li_2Te is present in the alloy (see following section for further discussion of the lithium-tellurium phase diagram). For the cell with a cathode composition of 17.4 at. % lithium, two changes of slope are noted in the emf-temperature

curve. The first, near 727°K, is assigned to the temperature at which " LiTe_3 " precipitates. The second, near 703°K, is assigned to the temperature at which a solid eutectic mixture of " LiTe_3 " and tellurium forms.

From the emf data for the cell with a cathode of 33.2 at. % lithium, the free energy of formation of Li_2Te at 720°K was calculated to be -77.9 kcal/mol (the same value as reported previously⁷ for 798°K). The free energy of formation of " LiTe_3 " was calculated to be -23.7 kcal/mol at 727°K from the emf data for the cell containing a cathode alloy of 17.4 at. % lithium.

A more complete thermodynamic analysis of the emf data of the lithium/tellurium cell is planned for the future.

3. Phase Equilibrium Studies of the Lithium-Tellurium System (M. S. Foster, C. E. Johnson, K. A. Davis, J. Peck, R. Schablaske⁸)

The solid-liquid equilibria in the lithium-tellurium system have been defined by thermal analysis and X-ray diffraction studies. The crystallization temperatures obtained from thermal analysis experiments are shown in Table V-2. Because cooling curves exhibited a supercooling phenomenon which reduced their usefulness, these data were obtained only from slow-heating curves. The compositions shown were obtained by chemical analysis.

Several lithium-tellurium alloys, which were prepared by direct combination of the elements and annealed at 350°C for 28 days, were examined by X-ray diffraction. The results, also shown in Table V-2, indicate the presence of a compound, tentatively designated as LiTe_3 , which has a body-centered cubic structure with a lattice constant of 6.162 Å. Although

an alloy of the exact 1:3 stoichiometry has not been examined, the pattern of the new phase, which is strongest at 78 at. % tellurium, suggests this stoichiometry. The characterization of this phase as LiTe_3 , rather than LiTe , is also consistent with the observation that the X-ray pattern is very weak for an alloy containing 43 at. % tellurium.

As mentioned in the preceding section, the emf data suggest that a new phase precipitates when an alloy containing 17.4 at. % lithium (82.6 at. % tellurium) is cooled to 727°C. If this phase were LiTe , then it should also precipitate from an alloy containing 33.2 at. % lithium (66.8 at. % tellurium) upon cooling. This does not seem to be the case, since the slopes and locations of the emf-temperature lines are considerably different for the two temperature regions where solids are present. Therefore, Li_2Te and LiTe_3 are as-

⁸ Analytical group, Chemical Engineering Division.

TABLE V-2. RESULTS OF THERMAL ANALYSIS AND X-RAY DIFFRACTION STUDIES OF THE LITHIUM-TELLURIUM SYSTEM

Composition (at. % Te)	Crystallization Temperature ^a (°C)		X-Ray Diffraction Analysis of Annealed Alloy ^b
	Liquidus	Eutectic	
94.6	442.9	423.7	Te
85.0	451.7	424.2	—
82.0	—	—	"LiTe ₃ " major phase, Te intermediate
77.9	467.0	427.1	"LiTe ₃ " major phase, Te very minor
70.0	(none observed)	453.3	—
43.0	—	—	Li ₂ Te major phase, "LiTe ₃ " very minor

^a From slow-heating curves.^b After annealing at 350°C for 28 days.

signed as the two compounds of lithium and tellurium in alloys containing more than 33 at. % tellurium.

The lithium-tellurium phase diagram from 50 to 100 at. % tellurium is shown in Fig. V-6. The phase diagram shows that the cathode alloy in a lithium/tellurium cell operating at 480–500°C can contain up to about 35 at. % lithium before the precipitation of solid Li₂Te occurs. At higher compositions of lithium, solid Li₂Te will be formed in the cathode and must be redissolved during recharge of the cell.

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FIG. V-6. Tellurium-Rich Portion of Lithium-Tellurium Phase Diagram.

4. Phase Equilibrium Studies of Lithium Halide-Containing Electrolytes (C. E. Johnson, M. S. Foster)

The application of fused-salt mixtures as electrolytes in electrochemical cells has resulted in increased interest in their physical and chemical properties. In selecting fused-salt mixtures for electrolytes, a variety of factors must be considered. For example, the use of low-melting cathode materials requires low-melting electrolytes. Also, high electrical conductivity is desirable to reduce ohmic losses within the cell. Fused alkali halides generally meet these requirements. Particular emphasis has been placed on the lithium halides, since these salts have the lowest melting points of the alkali halide series.

For a specific salt system which may be of interest, it is, of course, desirable to locate the minimum temperature, its corresponding chemical composition, and the general topological characteristics of the system with a minimum of effort. Such knowledge would be beneficial in choosing appropriate electrolytes without undue delay.

A perturbation theory, the conformal ionic solution

TABLE V-3. CRYSTALLIZATION TEMPERATURES FOR THE LiCl-LiI-KI System

Series I Mole Ratio LiCl:LiI 1:1		Series II Mole Ratio LiCl:LiI 3:7		Series III Mole Ratio LiI:KI 6:4	
mol % KI	Temperature (°C)	mol % KI	Temperature (°C)	mol % LiCl	Temperature (°C)
30.0	399.5	20.0	341.3	20.0	330.0
35.0	392.1	25.0	338.0		
47.3	436.8	31.5	330.0		
		38.3	346.1		

theory,⁹ has been used to calculate topological characteristics of reciprocal salt systems, i.e., systems having two anions and two cations. (This theory was reviewed briefly in ANL-7425, p. 176.) The advantage of this theory is that with a minimum of information (the melting point, heat of fusion, and standard Gibbs free

⁹ M. Blander, S. J. Yosim, *J. Chem. Phys.* **39**, 2610 (1963).

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FIG. V-7. Solid-Liquid Equilibrium Data for the LiCl-LiI-KI System. (Solid curves: experimental. Dashed curves: conformal ionic solution theory.)

energy of formation for each component and the eutectic temperature of each of the four nonreciprocal pairs in the system), the complete liquidus surface for the system can be computed.

One of the salt systems being considered for use as an electrolyte is LiCl-LiI-KI. This system was chosen for further investigation after preliminary experiments had indicated that it had a minimum melting point of 264°C (ANL-7425, Table V-3, p. 178), one of the lowest observed for ternary alkali halide mixtures. This ternary system, which consists of the binary eutectic systems LiCl-LiI, LiCl-KI, and LiI-KI, forms one-half of the reciprocal LiCl-KI system. Therefore, it also affords an opportunity to test the conformal ionic solution theory, which predicts a minimum temperature of 276°C at a composition of 6 mol % LiCl, 62 mol % LiI, 32 mol % KI.

Eight thermal analysis experiments were performed on the LiCl-LiI-KI system using apparatus and techniques that have been described elsewhere.¹⁰ These experiments provided solid-liquid equilibrium data

(Table V-3) for three pseudobinary mixtures that traversed the predicted minimum temperature-compositional regime.

A contour diagram of the liquidus isotherms for the ternary LiCl-LiI-KI system, given in Fig. V-7, was constructed from the pseudobinary data of Table V-3 and data for the three binary-component systems. Superimposed on the figure, as dashed lines, are the isotherms predicted by the conformal ionic solution theory. The experimental data indicated that the minimum temperature in the system was at 8.5 mol % LiCl, 59 mol % LiI, 32.5 mol % KI. A single thermal-analysis experiment at this composition showed no breaks other than a minimum at 265°C.

As stated above, the theoretical calculations had predicted a minimum temperature of 276°C at a composition of 6 mol % LiCl, 62 mol % LiI, 32 mol % KI. Since this agrees quite well with the experimental work, it is clear that the conformal ionic solution theory offers significant saving of experimental effort in the selection of low-melting electrolyte mixtures. Cesium- and rubidium-containing systems are among those to be investigated using this approach.

¹⁰ C. E. Johnson, C. E. Crouthamel, S. E. Wood, *Inorg. Chem.* **3**, 1487 (1964).

5. Spectroscopic Studies of Intermetallic Compounds and Halide-Containing Fused Salts (V. A. Maroni, E. J. Hathaway, E. J. Cairns)

A number of spectroscopic techniques are being applied to the task of characterizing the species present in intermetallic systems and in halide-containing fused salts. Raman spectroscopy has been used extensively (see ANL-7225, p. 219; ANL-7325, p. 184; ANL-7375, p. 168; and ANL-7425, p. 181); infrared, visible, and ultraviolet absorption spectroscopy have also been applied.

a. Intermetallic Compounds

The spectroscopic characterization of intermetallic systems has at times required the synthesis of pure intermetallic compounds. Lithium selenide has been prepared by vapor-phase transfer of selenium into molten lithium. The lithium and selenium react stoichiometrically in the ratio of 2:1 to produce high-purity Li_2Se , which has been shown by X-ray diffraction to have the CaF_2 structure. Samples of lithium telluride have been prepared in the same manner, but the stoichiometry of the reaction is not well characterized.

The systems $\text{Li}_2\text{Se-LiF-LiCl}$ and $\text{Li}_2\text{Te-LiF-LiCl}$ have been examined by Raman spectroscopy. Raman spectra of 5–10 mol % Li_2Se or Li_2Te in the LiF-LiCl eutectic did not contain bands that could be attributed to selenium- or tellurium-containing species. It was concluded from these studies that Li_2Se and Li_2Te dissociate completely in alkali halide melts.

Further evidence for the ionic nature of lithium selenide was obtained in a study of the infrared spectrum of solid Li_2Se as a function of pressure.¹¹ Samples of crystalline Li_2Se were introduced between two diamond windows set in a specially designed holder which allowed a known pressure to be applied across the faces of the diamonds. The infrared light was passed through the diamond windows and focused into the spectrophotometer. One strong band was observed for Li_2Se at 276 cm^{-1} at atmospheric pressure. The dependency of the energy of the band maximum on pressure is illustrated in Fig. V-8. From the large shift of the maximum to higher wave numbers with increasing pressure, we conclude that this band is the infrared-active lattice vibration expected for a crystal having the CaF_2 structure. The absence of any other bands that could be attributed to molecular vibrations indicates that Li_2Se is an ionic solid.

Solutions of Li_2Se in the LiF-LiCl eutectic have no

absorption maximum in the visible region, but their long wavelength absorption edge in the ultraviolet is at a lower energy than that of the pure fused eutectic. The absence of an absorption maximum in the visible or near ultraviolet offers further evidence that Li_2Se is completely ionized in fused-salt media.

b. Halide-Containing Fused Salts

(1) $\text{MgCl}_2\text{-KCl}$ System

A study of complex formation in MgCl_2 -containing fused-salt systems that are pertinent to compact pyrochemical processes has been carried out by means of Raman spectroscopy. There is a considerable amount of indirect evidence in the literature¹²⁻¹⁶ for the presence of complex species in these melts, as well as some evidence based on a cursory Raman investigation¹⁷ of MgCl_2 and two $\text{MgCl}_2\text{-KCl}$ mixtures.

Molten samples of MgCl_2 in various proportions with KCl were investigated to determine the effect of varying the $\text{Cl}^-/\text{Mg}^{+2}$ mole ratio on the Mg-Cl vibrational bands. Spectra obtained for $\text{Cl}^-/\text{Mg}^{+2}$ ratios in the range from 2.5 to 4.0 all show a strong polarized band in the region of $200\text{--}300\text{ cm}^{-1}$ and a broad depolarized band centered near 160 cm^{-1} . The spectrum for an $\text{MgCl}_2\text{-KCl}$ melt (550°C) with $\text{Cl}^-/\text{Mg}^{+2} = 4.0$, shown in Fig. V-9, is typical of the results obtained for the entire series of compositions. As the $\text{Cl}^-/\text{Mg}^{+2}$ ratio is increased from 2.5 to 4.0, the position of the maximum of the polarized band shifts continuously to higher frequency; this shift is illustrated in Fig. V-10.

Spectra of the $\text{MgCl}_2\text{-BaCl}_2$ and $\text{MgCl}_2\text{-KCl-NaCl}$ eutectics have also been obtained, and these data points are included in Fig. V-10. The point for each eutectic falls very close to the line determined from the $\text{MgCl}_2\text{-KCl}$ data; this agreement indicates that the substitution of other alkali and alkaline earth cations for potassium ion has relatively little effect on the frequency of the band maximum in the region of $200\text{--}300\text{ cm}^{-1}$.

These results suggest that a complex equilibrium, which involves several structurally different species, exists in MgCl_2 -containing melts. This equilibrium was studied in detail by subjecting the series of $\text{MgCl}_2\text{-KCl}$

¹² P. W. Huber, E. V. Potter, W. H. St. Clair, U.S. Bureau of Mines, Report of Investigation No. 4858 (1952).

¹³ E. G. Schrier, H. M. Clark, *J. Phys. Chem.* **67**, 1259 (1963).

¹⁴ S. Karpachev, A. Stromberg, *Z. Anorg. Allg. Chem.* **232**, 78 (1935).

¹⁵ O. G. Desyatnikov, *J. Appl. Chem. USSR (English Transl.)* **29**, 945 (1956).

¹⁶ H. Flood, S. Urnes, *Z. Elektrochem.* **59**, 834 (1955).

¹⁷ K. Balasubrahmanyam, *J. Chem. Phys.* **44**, 3270 (1966).

¹¹ This work was performed cooperatively with C. Postmus, Jr. and J. R. Ferraro of the Chemistry Division. The high-pressure diamond cell assembly and infrared spectrophotometer were supplied by the Chemistry Division.

spectra to a computerized Gaussian curve resolution analysis.³ The analysis of the spectrum in Fig. V-9 is shown in Fig. V-11, and results for the entire series of compositions are summarized in Table V-4.

The four bands at 282, 251, 234, and 217 cm^{-1} , which constitute the completely polarized envelope at 200–300 cm^{-1} , probably arise from species of the type $\text{MgCl}_n^{(2-n)}$

or from the solid-like lattice structure $(\text{MgCl}_2)_n$ persisting into the melt phase. A continuous-variations study of the integrated intensities for the resolved bands in Table V-4 indicates that the bands at 234 and 217 cm^{-1} arise from species with a $\text{Cl}^-/\text{Mg}^{+2}$ ratio of less than 3, that the band at 282 cm^{-1} arises from a species with a $\text{Cl}^-/\text{Mg}^{+2}$ ratio of about 3, and that the band at

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FIG. V-8. The Infrared Spectrum of the Li_2Se Lattice Vibration as a Function of Pressure.

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FIG. V-9. Photoelectrically Recorded Raman Spectrum of $\text{MgCl}_2\text{-KCl}$ at 550°C ; $\text{Cl}^-/\text{Mg}^{+2} = 4.0$.

FIG. V-10. Plot of $\text{Cl}^-/\text{Mg}^{+2}$ Mole Ratio vs. Maximum Frequency of Mg-Cl Band.

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FIG. V-11. Resolved Raman Spectrum of MgCl_2 -KCl at 550°C, $\text{Cl}^-/\text{Mg}^{+2} = 4.0$. (Points represent the recorded spectrum; solid lines, the computer-resolved Gaussian peaks and total calculated intensity curve.)

251 cm^{-1} arises from a species with a $\text{Cl}^-/\text{Mg}^{+2}$ ratio of greater than 3.

We conclude from these results that the bands at 234 and 217 cm^{-1} are due to symmetric stretching vibrations

of polymeric $(\text{MgCl}_2)_n$ units, and that the bands at 282 and 251 cm^{-1} arise from the totally symmetric stretching vibrations of MgCl_3^- and MgCl_4^{2-} , respectively. The intensity of the band at 163 cm^{-1} was relatively invariant over the range of the continuous-variations plot; this band has, therefore, been attributed to a composite of bond-bending vibrations for MgCl_3^- , MgCl_4^{2-} , and the polymeric lattice structure.

These studies may be extended to determine the effect of the structure of the fused-salt phase on distribution coefficients of various dissolved species between a fused-salt phase and one or more liquid-metal phases. This information should be useful in connection with compact pyrochemical processes.

(2) UO_2Cl_2 in MgCl_2 -KCl-NaCl Eutectic

The Raman spectrum of UO_2^{+2} in MgCl_2 -KCl-NaCl eutectic and the effect of dissolved UO_2Cl_2 on the magnesium (II)-chloride complex equilibrium have been investigated. The spectrum of 1.5 M UO_2Cl_2 in MgCl_2 -KCl-NaCl eutectic (uranium/magnesium = 0.18) at 600°C is shown in Fig. V-12. The band at 850 cm^{-1} is the totally symmetric UO_2^{+2} stretching vibration.¹⁸ The

¹⁸ G. K. T. Conn, C. K. Wu, *Trans. Faraday Soc.* **34**, 1483 (1938).

TABLE V-4. SUMMARY OF CURVE-RESOLUTION DATA FOR MgCl_2 -KCl SYSTEM

Frequency (cm^{-1}) at indicated $\text{Cl}^-/\text{Mg}^{+2}$ Ratio ^a				Average Frequency ^b (cm^{-1})	Assignment
4.0	3.6	3.0	2.5		
283 (0.6)	277 (0.3)	287 (0.3)	—	282 ± 5 , p	$\nu_1(A_1') \text{MgCl}_3^-$
257 (5.9)	257 (0.8)	254 (0.6)	245 (0.3)	251 ± 6 , p	$\nu_1(A_1) \text{MgCl}_4^{2-}$
236 (1.0)	238 (1.0)	227 (1.0)	241 (1.0)	234 ± 7 , p	$(\text{MgCl}_2)_n$ polymer
219 (1.0)	220 (0.6)	224 (0.6)	210 (0.4)	217 ± 7 , p	$(\text{MgCl}_2)_n$ polymer
158 (3.2)	158 (0.6)	168 (0.5)	167 (0.3)	163 ± 5 , dp	Cl-Mg-Cl bending modes

^a Numbers in parentheses indicate intensity relative to $234 \pm 7 \text{ cm}^{-1}$ band.

^b The average frequencies are used in the text to identify the bands; p = polarized, dp = depolarized.

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FIG. V-12. Raman Spectrum of 1.5 M UO_2Cl_2 in MgCl_2 -KCl-NaCl Eutectic at 600°C (uranium-to-magnesium mole ratio = 0.18).

broad band centered near 205 cm^{-1} is assigned to vibrations of the various magnesium (II)-chloride species, but this band is displaced to a significantly lower frequency, relative to that for the MgCl_2 -KCl-NaCl eutectic alone (238 cm^{-1} , see Fig. V-10). A plot of the magnitude of the displacement from the peak position expected in the absence of UO_2^{+2} is given in Fig. V-13 for four different uranium-to-magnesium mole ratios. The extent of shift increases linearly as the uranium-to-magnesium ratio is increased. From the direction of the shift (to lower frequency), it appears that UO_2^{+2} is complexing some of the chlorine atoms that give rise to the higher frequency vibrations in the region of 200 – 300 cm^{-1} . The band at 267 cm^{-1} is, therefore, assigned to vibrations associated with a structure having uranium-chlorine-magnesium bridges.

(3) MgBr_2 -KBr System

A Raman study has been made of complex formation in molten MgBr_2 -KBr mixtures as a function of the $\text{Br}^-/\text{Mg}^{+2}$ ratio for compositions having $\text{Br}^-/\text{Mg}^{+2}$

ratios in the range from 2.5 to 5.0. All the spectra show a strong polarized band in the region of 125 – 175 cm^{-1} and a broad weak band centered near 90 cm^{-1} . The spectrum for an intermediate composition, $\text{Br}^-/\text{Mg}^{+2} = 3.48$, is reproduced in Fig. V-14.

Curves A and B, taken at 530°C and 410°C , respectively, illustrate the negligible effects of temperature on the band shapes and peak positions; similar results were observed for the entire series of compositions. Curve C shows the results of depolarization studies.

A plot of the peak position of the polarized band for five $\text{Br}^-/\text{Mg}^{+2}$ ratios is shown in Fig. V-15. As in the case of the MgCl_2 -KCl system, the position of this maximum shifts steadily to higher frequency when the halide/magnesium (II) ratio is increased toward 4.0. Because of the lower melting temperatures in the MgBr_2 -KBr system, spectra could be taken at compositions up to a $\text{Br}^-/\text{Mg}^{+2}$ ratio of 5.0.

The data for the MgBr_2 -KBr system are interpreted in terms of a magnesium (II)-bromide complex equilibrium involving at least two species. There appear to

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FIG. V-13. Plot of Uranium-to-Magnesium Mole Ratio vs. Shift in Frequency of Mg-Cl Band Maximum.

be two components in the envelope at 125–175 cm^{-1} , one at 156 cm^{-1} and a second at a lower frequency; the latter grows in relative intensity as the $\text{Br}^-/\text{Mg}^{+2}$ ratio is reduced. The band at 156 cm^{-1} is assigned to the symmetric stretching motion, $\nu_1(A'_1)$, for planar MgBr_3^- (D_{3h}); however, the assignment of this band to $\nu_1(A_1)$ for tetrahedral MgBr_4^{2-} is also possible.

Of the remaining Raman active modes expected for planar MgBr_3^- or tetrahedral MgBr_4^{2-} , the predominantly bond-bending vibrations could be contained in the depolarized band at about 90 cm^{-1} . No depolarized band attributable to the antisymmetric stretching vibration of either species was observed. This band should be at a higher frequency than ν_1 for both planar MgBr_3^- and tetrahedral MgBr_4^{2-} , but as in the case of the MgCl_2 -KCl studies, it may be too weak in intensity to be detected. The lower frequency component of the envelope at 125–175 cm^{-1} could be associated either with residual lattice structure persisting into the melt phase or with a $\text{MgBr}_n^{(2-n)}$ species other than the one producing the band at 156 cm^{-1} .

(4) HgI_2 -LiI-KI System

Raman spectra have been obtained for pure molten HgI_2 and also for various molten mixtures of HgI_2 , LiI, and KI. The spectra of four melts having $\text{I}^-/\text{Hg}^{+2}$ ratios in the range from 2.0 to 7.0 are shown in Fig. V-16.

Curve a is the spectrum of pure HgI_2 , and curves b, c, and d are the spectra of melts with $\text{I}^-/\text{Hg}^{+2}$ ratios of 2.7, 4.5, and 7.0, respectively. The proportions of LiI, KI, and HgI_2 in these melts were adjusted to give samples of the desired $\text{I}^-/\text{Hg}^{+2}$ ratio that melted below the boiling point of pure HgI_2 (354°C).

The spectrum of pure HgI_2 contains a single polarized band at 143 cm^{-1} , which is assigned to ν_1 for the linear triatomic HgI_2 molecule with $D_{\infty h}$ symmetry. This band has been observed at 155 cm^{-1} in the gas-phase Raman spectrum of HgI_2 ,¹⁹ at 146 cm^{-1} in Raman spectra of melts containing mixed mercuric halides,²⁰ and at 138 cm^{-1} in a previous study of molten HgI_2 .²¹ As the $\text{I}^-/\text{Hg}^{+2}$ ratio is increased, the band maximum at 143 cm^{-1} shifts to lower frequencies. For $\text{I}^-/\text{Hg}^{+2} = 2.7$, the maximum is at 136 cm^{-1} ; for $\text{I}^-/\text{Hg}^{+2} = 4.5$, 131 cm^{-1} . No new bands are observed in either spectrum. At $\text{I}^-/\text{Hg}^{+2} = 7.0$, the maximum is at 126 cm^{-1} , and a second weak band appears at 185 cm^{-1} .

The above results are explained by assuming gradual formation of planar HgI_3^- as the $\text{I}^-/\text{Hg}^{+2}$ ratio is increased. The totally symmetric vibration, $\nu_1(A'_1)$, of the HgI_3^- species begins to grow on the low-frequency side of the HgI_2 fundamental at 143 cm^{-1} , thereby causing this band to broaden and shift to lower frequency. At $\text{I}^-/\text{Hg}^{+2} = 7.0$, there is sufficient HgI_3^- formed so that the antisymmetric stretching motion, $\nu_3(E')$, at 185 cm^{-1} becomes detectable. The $\nu_4(E')$ vibration, also expected in the Raman spectrum of planar HgI_3^- , is probably buried in the Rayleigh scattering. The formation of HgI_3^- in other media containing HgI_2 and added iodide has been demonstrated by previous investigators.²²⁻²⁴

(5) Gaseous Aluminum Chloride

A study of the Raman spectrum of aluminum chloride in the vapor phase (450°C and ~ 4 atm pressure) has been conducted in cooperation with D. M. Gruen and R. McBeth of the Chemistry Division. A normal coordinate analysis of the Al_2Cl_6 bridged dimer has been performed based on our gas-phase Raman data and gas-phase infrared data of Klemperer.²⁵

¹⁹ H. Braune, G. Engelbrecht, *Z. Phys. Chem. (Leipzig)* **B19**, 303 (1932).

²⁰ J. H. R. Clark, C. Solomons, *J. Chem. Phys.* **48**, 528 (1968).

²¹ A. J. Melveger, R. K. Khanna, B. R. Guscott, E. R. Lipincott, *Inorg. Chem.* **7**, 1630 (1968).

²² T. R. Griffiths, M. C. R. Symons, *Trans. Faraday Soc.* **56**, 1752 (1960).

²³ H. Specker, E. Jackwerth, H. G. Kloppenburg, *Z. Chem.* **183**, 81 (1961).

²⁴ E. L. Short, D. N. Waters, D. F. C. Morris, *J. Inorg. Nucl. Chem.* **26**, 902 (1964).

²⁵ W. Klemperer, *J. Chem. Phys.* **24**, 353 (1956).

FIG. V-14. Raman Spectrum of Molten $\text{MgBr}_2\text{-KBr}$; $\text{Br}^-/\text{Mg}^{+2} = 3.48$. FIG. V-15. Plot of $\text{Br}^-/\text{Mg}^{+2}$ Mole Ratio vs. Frequency of Mg-Br Band Maximum.

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FIG. V-16. Raman Spectra of Molten HgI_2 and Molten HgI_2 -LiI-KI Mixtures ($\text{I}^-/\text{Hg}^{+2} = 2.0$ to 7.0).

The results of this study are reported in Table V-5 and are discussed in detail elsewhere.²⁶ Ten observed frequencies were reproduced by an eight-constant force field with a maximum deviation between observed and calculated frequencies of 3%, confirming the frequency assignments of Klemperer for the Al_2Cl_6 species with D_{2h} symmetry.

²⁶ V. A. Maroni, D. M. Gruen, R. L. McBeth, E. J. Cairns, "Raman Spectrum and Vibrational Analysis for Gaseous Aluminum Chloride," *Spectrochim. Acta* (in press).

TABLE V-5. SUMMARY OF VIBRATIONAL ANALYSIS FOR Al_2Cl_6

Species	Frequency (cm^{-1})		Force Constants ($\text{mdyn}/\text{\AA}$)
	Observed	Calculated	
A_g { ν_1 ν_2 ν_3 ν_4	501	491	K_1 (Al-X stretching constant) = 1.31
	336	333	
	217	216	k_1 (Al-X, Al-X interaction) = -0.20
	115	117	
A_u { ν_5	—	85	
B_{1g} { ν_6 ν_7	438	425	K_2 (Al-Y stretching constant) = 2.75
	168	165	
B_{1u} { ν_8 ν_9 ν_{10}	625 ^b	617	k_2 (Al-Y, Al-Y interaction) = 0.36
	—	194	k_{12} (Al-Y, Al-X interaction) = 0.33
	—	— ^c	
B_{2g} { ν_{11} ν_{12}	608	615	H_α (X-Al-X bending constant) = 0.15
	—	142	
B_{2u} { ν_{13} ν_{14}	420 ^b	433	H_β (Y-Al-Y bending constant) = 0.23
	—	114	
B_{3g} { ν_{15}	—	163	
B_{3u} { ν_{16} ν_{17} ν_{18}	484 ^b	494	H_δ (X-Al-Y bending constant) = 0.13
	—	375	
	—	175	

^a Raman active modes.^b Observed by Klemperer²⁸ in the infrared.^c Ring deformation coordinates for $\nu_{10}(B_{1u})$ were neglected.

6. The Lithium/Tin Thermally Regenerative System (H. Shimotake, E. J. Cairns)

The lithium-tin system is currently being investigated for use in a thermally regenerative cell.⁶ Performance data have been obtained for lithium/tin cells

with immobilized (paste) electrolytes operating under various conditions (see Section V.A.8.b of this report). Figure V-17 shows typical voltage-current density

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FIG. V-17. Voltage-Current Density Curves for a Lithium/Tin Cell.

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FIG. V-18. Conceptual Design of Thermally Regenerative System with Paste Electrolyte.

curves for these lithium/tin cells. Because the partial pressure of lithium is low under regeneration conditions, special regenerator designs will be required for the lithium/tin system. An integrated cell-regenerator system design is presented in Fig. V-18. The mathematical analysis of the mass and energy transport processes occurring in this regenerator is developed below.

To obtain estimates of the temperature, pressure, and composition distributions in a regenerator of simple geometric configuration, a parallel-plate model of the regenerator was adopted, as shown schematically in Fig. V-19. The regenerator has been rotated clockwise 90° for ease in interpreting the temperature, composition, and pressure profiles. "Down" is now to the left, and "up" is to the right.

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FIG. V-19. Heat and Mass Transfer Processes in Regenerator-Condenser Section.

TABLE V-6. NOMENCLATURE USED IN DESIGN CALCULATIONS FOR LITHIUM-TIN SYSTEM REGENERATORS

C_A	concentration of lithium in tin, g-atom/cm ³
D_E	effective diffusivity, including eddy diffusivity, cm ² /sec
ΔH_v	partial heat of vaporization of lithium from lithium-tin alloy, cal/g-atom
J_A	atomic flux of anode metal, g-atom/(cm ²)(sec)
k	thermal conductivity of lithium-tin alloy, cal/(sec)(cm)(°C)
l	thickness of lithium-tin alloy, cm
M	atomic weight, g/g-atom
p_i	equilibrium vapor pressure of lithium above lithium-tin alloy of composition C_A ($x=l$) = C_{Ai} , dyn/cm ² or Torr
p_s	vapor pressure of lithium at the liquid-vapor interface of the condensate, dyn/cm ² or Torr
p_s^0	equilibrium vapor pressure of lithium above the condensate, dyn/cm ² or Torr
p_v	pressure in the bulk vapor, dyn/cm ² or Torr
R	gas constant, 82.057 (atm)(cm ³)/(mol)(°C)
T	temperature, °K
T_{air}	temperature of ambient air, °K
T_c	temperature at condenser surface, °K
T_{FIN}	temperature of condenser fin, °K
T_H	heat source temperature, °K
T_i	temperature at the liquid-vapor interface, °K
T_s	liquid temperature at the vapor-liquid interface of the condensate, °K
T_v	temperature of the bulk vapor, °K
U	overall heat transfer coefficient, cal/(sec)(cm ²)(°C)
W_{ia}	inlet cathode alloy flow rate, g-atom/sec
W_{out}	outlet cathode alloy flow rate, g-atom/sec
X_A	atom fraction lithium
X_{Ai}	atom fraction lithium at evaporation surface
X_{Ain}	atom fraction lithium in inlet stream
X_{Aout}	atom fraction lithium in outlet stream
x	axial distance perpendicular to the direction of the liquid flow, cm
α_c	condensation coefficient, dimensionless
α_e	evaporation coefficient, dimensionless
ρ	molar density of liquid alloy, mol/cm ³

The nomenclature used in the following mathematical treatment is presented in Table V-6. The overall process of regeneration is separated into steps for the purpose of the mathematical description. When the regenerator is operating at steady state, all of the processes occur at equal rates, and all the equations for the processes are linked.

1. Heat is transferred from the heat source at a uniform temperature through the lithium-tin alloy to the liquid-vapor interface:

$$J_A = \frac{k}{l} (T_H - T_i) \frac{1}{\Delta H_v} \quad (1)$$

2. Lithium is evaporated from the alloy under non-equilibrium conditions:

- a) Transport of lithium from the bulk liquid to the liquid-vapor interface,

$$J_A = -D_E \left. \frac{\partial C_A}{\partial x} \right|_{x=l} \quad (2)$$

- b) Vaporization of lithium,

$$J_A = \frac{\alpha_e}{M} \sqrt{\frac{M}{2\pi R}} \left(\frac{p_i}{\sqrt{T_i}} - \frac{p_v}{\sqrt{T_v}} \right) \quad (3)$$

3. Lithium vapor flows to the condensation surface with a negligible pressure drop; the negligible pressure drop allows us to equate p_v in Eqs. 3 and 4.
4. Lithium condenses, releasing its heat of condensation:

$$J_A = \frac{\alpha_c}{M} \sqrt{\frac{M}{2\pi R}} \Gamma \left(\frac{p_v}{\sqrt{T_v}} - \frac{p_s^0}{\sqrt{T_s}} \right) \quad (4)$$

where

$$\Gamma = e^{-\phi^2} + \phi \pi^{1/2} (1 + \operatorname{erf} \phi)$$

and

$$\phi = J_A M / \rho \left(\frac{2RT}{M} \right)^{1/2}$$

5. The heat of condensation is removed through a layer of lithium and the condenser wall and is transferred to air:

$$J_A = U(T_s - T_{air}) \frac{1}{\Delta H_v} \quad (5)$$

To determine the regenerator size for a given distillation rate (corresponding to a given cell power), heat-source temperature, heat-sink temperature, and cathode-alloy composition, the preceding equations must be solved simultaneously. In practice, the operating conditions of the cell are closely related to the cathode-alloy composition and to the distillation rate of the regenerator. Therefore, the design calculations for the regenerator and the cell should be conducted simultaneously to determine the optimum size of the total system for a given set of operating conditions. For the sake of simplicity, only the regenerator is discussed here; therefore, the results are not necessarily optimized for the system as a whole.

Calculations were carried out for several regenerator configurations. The physical properties of cathode alloys used for the calculations are presented elsewhere,⁶ along with a sample calculation. The results are summarized in Table V-7.

These results indicate that (1) a relatively high liquid-phase mass transport rate is obtainable because of a high eddy diffusivity (10^{-2} to 10^{-1} cm²/sec) (2) a very high vaporization mass flux is achievable (from Eq. 3). However, the condensation rate is limited by the air-side heat-transfer coefficient, which

TABLE V-7. SAMPLE REGENERATOR DESIGNS FOR THE LITHIUM-TIN SYSTEM

Power:	1 kW at 0.4 V
Lithium distillation rate required for power production:	93 g-atom/hr = 650 g/hr
Cathode-alloy composition	
At inlet:	30 at. % Li-70 at. % Sn
At outlet:	20 at. % Li-80 at. % Sn
Heat-source temperature:	1300°C
Heat-sink temperature:	50°C

Area Ratio, Condenser to Regenerator	Regenerator			Regeneration Rate		Required Overall Condenser Heat Transfer Coefficient [Btu/(hr) (ft ²) (°F)]	Condensate Surface Temperature (°C)
	Depth (cm)	Width (cm)	Length (cm)	g-atom/(cm ²) (sec)	A/cm ²		
1	0.3	10	7.15	3.61×10^{-4}	34.8	145	650
1	0.3	10	18.7	1.38×10^{-4}	13.3	50	715
3	0.3	10	7.15	3.61×10^{-4}	34.8	50	650
1	1	10	13.7	1.95×10^{-4}	18.8	72	700
1	0.3	20	3.6	3.61×10^{-4}	34.8	145	650

results in three alternatives for achieving a high mass flux at the vaporization surface: (1) use of a large condenser area, about three times as large as the vaporization area, (2) provision for a higher overall heat-transfer coefficient at the condenser by means of liquid cooling, or (3) reduction of the mass flux to suit the condenser capacity and to maintain equal vaporization and condensation areas. The choice will be determined by the application. In a location where cooling water is inexpensive, such as an undersea application, a high overall heat-transfer coefficient can be achieved, and the unit will be compact. However, in applications where natural-convection air cooling is desired, the size of the unit will be largely determined by the condenser area.

A higher mass flux can be obtained in the regenerator by reducing the depth of the flowing liquid. The

resulting reduction in required surface area is not directly proportional to the reduction of the depth; this is shown in Table V-7. However, it is preferable to have a small depth, since this reduces the inventory of liquid metal in the regenerator. The reduction of liquid depth will be limited by the requirement that the velocity of the liquid metal be kept reasonably low (because of mass-transfer corrosion).

In summary, this analysis points out the possibility of a high rate of regeneration, up to 35 A/cm², even at pressures near 2 Torr. If a liquid coolant is available for the condenser, this high regeneration rate may be achieved, provided the vapor-phase pressure drop across the regenerator and condenser remains insignificant. For the case of an air-cooled condenser, the regeneration rate would be limited to about 13 A/cm², which is still a reasonable rate.

7. Lithium/Chalcogen Secondary Cells (*H. Shimotake, G. L. Rogers, J. Peck*)

a. Lithium/Selenium Cell

A secondary cell with a liquid lithium anode, an electrolyte of the molten ternary eutectic LiF-LiCl-LiI (mp, 340.9°C), and a liquid selenium cathode has been operated in the temperature range 350 to 400°C.⁵ The cell reaction on discharge is the transfer of lithium from the anode to the cathode to form a lithium-selenium alloy at the cathode. The capacity of the cell, which was determined by the amount of lithium in the anode, varied from 4 to 8.9 A-hr; selenium was always present in excess. The maximum ratio of lithium to selenium in the cathode corresponded to 60 at. % lithium at complete discharge.

Because of the relatively high resistivity of selenium,

an efficient cathode current collector was needed to maximize cell performance. Experiments with various forms of iron had shown (ANL-7425, p. 185) that cells having iron wires as the current-collecting network gave the best cell performance (short-circuit current density of 8.7 A/cm²). Better cell performance has since been obtained by using a stack of five expanded iron meshes welded to the cathode cup (short-circuit current density of 11 A/cm²). In the cell study described below, iron mesh was used as the cathode current collector and a stainless steel spiral as the anode current collector; both electrodes were 10 cm² in area.

The performance of the cell on discharge was measured in two ways: (1) short-term performance meas-

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FIG. V-20. Voltage-Current Density Curves for a Lithium/Selenium Cell with an Iron Mesh Cathode Current Collector.

ured from the fully charged condition for each datum point, corresponding to a cathode composition of about 5 at. % lithium; (2) "steady-state" performance measured on the voltage plateau, corresponding to a cathode composition of about 25 at. % lithium. These performance curves are shown in Fig. V-20. The behavior on charging is representative of that of a fully discharged cell, hence the steeper slope of the voltage-current density curves for charging.

The voltage-current density curves for discharge in Fig. V-20 show that 2.3 to 2.4 V is available at open circuit, and short-circuit densities of 11 to 13 A/cm² can be achieved. The maximum power density for short-term operation is 7.8 W/cm² (at 1.2 V) and at "steady-state" is 6.3 W/cm² (at 1.2 V). Measurements of the overvoltage by a current-interruption technique indicated that in the range 1 to 4 A/cm², the overvoltage was 90% resistive (mostly due to the electrolyte); the remaining overvoltage was associated with the diffusion of lithium into the cathode alloy.

Constant-current charge and discharge voltage-capacity curves for this cell are shown in Fig. V-21. The cathode alloy composition at complete discharge was 59.6 at. % lithium; thus solid Li₂Se was present during the latter part of the discharge curve. The accumulation of solid Li₂Se causes the second plateau in the discharge curves (3 to 5 A-hr). The first plateau

(0.5 to 2 A-hr) corresponds to an all-liquid cathode, in which the lithium probably forms soluble Li₂Se. The voltage differences between the various charge and discharge curves are primarily due to resistive losses in the cell, which are largely electrolytic in nature. The voltage-capacity curves show that this cell can be completely charged (6 A-hr) in less than 15 min. The stability of the open-circuit voltage indicates a low rate of self-discharge.

In summary, the lithium/selenium cell with a molten lithium halide electrolyte is capable of operation at current densities of 11–13 A/cm², and has power densities of 6.3–7.8 W/cm² available at 1.2 V. Complete recharge can be achieved in less than 15 min. Design calculations based on these results indicate that lithium/selenium batteries operating at 370°C can be expected to deliver 130 W-hr/lb (1-hr rate) and 380 W/lb (~10-min rate). These calculations indicate that this cell may provide a basis for a wide range of special applications which require high power densities, high efficiency, and a capability of fast recharge.

b. Lithium/Sulfur Cells

Two types of experimental lithium/sulfur cells have been studied: a cell with a liquid electrolyte and a cell with a paste electrolyte.

The first cell employed a molten salt electrolyte

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FIG. V-21. Voltage-Capacity Curves at Constant Current for a Lithium/Selenium Cell.

(26 mol % LiCl, 54 mol % LiI, 20 mol % KI) held in an alumina crucible. Both the cathode and anode had effective areas of 10 cm². The cathode consisted of an iron cup that contained 13.78 g of sulfur and twelve layers of expanded Armco iron mesh, the latter aiding in current collection. The anode current collector consisted of concentric rings of corrugated stainless steel sheet. Approximately 1.5 g lithium was added to the anode by prewetting it in a lithium bath at ~400°C. In the fully discharged condition, the ratio of lithium to sulfur corresponded to a cathode alloy composition of 33 at. % lithium in sulfur. The cell was operated under a helium atmosphere at 347°C. The maximum capacity of the cell was 5.7 A-hr.

The short-term voltage-current density curve for

this cell at a temperature of 347°C is shown in Fig. V-22. An open-circuit voltage of 2.1 V and a short-circuit current density of 7.5 A/cm² were obtained. The cell was charged between experiments in which the discharge data were obtained. After 18 hr of operation, the iron mesh current collector was found to be dissolved in the sulfur. (Recent tests show tantalum or niobium current collectors to be suitable.)

The experimental lithium/sulfur cell with a paste electrolyte was constructed of type 304 stainless steel and had electrodes of 3.8-cm² area. The paste electrolyte consisted of a mixture of 26 mol % LiCl, 54 mol % LiI, 20 mol % KI and an inert ceramic powder in a one-to-one weight ratio.

Special care was taken in constructing the cathode

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FIG. V-22. Voltage-Current Density Curve for a Lithium/Sulfur Cell.

to minimize electronic resistivity. The molten sulfur was mixed with graphite powder (which served as a current collector) at 150°C under a helium atmosphere. The resulting 75 wt % sulfur, 25 wt % carbon mixture formed a plastic paste with a specific resistance at room temperature of about 75 ohm-cm. The mixture was pressed into the cathode compartment in five layers with sheets of expanded stainless steel mesh separating the layers. The anode compartment contained lithium without any current collectors.

This cell, which was operated at 310°C, yielded an open-circuit voltage of 2.2 V and a short-circuit current density of 0.67 A/cm². The cell resistance was 0.9 ohm. Such a high resistance means that carbon is not a satisfactory current collector. In future experiments, other methods of current collection will be investigated.

c. Lithium/Phosphorus Cell

An experimental lithium/phosphorus cell with a liquid electrolyte of LiF-LiCl-LiI eutectic has been operated from 374 to 425°C under a helium atmosphere. The cathode consisted of an Armco iron cup

with an effective cathode area of 10 cm² and contained several layers of expanded Armco iron mesh to aid in current collection. The cathode material was a 50 at. % lithium, 50 at. % phosphorus mixture prepared by successive additions of red phosphorus to liquid lithium at 200°C. The anode, also 10 cm² in area, consisted of two concentric rings made from corrugated stainless steel sheet, prewetted with lithium.

The open-circuit voltage of this cell ranged from 0.89 V at 374°C to 0.875 V at 425°C; the maximum short-circuit current density observed was 1.7 A/cm². These results correspond to a maximum power density of 0.36 W/cm² at 0.4 V. The cell resistance was 0.052 ohm; this may be compared with a theoretical value of 0.013 ohm, calculated from the thickness of the electrolyte (0.3 cm) and from its specific resistance (0.44 ohm-cm). This disagreement could have been caused by the fact that the cathode was probably solid at the operating temperature.

An open-circuit voltage of about 1.3 V was observed at 386°C after charging the cell for over 2 A-hr; at this point the cathode composition was 29 at. % lithium and 71 at. % phosphorus. On slow discharge

TABLE V-8 SUMMARY OF PERFORMANCE DATA FOR LITHIUM/CHALCOGEN CELLS

Cells with Liquid Electrolytes					
Cell	Open-Circuit Voltage (V)	Short-Circuit Current Density (A/cm ²)	Maximum Power Density (W/cm ²)	Temperature (°C)	
Li/Te	1.75	8	3.5	470	
Li/Se	2.3	11	6.3	365	
Li/S	2.1	7.5	3.9	347	
Li/P	0.89	1.7	0.38	374	
Cells with Paste Electrolytes					
Cell	Open Circuit Voltage (V)	Short Circuit Current Density (A/cm ²)	Maximum Power Density (W/cm ²)	Temperature (°C)	Resistivity Ratio ^a
Li/Te	1.75	2.1	0.96	475	7.6
Li/Se ^b	2.3	4.0	2.7	375	3.9
Li/S ^c	2.2	0.67	0.37	310	— ^d

^a Resistivity of the paste divided by the resistivity of the pure fused salt electrolyte

^b Preliminary results given, not detailed in text

^c Preliminary results given, considerable improvement anticipated

^d The resistivity was not calculated because part of the electrolyte was solid

(<0.5 A), the cell maintained a voltage plateau of 1.3 V for about 40 min, the voltage then dropped rather quickly to another plateau at 0.98 V. The plateau at 1.3 V is attributed to the P-Li₂P₅ equilibrium, whereas the plateau at 0.98 V is attributed to the Li₂P₅-Li₃P equilibrium.

More experiments are planned with the lithium/phosphorus cell, however, a different type of current collector will be used to improve the current density. Although the anticipated cell performance was not attained in this preliminary experiment, the advantages of a lithium/phosphorus cell, e.g., low mass, low cost, and good availability of phosphorus, warrant further experimental work.

d. Performance Comparison

To put the capabilities of the various cells studied into perspective, the performance data presented above, along with data reported previously,^{2, 5, 27, 28}

²⁷ H. Shimotake, G. L. Rogers, E. J. Cairns, "Performance Characteristics of a Lithium Tellurium Cell," presented at the Electrochem Soc Meeting, Chicago, Illinois, Oct 15-19, 1967 (see extended abstracts of the Battery Div.), also, ANL 7450, pp 92-100.

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FIG. V-23 Design of Lithium/Chalcogen Battery with Immobilized (Paste) Electrolyte

are summarized in Table V-8. These performance data were used, together with the battery design shown in Fig. V-23, to calculate the expected performance for fully engineered batteries with paste electrolytes. The calculations (based on a 10-min rate for specific power and a 1-hr rate for specific energy) indicate the following: a lithium/tellurium battery would have a specific power of 250 W/lb and a specific energy of 90 W-hr/lb, a lithium/selenium battery would have a specific power of 380 W/lb and a specific energy of 130 W-hr/lb, and a lithium/sulfur battery would have a specific power of 500 W/lb and a specific energy of 160 W-hr/lb. The specific power-specific energy characteristics for these three types of secondary batteries are compared with those for some other secondary batteries in Fig. V-24.

Some of the applications that could be considered for a practical lithium/chalcogen battery include power for spacecraft, military communications, materials-handling vehicles, military vehicles, boats and submarines, remote locations, buses and trucks, urban automobiles, and off-peak energy storage for central stations. (This list is arranged in a possible order of higher-probability applications first.)

²⁸ H. Shimotake, E. J. Cairns, "Lithium/Chalcogen Secondary Cells," Preprints of papers, presented at the Fourth Advances in Battery Technology Symposium, Los Angeles, California, December 1968.

FIG. V-24. Specific Energy-Specific Power Characteristics of Various Batteries.

8. Immobilization of Lithium Halide Electrolytes

An important phase of the development of practical cell configurations is the immobilization of one or more of the three liquid phases. Recently, a program was initiated with the goal of understanding and optimizing the immobilization of electrolytes by using disks of paste electrolyte. The paste electrolyte disk is a pressed composite of an inert infusible filler and the electrolyte proper, which is an ionic lithium salt mixture. At the operating temperature of an electrochemical cell, the electrolyte is above its melting point; however, the paste, being a highly viscous material, remains essentially solid. This pseudo-solid functions both as a mechanical separator between the electrodes and as an ionic conductor between them.

a. Lithium Aluminate Preparation and Characterization (A. K. Fischer, K. A. Davis, G. H. Kucera)

The paste electrolyte filler that is being studied at the present time is meta-lithium aluminate, LiAlO_2 , which appears to have the important property of being

stable toward molten lithium. (In Section V.C.1 of this report, the use of LiAlO_2 as an insulator in lithium-containing systems is discussed.) Other important factors are particle size and shape, since these influence the strength and rheological properties of the disk. Fine particle size favors the high surface tension forces that are believed to be the main contributor to the strength of the pellet. The shapes of the particles, insofar as they promote their own interlocking, are also expected to be important. This program, then, is concerned with the preparation of lithium aluminate and other fillers, and with their characterization with respect to both particle size and shape and to performance in a paste.

Two crystalline modifications of LiAlO_2 are known: a low-temperature, high-density α form (3.4 g/cm^3) and a high-temperature, low-density γ form (2.6 g/cm^3). The α -to- γ transition proceeds at an appreciable rate above 600°C . The reverse transformation can be achieved only under pressure (about 35 kbar at 850°C).

The reactions by which LiAlO_2 is being prepared are

TABLE V-9. SUMMARY OF SELECTED EXPERIMENTS ON THE PREPARATION OF LiAlO_2

Reactants	Experimental Conditions	Product
$\text{Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$	24 hr at 550°C in helium and 48 hr at 625°C in air	$\alpha\text{-LiAlO}_2$
$\text{Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3$	114 hr at 751°C in helium	Approximately equal amounts of α - and γ - LiAlO_2
$\text{AlOOH} + \text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$	20 hr at 525°C, 0.25 hr at 800°C in oxygen	About 70% γ - LiAlO_2 and 30% α - LiAlO_2
$\text{Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3$	14 hr at 800°C in oxygen	γ - LiAlO_2
$\text{AlOOH} + \text{Li}_2\text{CO}_3$	15 hr at 800°C in oxygen	Approximately equal amounts of α - and γ - LiAlO_2

and

The conditions necessary for the preparation of LiAlO_2 in either the pure α or the pure γ form are being investigated. Preparing γ - LiAlO_2 , the high-temperature form, presents no particular problem because all that is required is to carry out the reaction at a high enough temperature, about 800°C, for a long enough time. To favor the formation of α - LiAlO_2 , a lower reaction temperature, preferably below 600°C, is required. No interaction seems to take place when solid Li_2CO_3 (mp, 723°C) and AlOOH or Al_2O_3 are heated at 500°C. However, if the reaction is carried out at 500°C in a fluid medium, e.g., in low-melting mixtures of Li_2CO_3 - LiCl or Li_2CO_3 - Na_2CO_3 , α - LiAlO_2 is formed as either a partial or dominant product. Work is under way to define the conditions that maximize the yield of α - LiAlO_2 . Selected examples of the experiments performed thus far are presented in Table V-9.

The factors that affect particle size and shape of LiAlO_2 products are also being examined. Since fine particle size in the product is a desirable characteristic, finely divided Al_2O_3 and AlOOH were used in the preparations. The Al_2O_3 had a nominal particle size of 0.03 μm (300 Å), whereas the AlOOH had a mean particle diameter near 0.01 μm . The particle size of the Li_2CO_3 is immaterial, since the reaction must take place in the presence of a liquid phase (i.e., molten Li_2CO_3) to achieve an appreciable reaction rate.

Assay of particle size of the reaction product can be accomplished rapidly by measurement of specific surface area. A BET surface area analyzer has recently been acquired for this purpose. For particle shape determinations, an electron microscope provides the only feasible method, since the particle sizes are below the range of usefulness of optical microscopes.

In the preparations of LiAlO_2 from Al_2O_3 , an investigation was made of the effect of atmospheric composition on particle characteristics. It is known that the sintering rate of alumina is controlled by the presence of vacancies in the oxide lattice, and that the concentration of these vacancies is determined by the atmosphere in which the sintering proceeds.²⁹ In reducing atmospheres, the sintering rate is high; in oxidizing atmospheres, it is low. In the preparation of LiAlO_2 from Al_2O_3 , it was expected that a product of fine particle size would result only if both the Al_2O_3 and the LiAlO_2 did not sinter. If the mechanism of mass transfer that operates during sintering of pure Al_2O_3 is the same in the preparative reaction, an oxidizing atmosphere should be beneficial.

To test this hypothesis, LiAlO_2 was prepared from Al_2O_3 and Li_2CO_3 at 800°C in three different atmospheres: oxidizing (O_2), neutral (Ar), and reducing (H_2). The Al_2O_3 and the reaction products were then examined with an electron microscope, through the cooperation of R. Hart and D. Plincy of the Metallurgy Division. The results showed essentially no particle growth in the products made in oxidizing or neutral atmospheres, but there was evidence of considerable accretion of originally spherical particles into agglomerates in the reducing atmosphere.

Additional studies are being carried out on the methods of preparation of other lithium aluminates such as Li_3AlO_4 and LiAl_5O_8 .

b. Paste Electrolyte Preparation and Properties (H. Shimotake, J. Cassulo, L. Anderson³⁰)

A necessary part of the development of practical cells employing past electrolytes is the selection of pastes with suitable electrochemical and physical characteristics. Recent work has been directed toward the preparation of paste electrolyte disks of various compositions and the determination of the properties of the disks.

²⁹ F. A. Kröger, *The Chemistry of Imperfect Crystals*, p. 820, North Holland Publishing Co., Amsterdam (1964).

³⁰ Co-op student from Northwestern University.

Candidate filler materials, which were either prepared as described above or obtained commercially (see Table V-10), were combined with LiF-LiCl-LiI eutectic (mp, 340.9°C) and molded into disks. The

TABLE V-10. CERAMIC FILLERS FOR PASTE ELECTROLYTE PREPARATIONS

Filler Designation	Synthesis Method	Filler Constituents ^a
GK-1	Vitro Al ₂ O ₃ + Li ₂ CO ₃ in air at 850°C	γ -LiAlO ₂
GK-2	Vitro Al ₂ O ₃ + Li ₂ CO ₃ -Na ₂ CO ₃ in air at 550°C	α -LiAlO ₂
KD-7	Vitro Al ₂ O ₃ + Li ₂ CO ₃ in oxygen at 800°C	γ -LiAlO ₂
KD-9	Vitro Al ₂ O ₃ + Li ₂ CO ₃ in vacuum at 450°C	Li ₂ CO ₃ + γ -Al ₂ O ₃
KD-11	LiOH + Al in oxygen at 450°C	LiAl ₂ O ₃ + minor LiAlO ₂
KD-15	Dispal AlOOH + LiCO ₃ in oxygen at 800°C	γ - + α -LiAlO ₂
Gallard and Schlesinger	Proprietary	γ -LiAlO ₂
Electronic Space Products	Proprietary	γ -LiAlO ₂
Vitro	Proprietary	γ -Al ₂ O ₃
Dispal	Proprietary	AlOOH
Ceramic Filler X	Proprietary	Proprietary

^a Determined by X-ray analysis.

dried, finely divided filler was first ground under helium atmosphere with a preselected amount of the electrolyte (50, 60, or 70 wt %). Homogeneity was achieved by repeated heating (at 360°C for ~3 hr), cooling, and grinding. A disk was formed by pressing a weighed portion of the mixture in a 2.5-cm dia mold with a force of 3250 lb. Before ejection from the mold, the disk was heat treated at 120°C for ~1 hr.

The mechanical properties of the disks were influenced by the particle size of the filler material. When the filler was very finely divided (e.g., Vitro Al₂O₃ and GK-2 α -LiAlO₂), a 50 wt % electrolyte paste was too brittle for use in a cell. On the other hand, when the filler was a coarse powder (e.g., Electronic Space γ -LiAlO₂), a 60 wt % electrolyte mixture was too soft to form a suitable paste.

The electrochemical properties of the paste electrolytes were determined by testing the performance of lithium/tin cells that incorporated the pastes. The cells consisted of 2.5-cm dia paste electrolyte disks held between 2.2-cm dia lithium and tin electrodes. The anodes were prepared by immersing sintered fiber disks of type 430 stainless steel in liquid lithium at 550°C; the disks were completely wetted by the lithium and retained an average of 0.53 g of lithium. The cathodes, which were also made from disks of sintered stainless steel fiber, were pretreated, either with an HCl-ZnCl₂ solution or with powdered NH₄Cl.

TABLE V-11. PROPERTIES OF PASTE ELECTROLYTE DISKS

Electrolyte Concentration ^a (wt %)	Filler ^b	Thickness (cm)	Density ^c (g/cm ³)	Durability	Wetting by Liquid Metals	Resistivity Ratio ^d at 400°C	Short-Circuit Current Density ^e (A/cm ²)				Appearance of Disk after Experiment
							350°C	400°C	450°C	500°C	
50	GK-2	0.465	1.69	Brittle	—	—	—	—	—	—	Broken
	KD-15	0.458	1.74	Brittle	—	—	—	—	—	—	Broken
	Vitro	—	—	Brittle	—	—	—	—	—	—	Broken
	KD-7	0.332	2.426	Small crack	Good	11.9	—	0.515	—	—	Slightly deformed
	G & S	0.338	2.42	Soft	Good	8.7	0.252	0.70	0.98	1.17	Slightly deformed
	ESP	0.335	2.389	Satisfactory	Good	8.55	0.60	0.715	1.11	1.30	Chipped, deformed
	KD-11	0.317	2.53	Satisfactory	Good	5.45	—	1.18	1.20 ^f	—	Edge chipped
60	KD-15	0.414	1.932	Very strong	No (Sn)	—	0.013	<0.1	<0.1	—	Satisfactory
	X	0.358	2.237	Split, crack	No (Li)	10.0	0.260	0.57	0.74	1.06	Satisfactory
	Vitro	0.295	2.686	Satisfactory	Good	48.5	0.137	0.143	0.56	1.29	Satisfactory
	KD-9	0.338	2.435	Satisfactory	Good	7.07	—	0.856	0.915	1.86	Satisfactory
	GK-2	0.297	2.73	Satisfactory	Very good	3.72	—	1.58	1.85 ^f	—	Slightly deformed
	GK-2	0.297	2.73	Satisfactory	Very good	5.5	0.78	1.23	1.60	1.80	Slightly deformed
70	KD-9	0.312	2.588	Soft	Satisfactory	5.27	0.57	1.15	0.97	—	Became black

^a LiF-LiCl-LiI eutectic.

^b See Table V-10 for filler properties.

^c Calculated on basis of the formula density: wt of paste/(circular area) (thickness).

^d Ratio of resistivity of the paste to resistivity of the pure electrolyte; resistivity of the pure electrolyte is 0.44 ohm-cm.

^e Open-circuit voltages = 0.8 to 1.0 V (see Fig. V-17); electrode area = 3.5 cm².

^f Current density measured at 410°C.

Upon immersion in liquid tin, the pretreated stainless steel disks were completely wetted and retained an average of 5.5 g of tin. The tin-wetting operation was performed in air. Both the lithium and tin electrodes were pressed in a vise to produce flat surfaces.

The assembled cell was placed in a tube furnace, and the cell temperature was gradually raised to 500°C. Cell performance data were taken at 350, 400, 450, and 500°C. At the start of cell operation, a high open-circuit voltage, ~2 V, was observed. This may have been produced by residual zinc chloride in the cathode from the pretreatment. However, as current was drawn from the cell, the voltage decreased to a normal open-circuit voltage of 0.7 to 1.0 V.

Good wetting of the paste electrolytes by the liquid metals was achieved by raising the cell temperature to about 400°C. There were two exceptions: elec-

trolytes containing KD-15 (a mixture of γ - and α -LiAlO₂) were not wetted by tin, and the electrolyte containing Ceramic Filler X was not wetted by lithium.

The data obtained from the paste electrolyte disks tested to date are presented in Table V-11. (A typical voltage-current density curve for the lithium/tin cell with paste electrolyte was shown in Fig. V-17 in Section V.A.6 of this report.) As indicated in the table, the highest short-circuit current densities thus far were achieved with a paste electrolyte of 60 wt % electrolyte-40 wt % GK-2 (α -LiAlO₂). Further tests now under way may result in a paste electrolyte that shows even higher current densities. A reasonable goal is a paste electrolyte having a resistivity 2.5 times that of the corresponding fused salt with no filler, and of sufficient strength that it can be used in sheets about 2 mm thick.

B. CELLS WITH SODIUM ANODES

Cells with sodium anodes have been of particular interest in connection with thermally regenerative systems for use with heat sources having temperatures in the range 800 to 1000°C. The sodium-bismuth system has been thoroughly investigated using emf,

vapor-liquid equilibrium, and thermal-analysis methods. Recently, all of these data have been used in a detailed thermodynamic treatment of the results using the quasi-ideal solution theory. A portion of this treatment and some new results are presented below.

1. Thermodynamics of the Sodium-Bismuth System by an Emf Method

(M. S. Foster, E. J. Cairns)

The quasi-ideal solution theory^{31, 32} has been used to correlate the thermodynamic properties of sodium-bismuth alloys as calculated from vapor-liquid equilibrium measurements by the transpiration and total pressure methods.³³ Application of this theory has now been extended to include emf data as a function of temperature and composition, as observed for cells of the type

The quasi-ideal solution theory, as applied to the sodium-bismuth system, assumes that the compounds Na₃Bi and NaBi persist in the melt, and that the compound species, as well as Na and Bi, behave ideally. Experimental data obtained at 1173°K³³ were used to calculate the activity coefficients of sodium and bis-

mut as components of the sodium-bismuth system. More recently, the activity coefficient of sodium as a component was obtained from cell emf data as a function of temperature and composition of the liquid alloy (ANL-7375, p. 160). The emf data were obtained over the temperature range 550 to 1050°K. The composition of the alloy ranged between 40 and 90 at. % bismuth in sodium, although at the lower temperatures it was not possible to reduce the bismuth concentration below 70 at. % owing to the precipitation of the solid compounds NaBi or Na₃Bi.

The two parameters required for a description of the quasi-ideal sodium-bismuth system are the equilibrium constants for the formation of the species NaBi (K_1) and Na₃Bi (K_2). At a single temperature, these may be determined by a nonlinear least-squares technique using the observed activity coefficients of sodium and bismuth as components.

A plot of K_1 and K_2 as a function of temperature is shown in Fig. V-25. The data were calculated by

³¹ E. Högfeldt, *Arkiv Kemi* **7**, 315 (1954).

³² E. Högfeldt, *Rec. Trav. Chim.* **75**, 790 (1956).

³³ A. K. Fischer, S. A. Johnson, S. E. Wood, *J. Phys. Chem.* **71**, 1465 (1967).

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FIG. V-25. Equilibrium Constants for NaBi (K_1) and Na₃Bi (K_2) from Quasi-ideal Theory.

multiple regression for temperatures greater than 700°C. At lower temperatures, the smaller range of the bismuth concentration allowed only an estimation of K_2 by extrapolation and a calculation of K_1 using a single nonlinear least-squares technique.

The values of K_1 and K_2 , as given by the straight lines in Fig. V-25, were used to calculate the expected emf of the experimental cells. The standard deviation of the calculated emf values from the observed data was 10 mV, which is within the accuracy of the measurements. The calculated curves of the activity coefficients of sodium and bismuth are compared with experimental data points in Fig. V-26. Also included for comparison are the vapor pressure-transpiration measurements at 1173°K.³³

The two parameters, K_1 and K_2 , expressed as a function of temperature, were used as the basis for calculating the equilibrium vapor composition and

pressure above sodium-bismuth alloys. At equilibrium, the activity of sodium as a species in the quasi-ideal solution is equal to its concentration. Also, the activity of sodium as a species in the solution is equal to the activity of Na monomer in the vapor phase in equilibrium with the solution. Assuming that the species in the gas phase behave ideally, the activity of Na monomer may be calculated as the ratio of its partial pressure over the solution to its partial pressure over pure sodium. Since the activity of Na monomer and its partial pressure over pure sodium are known, the partial pressure of Na monomer in the gas phase could be calculated. Similar reasoning can be applied to the Bi monomer.

The vapor above the liquid alloy was assumed to contain Na, Na₂, Na₄, Bi, and Bi₂, i.e., the species usually found or postulated to explain the behavior of pure sodium and pure bismuth vapors. The partial

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FIG. V-26. Calculated and Observed Activity Coefficients in Sodium-Bismuth Alloys (calculated values were derived from the quasi-ideal solution theory).

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FIG. V-27. Phase Relationships in the Sodium-Bismuth System for a Total System Pressure of 240 Torr.

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FIG. V-28. Liquid-Vapor Composition Relationship for Sodium-Bismuth System from Quasi-ideal Theory (system pressure, 240 Torr).

pressure of each of these species was calculated, and the sum was used as the total pressure over the solution.

The results are shown in Figs. V-27 and V-28. In Fig. V-27, the compositions of the liquid and vapor phases are shown as a function of temperature for a total system pressure of 240 Torr. In addition, liquid-solid phase equilibrium data reported in the following section are shown for comparison. The proximity of the liquid-vapor loop to the liquid-solid curve should be noted. At lower pressures, overlap would occur, creating a solid-vapor region.

The relationship of the composition of the vapor phase to the composition of the liquid phase is shown in Fig. V-28. These data are for the same conditions as those of Fig. V-27, i.e., the temperature varies such that a constant system pressure of 240 Torr is maintained.

The results presented above illustrate the usefulness of the quasi-ideal theory in the treatment of thermodynamic data for the sodium-bismuth system over a wide range of temperatures and over the full composition range. The success of this treatment in the prediction of the vapor-liquid loop and other thermodynamic behavior is not offered as a proof of the existence of the species NaBi and Na_3Bi in the liquid alloy. This question may best be answered by direct experimental observation.

2. Phase Equilibrium Studies of the Sodium-Bismuth System

(C. E. Johnson, A. K. Fischer, M. S. Foster, E. J. Cairns)

In a report on the liquid-vapor equilibria for the sodium-bismuth system,³³ certain experimental results were discussed that indicated an error in the published sodium-bismuth phase diagram,³⁴ which was based on the work of Kurnakov and Kusnetzow³⁵ and Mathewson.³⁶ Experimental difficulty in the earlier studies is evident from the fact that the thermal analysis results of Kurnakov and Kusnetzow show a melting point for Na_3Bi (730°C) that is 45° lower than that measured by Mathewson (775°C). In their compilation, Hansen and Anderko³⁴ discounted the lower value, presumably because possible impurities could have depressed the melting point, but also perhaps because Kurnakov and Kusnetzow reported only one point in this composition region. From the thermal analyses and solubility work reported herein, a more accurate phase diagram for the sodium-bismuth system has been constructed.

The apparatus and techniques used in the thermal analysis study are described elsewhere.¹⁰ A modification was made in the design of the sample capsule to allow thermal analysis of the sodium-rich samples, whose high vapor pressure might cause vaporization losses and composition changes. The new sample capsule is a closed right circular cylinder with a centrally located thermowell and an extended tube for loading the sample. Appropriate amounts of sodium and bismuth were weighed into the capsule, and the loaded capsule was evacuated and closed by welding. The volume of vapor space in the capsule was small enough (3 to 5 cm³) that loss of material from the condensed phase to the vapor phase would be negligible. Thermal analyses of bismuth-rich samples were conducted in open crucibles; the vapor pressures were low enough that no appreciable change in composition resulted from vaporization of part of the sample.

In the solubility study,³⁷ solid Na_3Bi and sodium were equilibrated for 5 or more hours, and the resulting solutions of bismuth in sodium were then filtered and analyzed.

The thermal analysis data and the solubility data are presented in Tables V-12 and V-13, respectively.

³⁴ M. Hansen, K. Anderko, *Constitution of Binary Alloys*, p. 321, McGraw-Hill, New York (1958).

³⁵ N. S. Kurnakov, A. N. Kusnetzow, *Z. Anorg. Chem.* **23**, 455 (1900).

³⁶ C. H. Mathewson, *Z. Anorg. Chem.* **50**, 187 (1906).

³⁷ This problem was selected for study by the 1968 AUA-ANL Summer Engineering Practice School. Students participating in this study were L. E. Brown (Michigan Technological University), C. H. Lewis (University of Arizona), and K. A. Williams (Purdue University).

TABLE V-12. THERMAL ANALYSIS DATA FOR THE SODIUM-BISMUTH SYSTEM

Liquid Phase Composition (at. % Bi)	Crystallization Temperature (°C)	Peritectic or Eutectic Temperature (°C)
5.0	650.0	—
10.0	714.9	97.6
15.0	751.4	—
17.5	769.8	97.7
20.0	792.6	—
25.0	848.1	—
35.0	703.7	—
43.0	553.8	443.7
51.8	444.4	217.0
53.0	441.0	215.7
65.0	372.1	215.8
75.0	249.2	216.2
78.1	226.3	215.5
80.0	236.2	215.7
90.2	261.3	215.8

TABLE V-13. SOLUBILITY OF BISMUTH IN SODIUM

Temperature (°C)	Solubility (10 ⁻⁴ at. % Bi)
125	0.708
125	0.779
150	2.67
175	2.29
175	3.31
200	7.84
225	13.5
250	22.8

Compositions between those examined in the thermal analysis studies and those in the solubility studies have been investigated by Walker, Pratt, and Mott.³⁸ All of these data have been used to construct the phase diagram shown in Fig. V-29 (solid lines). Two points derived from earlier vapor-pressure measurements,³³ also shown on the diagram, agree well with the curve drawn from the thermal analysis data. The melting point of Na_3Bi is a major point of disagreement with the earlier measurements.^{35, 36} Our work indicates a melting point temperature of 848.1°C, approximately 75° higher than the previously accepted value of 775°C.

Walker et al.³⁸ reported that for the temperature range 252 to 563°C, the solubility of bismuth in sodium is given by the relationship

³⁸ R. A. Walker, J. N. Pratt, B. W. Mott, "The Solubility of Metallic Elements in Liquid Sodium," presented at the 1968 AEC Corrosion Symposium, Battelle Memorial Institute, Columbus, Ohio, May 6-8, 1968

$$\log (\text{at. \% Bi in Na}) = 5.0038 - 4188.9/T \quad (8)$$

from which the heat of solution of Na_3Bi in sodium is calculated to be 19.17 ± 1.47 kcal/mol. In the temperature region $550\text{--}775^\circ\text{C}$, the heat of solution was previously deduced (ANL-7316, p. 74) from the solubility of Na_3Bi in molten NaF-NaCl-NaI mixtures as 10.7 kcal/mol.

The solubility data shown in Table V-13 may be represented by the relationship

$$\log (\text{at. \% Bi in Na}) = 2.0266 - 2424.7/T \quad (9)$$

The heat of solution of Na_3Bi in sodium calculated from Eq. 9 is 11.1 ± 0.9 kcal/mol. The solubilities reported in Table V-13 are larger than would be expected from an extrapolation of Walker's data, whereas the indicated heat of solution is smaller. These results indicate that the system cannot be considered a simple ideal solution of Na_3Bi in sodium. The more dilute solutions studied in our experiments should yield a better approximation of the heat of solution of Na_3Bi , since these solutions are presumably more ideal.

The shape of the sodium-bismuth phase diagram is unusual in that there is a fairly sharp peak at the

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FIG. V-29. Solid-Liquid Phase Diagram for the Sodium-Bismuth System.

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FIG. V-30. Solid-Liquid Phase Diagram for the Lithium-Bismuth System.

congruent melting point of Na_3Bi caused by the upward concavity of the solubility curves defining the equilibria between solid Na_3Bi and the liquid near the peak. Such behavior is not unprecedented, although solubility curves associated with compound formation are most commonly concave downward. The published³⁴ diagram shows a concave-downward configuration throughout the Na_3Bi solubility curves.

Our sodium-bismuth phase diagram, although unusual, bears a close resemblance to the lithium-bismuth phase diagram, if the latter is drawn strictly through the experimental points determined by Grube, Vossühler, and Schlecht.³⁹ The curves in the lithium-bismuth diagram, as originally presented by Grube et al, deviate from some of the experimental points by as much as 50° (or about 2 at. %) with no reason given for expecting these data to be so badly in error. The data of Grube et al in the region of the Li_3Bi peak have been replotted in Fig. V-30 for comparison with Fig. V-29. The familial resemblance between the two systems is apparent in the peaks at 25 at. % bis-

³⁹ G. Grube, H. Vossühler, H. Schlecht, *Z. Electrochem.* **40**, 270 (1934).

moth. Just to the left of the peaks, both curves show an upward concavity; to the right of the peaks, the curves are initially concave downward and then inflect to concave upward. Similar characteristics can also now be recognized in the rubidium-bismuth and cesium-bismuth systems (data are sparse for the potassium-bismuth system), if literal curve fitting is done.

The experimental data from the thermal analysis and solubility studies were compared with theoretical calculations for the sodium-bismuth system. A theoretical phase diagram was constructed using an ideal-solution model including Na, Na₃Bi, NaBi, and Bi as species in the system. The choice of Na and Bi as species is obvious since they are the components making up the system. Na₃Bi and NaBi species were chosen since they correspond to the principal compounds found in the solid state in this system. The phase diagram was consequently divided into the following regions: Bi-NaBi, NaBi-Na₃Bi, and Na₃Bi-Na. The pertinent data for each region of the diagram follow:

Bi: $T_m = 271.3^\circ\text{C}$	$\Delta H_m = 2,600 \text{ cal/mol}$
NaBi: $T_m \simeq 500^\circ\text{C}$	$\Delta H_m \simeq 3,600 \text{ cal/mol}$
Na ₃ Bi: $T_m = 848.1^\circ\text{C}$	$\Delta H_m = 11,100 \text{ cal/mol}$

(The data for bismuth were taken from Hultgren et

al,⁴⁰ those for NaBi were estimated by conventional methods, and the heat of fusion of Na₃Bi was taken from the low-temperature solubility studies.)

Calculations based on the Clausius-Clapeyron equation,

$$\ln \frac{X_2}{X_1} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (10)$$

were made of the liquidus-solidus equilibrium compositions. These calculations yielded the equilibrium (dashed) lines of Fig. V-29. The agreement with the experimental data over the region from pure bismuth to the compound Na₃Bi is fair. However, the obviously poor agreement on the sodium-rich side indicates the need for a more complex model for the liquid behavior in this region. The direction of the deviation of the data from the calculated curve is consistent with the possibility of association of sodium to form polymers. A provision for this type of behavior can be incorporated into the calculations. Work is continuing to develop a theoretical model that is consistent with the experimental data.

⁴⁰ R. Hultgren, R. L. Orr, P. D. Anderson, K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys*, p. 53, John Wiley & Sons, New York (1963).

C. MATERIALS STABILITY

Because many of the systems of interest in the electrochemical energy conversion program represent couples having high reactivity, materials compatibility is a difficult problem. The experimental program requires that apparatus be constructed of very stable materials to avoid contamination and corrosion and to allow thermodynamically meaningful results to be obtained. In addition, the construction of laboratory

cells for power production requires that long lifetimes be achievable. Both metallic and ceramic (insulator) materials that are stable to molten alkali metals, fused alkali halides, and molten heavy metals or chalcogens are required. A continuing program is being carried out to identify metals, alloys, and ceramics that resist the corrosive action of the systems being investigated.

1. Ceramic Materials (*M. S. Foster, G. H. Kucera*)

To have efficient utilization of space in cells and batteries, effective electrical insulators must be developed. Aluminum oxide (Al₂O₃) is suitable as an insulator material for cells or batteries containing sodium and sodium alloys. However, the development of insulators for cells containing lithium and its alloys is a more difficult problem.

The potential use of double oxides as insulators in lithium-containing cells was discussed previously

(ANL-7375, p. 175). Recently, three double oxides, LiAlO₂, Li₂ZrO₃, and CaZrO₃, were evaluated as insulator materials. To test their behavior in a quasi-cell environment, pellets of each were fabricated under varying conditions of (1) reactants, (2) particle size, (3) pressing force, and (4) sintering temperature, and then exposed to liquid lithium at temperatures ranging from $\sim 400^\circ\text{C}$ to $\sim 550^\circ\text{C}$. Periodically, the pellets were inspected visually to determine their general

TABLE V-14. TESTS OF CERAMIC INSULATORS: FABRICATION CONDITIONS AND COMPATIBILITY WITH LIQUID LITHIUM

Sample Designation	Double Oxide Preparation Method	Insulator Fabrication Conditions			Insulator Compatibility with Lithium			
		Molding Pressure (psi)	Percent of Theoretical Density	Sintering Temperature ^a (°C)	Lithium Temperature (°C)	Duration of Test (hr)	Pre-soaked in LiF-LiCl-LiI	Final Condition of Pellet
Li ₂ ZrO ₃ -1	Reagent Grade Li ₂ CO ₃ + ZrO ₂	2 × 10 ⁴	—	1500	460	66	yes	Surface loss of Li ₂ O; attacked and deeply penetrated by Li
-2		1 × 10 ⁴	—	825	—	—	—	No test; pellet too powdery
-3		1 × 10 ⁴	—	1100	550	137	yes	Attacked and penetrated by Li
-4		3 × 10 ⁴	—	1100	454	66	yes	Nonuniform attack and penetration by Li
CaZrO ₃ -1	Commercial preparation; ground 24 hr in ball mill	3 × 10 ⁴	—	1100	444	17	yes	Half deteriorated; remainder completely penetrated by Li
LiAlO ₂ -1	Reagent-grade Li ₂ CO ₃ + Linde Al ₂ O ₃	2 × 10 ⁴	—	1500	450	145	yes	Surface loss of Li ₂ O; no appreciable attack and only slight penetration by Li
-2		1 × 10 ⁴	—	825	—	—	—	No test; pellet too powdery
-3		1 × 10 ⁴	—	1100	—	—	—	No test; H ₂ S odor from pellet ^b
-4		3 × 10 ⁴	—	1100	—	—	—	No test; pellet too powdery
-5	Same with Carbowax binder added	3 × 10 ⁴	—	1100	—	—	—	No test; pellet too powdery
-6	Same with Carbowax binder added; ground 24 hr in ball mill	3 × 10 ⁴	—	1100	460	18.5	yes	Soft
-7		3 × 10 ⁴	—	1100	450 ^c 450	21.5 23	yes yes	Hard and in good condition Deteriorated
-8	Recrystallized Li ₂ CO ₃ + Vitro Al ₂ O ₃	3 × 10 ³	—	1100	500	170	no	Attacked
-9		3 × 10 ³	—	1100	400	172	no	Moderate attack and penetration by Li
-10		3 × 10 ⁴	—	1100	—	—	—	No test; pellet slightly powdery
-11		8 × 10 ^{4 d}	78	1100	440	162	no	Moderate attack and penetration by Li
-12	Recrystallized Li ₂ CO ₃ + Linde Al ₂ O ₃	3 × 10 ⁴	56	1100	—	—	—	No test; H ₂ S odor from pellet ^b
-13	Reagent-grade Li ₂ CO ₃ + Vitro Al ₂ O ₃	8 × 10 ^{4 d}	66	1100	400	123	no	Moderate attack and deep penetration by Li
-14		8 × 10 ^{4 d, e}	73	1100	400	123	no	Mild attack and moderate penetration by Li
-15		8 × 10 ^{4 d}	69	1100	380	172	yes	No attack and moderate penetration by Li
-16		8 × 10 ^{4 d, e}	76	1100	380	172	yes	No attack and very minor penetration by Li

^a All pellets sintered for ~17 hr.^b Odor occurred after sintering, indicating contamination.^c Pellet heated in LiF-LiCl-LiI eutectic mixture only for 21.5 hr, inspected, and then heated in lithium for 23 hr.^d Stearic acid used as die lubricant.^e Product ground for ~15 min before pressing and sintering.

condition. The pellets that appeared to have suffered attack were removed from the liquid lithium, washed with absolute methanol, and examined.

Table V-14 summarizes the fabrication conditions and the compatibility of the double oxides with liquid lithium. Of the three tested, only LiAlO_2 appeared to be suitably resistant to lithium attack. (From these experiments, LiAlO_2 was also selected for testing as an inert infusible filler in the preparation of paste electrolytes.) The LiAlO_2 , both commercial and synthesized, used in these tests, was the γ or high-temperature form. A discussion of the reactions by which LiAlO_2 is synthesized as well as the conditions necessary for the preparation of both the α and γ forms of LiAlO_2 can be found in Section V.A.8.a.

In general, the results in Table V-14 indicate that LiAlO_2 insulators will satisfactorily resist corrosion by liquid lithium under certain conditions. For example, the degree of attack on the pellets is directly related to the density; as the density of the pellet is increased, the amount of attack by the molten lithium decreases significantly. A high pellet density was achieved by increasing the pressing force and decreasing the particle size of the product. A maximum pressing force of 8×10^4 psi was obtained by using a die lubricant (stearic acid) to prevent galling of the

mold at high pressures. The fine particle size of the product was enhanced by grinding the product aggregate. As previously discussed in Section V.A.8.a, the Li_2CO_3 particle size is not an important variable, since it is in the molten state during the synthesis reaction. Powdered Li_2CO_3 ranging from very fine recrystallized material to ground reagent-grade material was used as indicated in the table without any apparent change in the final product.

Presoaking the pellets in molten LiF-LiCl-LiI eutectic, to simulate more closely the environment of an operating cell, also reduced the extent of lithium penetration and improved the resistance of the pellet to attack. At lithium temperatures below 450°C , a value above that expected in an operating cell, attack was moderate to negligible if the pellet was initially in good condition and it was presoaked in the eutectic mixture. However, molten lithium at 500°C did cause appreciable attack on a LiAlO_2 pellet.

In summary, the tests indicate that, for compatibility with liquid lithium, the optimum conditions for fabrication of LiAlO_2 shapes include a pressing force of about 8×10^4 psi, a sintering temperature of about 1100°C , and a powder fine enough so that the pellet density approaches the theoretical density of LiAlO_2 .

2. Metals

a. Corrosion of Metals by Liquid Tellurium (*M. S. Foster, H. Shimotake, K. A. Davis, G. H. Kucera*)

Tungsten has been found to provide suitable resistance to attack by tellurium and lithium-tellurium alloys at temperatures up to 525°C . However, because of the high density and difficulty of fabrication of tungsten, as well as its cost, other metals have been sought for use in constructing lithium/tellurium cells.

An attempt to contain tellurium in molybdenum at 500°C failed when the tellurium reacted completely in 18 hr to form a solid (ANL-7425, p. 189). Subsequently, an investigation of the practicality of using Armco iron in lithium/tellurium cells was undertaken.

In several experiments, tellurium was observed to react with iron, forming a solid scale of FeTe_2 . The ability of this FeTe_2 scale to reduce or prevent further attack was investigated. When the system is quiescent, the rate of attack is reduced. However, when the liquid is agitated, no reduction in rate of attack is apparent. For example, with agitation, tellurium at 480°C in an Armco iron crucible completely reacted and formed a solid in 30 hr. In contrast, without agitation, Armco iron coupons which were initially 0.036 in. thick were reduced to a 0.025-in. thickness in 100 hr of

immersion in liquid tellurium at 455°C . The addition of up to 10 at. % lithium to the tellurium did not appreciably reduce its rate of reaction with iron.

Although no substitute for tungsten has yet been found, additional tellurium corrosion tests are being held in abeyance because of greater interest in other lithium/chalcogen cells.

b. Corrosion of Metals by Liquid Selenium (*H. Shimotake, M. S. Foster, M. L. Kyle, K. A. Davis*)

The use of molten selenium as the cathode material in a cell creates problems in the selection of corrosion-resistant, electrically conductive containment materials. Selenium is a particularly difficult material to contain in metals because selenides of most common metals can be prepared by direct contact of the two elements at temperatures below 1000°C .

Several static corrosion tests were conducted to determine the corrosion resistance of various materials to molten selenium at 375°C . The results of these tests (Table V-15) show that neither Fansteel 85 alloy nor niobium is severely attacked by selenium under static conditions. However, tantalum and a tantalum-10 wt % tungsten alloy are less corrosion-re-

TABLE V-15. STATIC CORROSION OF VARIOUS MATERIALS BY MOLTEN SELENIUM AT 375°C

Material Tested	Test Duration (hr)	Corrosion Rate (mils/yr)
Fansteel 85 ^a	98.5	12
Niobium	99.5	18
Tantalum	99	35
Ta-10 wt % W	120	48
Armco Iron	260	220
Molybdenum	18	75000

^a Nb-27 wt % Ta-11 wt % W-1 wt % Zr.

sistant, and both Armco iron and molybdenum are severely attacked. The corrosion rates in molten selenium of the latter two materials are higher than those reported in preliminary tests (ANL-7425, p. 189). It appears that these metals form loosely adherent reaction films with highly variable rates of sloughing. In further testing, a molybdenum crucible (1 in. OD with a 0.125-in. thick wall) was exposed to molten selenium at 300°C for 262 hr with agitation. At the end of the experiment, the crucible contents had solidified, indicating almost complete reaction of the selenium with the molybdenum crucible.

The corrosion resistance of other materials to molten selenium will be tested under conditions of mild agitation.

c. Corrosion of Metals by Liquid Tin (*H. Shimotake, G. L. Rogers*)

Liquid tin has been proposed as a liquid-metal cathode in thermally regenerative bimetallic cell systems using fused-salt electrolytes and alkali-metal anodes. However, little information on corrosion by tin is available for temperatures above 800°C. Since common metals such as iron, nickel, and chromium have high solubilities in tin at temperatures above 800°C, corrosion studies were carried out on refractory metals.

Tests were conducted at 1300°C either by suspending coupons of the test material in liquid tin or by containing the liquid tin in a crucible made of the test material. After exposure to tin, specimens cut from the coupon or the crucible were mounted in plastic for

TABLE V-16. CORROSION OF REFRACTORY METALS BY TIN AT 1300°C

Material Tested	Form of Test Material	Test Duration (hr)	Result
Tungsten	Crucible	211	No corrosion
Mo-30 wt % W	Crucible	123	No corrosion
Re-50 wt % W	Coupon	136	No corrosion
Nb-10 wt % W-2.5 wt % Zr	Crucible	100	50 μ m penetration by Sn; Nb-Sn interaction
Nb-27 wt % Ta-11 wt % W-0.8 wt % Zr	Crucible	114	60 μ m penetration by Sn; Nb-Sn interaction
Mo-0.5 wt % Ti-0.08 wt % Zr	Coupon	137	50 μ m penetration by Sn; Ti found in Sn and Zr at Sn-sample interface

examination with an electron probe microanalyzer having a resolution of about 2 μ m. The results are shown in Table V-16.

No interaction was found between the tin and the following metals: tungsten, Mo-30 wt % W, and Re-50 wt % W. A reaction layer (~ 50 μ m) of Nb-Sn formed at the tin-metal surface of the following niobium-containing alloys: Nb-10 wt % W-2.5 wt % Zr and Nb-27 wt % Ta-11 wt % W-0.8 wt % Zr. The test of a Mo-0.5 wt % Ti-0.08 wt % Zr alloy showed that titanium dissolved in the liquid tin leaving a 50- μ m-thick zone depleted in titanium; zirconium was completely removed from the alloy and formed a thin layer at the tin-sample interface. The zirconium is believed to have formed an oxide by reaction with a trace amount of dissolved oxygen in the tin. The corrosion of the niobium alloys and the Mo-0.5 wt % Ti-0.08 wt % Zr alloy by liquid tin occurs intergranularly.

Of the materials tested, tungsten, Mo-30 wt % W, and Re-50 wt % W are suitable for construction materials in a lithium/tin thermally regenerative system. The Mo-30 wt % W is the most promising of the three because of its relative ease of fabrication.

VI

Nuclear Constants¹

(*N. D. Dudey, C. E. Crouthamel*)

An understanding of fast-neutron processes is essential to the design and development of fast breeder reactors. The objective of the nuclear constants program is to obtain cross-sectional data for neutron reactions of fuel, structural, and control materials that are of interest to the overall fast breeder reactor program. In one method being used, the cross section for a given reaction is measured as a function of monoenergetic neutron energy. Frequently, however, this approach is impossible or impractical because of the relatively low monoenergetic neutron fluxes obtainable. In such cases, it is necessary to measure cross sections directly in the broad neutron energy spectrum of a fast reactor. These measurements provide an in-

tegral cross section value that is dependent upon the neutron energy distribution in the reactor. Cross-section measurements are also important in evaluating the accuracy of theoretical calculations and in providing insight into improvements of the theoretical descriptions.

Current progress is reported for (n,γ) , (n,p) , and (n,α) cross-section measurements of LMFBR structural and cladding materials, capture-to-fission ratios in various uranium and plutonium isotopes irradiated in EBR-II, and capture cross-section measurements of some fission product nuclides. The status of an experiment to measure the fast fission yields of low-mass particles is also described.

¹ A summary of this section is given on page 14.

A. MONOENERGETIC NEUTRON CROSS-SECTION MEASUREMENTS

(*N. D. Dudey, R. R. Heinrich, A. A. Madson*)

Nuclear-reactor neutronic calculations are critically dependent upon an accurate knowledge of unproductive neutron-absorption reactions that occur within a reactor. The most important unproductive process is the neutron capture (n,γ) reaction, which can occur in fuel, cladding, structural, coolant, and fission product material located within the reactor. Other reactions, such as (n,p) and (n,α) , in addition to being unproductive, are deleterious because they can produce radiation damage in fuel, cladding, and structural materials.

In the current program, emphasis is being placed upon measurements of neutron-capture cross sections as a function of neutron energy between about 30 keV and 1.7 MeV. The monoenergetic neutrons are produced by bombarding lithium targets with protons from a Van de Graaff accelerator. The target nuclides

of interest are irradiated in the form of pressed pellets or metallic foils. The number of neutrons incident upon the targets is monitored by thin gold foils in the front and back of the target and by a ^{235}U fission counter located immediately behind the back gold monitor foil. The reaction products are assayed by counting the gamma-ray, X-ray, or beta activity associated with the activation product.

A computer code has been written to reduce the experimental data to the desired cross sections. The code computes disintegration rates from the counting data by a least-squares method. The solid angles intercepted by the front gold foil, the back gold foil, and the fission counter are calculated from the geometry of the experiment, including the dimensions of the target and the neutron source. From the computed neutron energy, the neutron flux incident upon

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FIG. VI-1. Capture Cross Section of ^{51}V .

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FIG. VI-2. Capture Cross Section of ^{50}Ti .

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FIG. VI-3. Capture Cross Section of ^{89}Y for the Production of $^{90\text{m}}\text{Y}$.

308-1812

FIG. VI-4. Capture Cross Section of ^{85}Rb for the Production of $^{86\text{m}}\text{Rb}$.

308-1816

FIG. VI-5. Capture Cross Section of ^{87}Rb .

each of the three monitors is determined. The flux incident upon the target is then computed from the monitor flux values and the geometry of the experiment. The average difference in the values of the flux calculated for the ^{235}U monitor and the adjacent gold monitor was found to be less than 1% for 54 neutron

energy points between 150 keV and 1.3 MeV, when recommended cross-section values² were used. Corrections for neutron source spread and solid angles subtended by monitor foils and targets may account for

² Brookhaven National Laboratory, "Neutron Cross Sections," BNL-325, 2nd ed., Suppl. 2 (February 1966).

our excellent agreement between the gold and ^{235}U monitors (discrepancies as large as 15% between gold and ^{235}U flux monitors have been reported in the literature).

The final results of capture cross sections measured for the $^{51}\text{V}(n,\gamma)^{52}\text{V}$ and $^{50}\text{Ti}(n,\gamma)^{51}\text{Ti}$ reactions are shown in Figs. VI-1 and VI-2. Data of other investigators³⁻⁵ are also given for comparison. The error bars on the figures indicate the rms standard deviations in the absolute values of the cross sections. Cross sections for the reactions $^{89}\text{Y}(n,\gamma)^{90\text{m}}\text{Y}$, $^{85}\text{Rb}(n,\gamma)^{86\text{m}}\text{Rb}$, and $^{87}\text{Rb}(n,\gamma)^{88}\text{Rb}$ are shown in Figs. VI-3 to VI-5, respectively; the data of Grench⁶ are included in Fig. VI-3 for the reaction $^{89}\text{Y}(n,\gamma)^{90\text{m}}\text{Y}$. No assessment of errors has been made as yet for these three reactions. Measurements are in progress to determine cross sections for the $^{86}\text{Sr}(n,\gamma)^{87\text{m}}\text{Sr}$, $^{84}\text{Sr}(n,\gamma)^{85\text{m}}\text{Sr}$, and $^{87}\text{Sr}(n,n')^{87\text{m}}\text{Sr}$ reactions.

³ A. E. Johnsrud, M. G. Gilbert, H. H. Barschall, *Phys. Rev.* **116**, 927 (1959).

⁴ Y. Y. Stavisskii, V. A. Tolstikov, *J. Nucl. Energy* **16**, 496 (1962).

⁵ W. S. Lyon, R. L. Macklin, *Phys. Rev.* **114**, 1619 (1959).

⁶ H. A. Grench et al., *Nucl. Phys.* **A94**, 157 (1967).

Theoretical calculations for the (n,γ) reactions of ^{51}V , ^{50}Ti , and ^{87}Rb were performed using the computer codes Abacus and Nearrex. The theoretical description of Moldauer, which has been previously described,⁷⁻⁹ was used in the calculations. The calculated values are shown as the solid lines in Figs. VI-1, VI-2, and VI-5. The experimental and calculated values were in good agreement for ^{87}Rb . However, the experimental measurements for ^{51}V and ^{50}Ti showed deviations from theoretical calculations that were considerably greater than the experimental uncertainties. One such deviation can be seen clearly in the data for ^{50}Ti at about 400 keV (see Fig. VI-2). This deviation is attributed to a resonance-type structure that is not predicted by our energy-averaged compound-nuclear theoretical calculations. The nature of the structure is presently being investigated.

⁷ P. A. Moldauer, *Rev. Mod. Phys.* **63**, 1079 (1964).

⁸ P. A. Moldauer, C. A. Engelbrecht, G. J. Duffy, "Nearrex, A Computer Code for Nuclear Reaction Calculations," USAEC Report ANL-6978 (1964).

⁹ D. C. Stupegia, M. Schmidt, C. R. Keedy, A. A. Madson, *J. Nucl. Energy* **22**, 267 (1968).

B. INTEGRAL CROSS-SECTION MEASUREMENTS (N. D. Dudey, R. R. Heinrich, J. W. Williams)

Many reactions that cannot be readily measured by monoenergetic techniques can be measured in a fast-reactor neutron flux. These spectral-averaged or integral cross sections are valuable for evaluating differential data, for monitoring the number of neutrons present in a given position of a reactor, and for evaluating the spectral shape of the neutron-energy distribution. Since the neutron-energy distribution varies as a function of position within a reactor, integral measurements at various positions can give some indication of the energy dependence of reactions whose differential cross sections are unknown.

Integral measurements have been made on specimens of type 304L stainless steel irradiated at various positions throughout the core and blankets of EBR-II. The principal purposes of this study were (1) to measure the neutron flux of EBR-II as a function of radial position and (2) to estimate the integral cross sections of important (n,p) , (n,γ) , and (n,α) reactions occurring in irradiated stainless steel.

After suitable radiochemical separations, the reaction products ^{58}Co , ^{60}Co , and ^{54}Mn were determined

by gamma spectrometry using a Ge(Li) detector, ^{55}Fe was determined by 4π X-ray counting, and ^{63}Ni was determined by liquid scintillation counting techniques. From these results, calculations were made of the specific atom production rates, that is, the number of atoms of each of these nuclides produced per megawatt-day per gram of type 304L stainless steel; these data are shown in Fig. VI-6.

Differential cross sections for the two reactions $^{54}\text{Fe}(n,p)^{54}\text{Mn}$ and $^{58}\text{Ni}(n,p)^{58}\text{Co}$ were used to determine the total EBR-II flux per megawatt at eight radial positions. These values are shown in Fig. VI-7, where they are compared with a diffusion-theory calculation of the flux, and with values reported by Jackson and Ulseth¹⁰ for an EBR-II power level of 20 kW. The excellent agreement between our full-power measurements and the low-power values of Jackson and Ulseth¹⁰ indicates that the flux per megawatt is independent of EBR-II reactor power level, contrary to previous conclusions.¹⁰ From the

¹⁰ J. L. Jackson, J. A. Ulseth, *Nucl. Appl.* **5**, 275 (1968).

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FIG. VI-6. Specific Atom Production Rates in Type 304L Stainless Steel as a Function of Irradiation Position in EBR-II.

measured value of the EBR-II flux, integral cross sections were calculated for four reactions of stainless steel at the core center and estimated for three additional reactions. These data are summarized in Table VI-1 and are compared with the data of Jackson and Ulseth.¹⁰

The ratio of the atom production rates of ^{54}Mn and ^{55}Fe , both of which are produced from ^{54}Fe , can serve as a very sensitive indicator of a reactor's spectral shape. This ratio at eight radial positions in EBR-II is shown in Table VI-2; the median neutron energy calculated by a diffusion theory is also included to demonstrate the sensitivity of this indicator.

In an extension of this work, specimens of Ti, V, S, Fe, Ni, Co, Sc, Cu, and Au were irradiated in EBR-II, and analysis of all radiochemically measur-

able (n,γ), (n,p), (n,α), and ($n,2n$) reaction products is in progress.

In evaluating the long-term behavior of reactors, it is necessary to know fission and capture cross sections of the uranium and plutonium isotopes, which build up through successive captures in the primary fuel isotopes. In the first subassembly loading in EBR-II (ANL-7425, p. 191), 65 samples consisting of ^{233}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu , and ^{242}Pu were irradiated in various positions of the core and blanket. All of the samples have now been decanned, and the uranium samples have all been dissolved. Considerable difficulties were encountered in dissolving these samples because of the behavior of the irradiated stainless steel containers. After dissolution of a sample in perchloric acid, a silicon residue remained, which occluded some fission products. To eliminate

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FIG. VI-7. EBR-II Radial Flux per Megawatt Measured at Full Power.

TABLE VI-1. EBR-II SPECTRUM-AVERAGED CROSS SECTIONS OF TYPE 304L STAINLESS STEEL CONSTITUENTS

Reaction	Cross Section at EBR-II Core Center (mb)	
	This Work	Jackson-Ulseth ^a
$^{54}\text{Fe}(n,p)^{54}\text{Mn}$	26	24
$^{58}\text{Ni}(n,p)^{58}\text{Co}$	36	35
$^{60}\text{Ni}(n,p)^{60}\text{Co}$	≈ 0.5	
$^{58}\text{Ni}(n,\alpha)^{55}\text{Fe}$	≈ 0.1	
$^{62}\text{Ni}(n,\gamma)^{62}\text{Ni}$	9.6	
$^{54}\text{Fe}(n,\gamma)^{55}\text{Fe}$	9.3	
$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$	≈ 8.7	

^a Ref. 10.

the possibility of uranium loss, the precipitate was dissolved in HF and analysis was carried out on the combined solutions. Measurements of alpha (cap-

TABLE VI-2. "SPECTRAL HARDNESS" INDICATOR IN EBR-II: ATOM RATIO $^{54}\text{Mn}/^{55}\text{Fe}$ PRODUCED FROM ^{54}Fe

Radial Position ^a (cm)	Atom Ratio $^{54}\text{Mn}/^{55}\text{Fe}$	Calculated Median Neutron Energy (keV)
2.86	2.18	470
10.21	1.98	465
21.25	1.63	405
30.62	0.893	320
40.83	0.320	206
51.03	0.102	
61.24	0.056	140
71.45	0.040	

^a Distance from core center.

ture-to-fission cross-section ratios) for ^{233}U are nearly complete, and ^{235}U and ^{238}U measurements are in progress.

C. LOW-MASS FAST-NEUTRON FISSION YIELDS (*N. D. Dudey, A. A. Madson*)

A knowledge of the yields of the low-mass particles tritium, hydrogen, and helium in fast-neutron fission is important to the LMFBR program. Information on the production of tritium in fast reactors is particularly needed because of the problems of tritium disposal in fuel reprocessing and, possibly, in reactor operations. The production of hydrogen and helium is of interest because of the chemical and physical effects of their interactions, mainly with cladding materials. Measurements of the fission yields of these particles should also contribute to the theoretical understanding of the fission process.

An experiment has been designed to measure the fast-fission yields of these low-mass particles as a function of neutron energy. Monoenergetic neutrons will be produced by Li(p,n) or D(p,n) reactions in a new ANL neutron generator now under construction. The low-mass particles produced in the fast fis-

sion of various uranium and plutonium isotopes will be detected in a three-detector telescope array. After appropriate electronic manipulation, the energy of a particle will be determined from the sums of the signals from the three detectors; the type of particle will be determined from the relative energy loss in each of the three detectors.

A scattering tube has been designed and built which will house a wheel containing several targets, the telescope array, and the neutron monitoring equipment. The hardware and electronics have been assembled and calibrated. Final checkout of the instrumentation is awaiting receipt of a ^{252}Cf source, which will yield low-mass particles by spontaneous fission. On-beam experiments with ^{235}U and ^{239}Pu are expected to begin when the new neutron generator is available for measurements.

VII

Determination of Burnup of Fast Reactor Fuels¹

(*R. P. Larsen, R. J. Meyer, C. E. Crouthamel*)

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 to

develop accurate analytical methods for determining the concentration of fission products that can be used as burnup monitors and to establish accurate values for their fast fission yields.

¹ A summary of this section is given on pages 14 and 15.

A. EVALUATION OF RARE EARTHS, MOLYBDENUM, AND TECHNETIUM AS BURNUP MONITORS FOR URANIUM OXIDE FUEL (*R. J. Meyer, R. D. Oldham, R. J. Popek*)

A necessary part of developing methods for burnup analysis is the demonstration that a fission product monitor is suitable for a particular type of fuel (e.g., metal, oxide, carbide). The criteria that must be met in selecting a monitor were presented previously (ANL-6900, p. 335). One of the most important of these is that the monitor must be quantitatively retained in the sample for burnup analysis. Both technetium-99 and lanthanum-139 met this criterion for metallic EBR-II fuel. However, in oxide fuels, many fission products are expected to behave differently, and potential monitors for these fuels must be carefully evaluated.

Investigations being performed in a separate program on the chemistry of irradiated fuels (see ANL-7425, pp. 104-113, and this report, Section III.B.2) provided valuable guide lines in the selection of burnup monitors. For example, the studies on the chemistry of irradiated oxide fuels have shown that certain nuclides (e.g., the rare earths) do not appear to migrate during irradiation; therefore, these nuclides are considered excellent candidates for burnup monitors. When extreme migration of a fission product (e.g., cesium) is demonstrated, the nuclide is not a satisfactory monitor. However, for fission products with intermediate degrees of migration (e.g., molybdenum, technetium, ruthenium, barium), the decision is not clear cut, and further investigation is necessary to

establish whether or not a cross-sectional cut of a fuel pin will provide a representative sample of the fission product under consideration.

To clarify the situation with respect to the suitability of molybdenum and technetium as monitors for oxide fuels, a series of analyses was performed on three sections of a 13% enriched UO₂ fuel pin irradiated to ~6 at. % burnup. These sections were 1/8 in. thick and were cut from the top, middle, and bottom portions of the fuel rod. Each section was analyzed for burnup and for uranium, molybdenum, and technetium content. Burnup was determined by pre- and post-irradiation uranium isotopic analysis, and uranium by mass-spectrometric isotopic-dilution analysis. Both molybdenum and technetium were determined spectrophotometrically as their respective thiocyanate complexes after separation from interfering ions by ion exchange and/or solvent extraction. Each of the fuel sections was also analyzed gamma-spectrometrically for ¹⁴⁴Ce (285 days) with a Ge(Li) detector system; the ¹⁴⁴Ce count rate was determined by integration of the photopeak at 134 keV.

The results of the analyses for molybdenum, technetium, ¹⁴⁴Ce, and burnup have been correlated, and these correlations are summarized in Table VII-1. The variations in molybdenum-to-fission and technetium-to-fission ratios in the three sections of the

TABLE VII-1. FISSION PRODUCT-TO-FISSION RATIOS
FOR SECTIONS OF A UO_2 FUEL PIN
(6 AT. % BURNUP)

Sample	Molybdenum- to-Fission Ratio	Technetium- to-Fission Ratio	^{144}Ce Count Rate-to-Fission Ratio
Top	0.209	0.0492	1.66×10^4
Middle	0.242	0.0514	1.66×10^4
Bottom	0.249	0.0528	1.67×10^4

fuel pin indicate that neither molybdenum nor technetium was quantitatively retained in the fuel during irradiation. It is, therefore, concluded that

neither fission product is a satisfactory monitor for oxide fuels. This information is of particular significance because both molybdenum and technetium have been used, or have been considered for use, in other programs for determining burnup in oxide fuels. The good agreement among the cerium-to-fission ratios in the three sections of the fuel pin indicates that cerium was quantitatively retained in the fuel. These data on the behavior of cerium, a typical rare earth, provide further substantiation that the rare earths do not migrate in oxide fuels. Since the rare earths also appear to meet the other selection criteria, they are considered excellent candidates as burnup monitors for oxide fuels.

B. DEVELOPMENT OF ANALYTICAL METHODS FOR MONITORING BURNUP

Two methods of determining the concentration of rare earth fission products in irradiated fast reactor fuels are under development. As discussed in the preceding subsection, the rare earths are considered ex-

cellent candidates as burnup monitors for oxide fuels because they are immobile in the fuel during irradiation. Current work on the two methods of analysis is discussed below.

1. Photometric Titration of Total Rare Earths (*R. J. Meyer, R. D. Oldham*)

Developmental work has continued on a method of determining total rare earths by a photometric titration with EDTA. A detailed outline of the procedure was given in a previous report (ANL-7425, p. 193). Separation of the rare earths from major interferences is achieved in two steps of the procedure: (1) anion exchange in concentrated hydrochloric acid to remove the bulk of the fuel and cladding constituents and some fission products and (2) anion exchange in a methanol-nitric acid solution to remove the alkali metals, the alkaline earths, and yttrium. Recent minor modifications in both of these steps have resulted in improved separations.

The anion-exchange separation with concentrated hydrochloric acid has been altered to provide a better separation of plutonium from the rare earths. This was accomplished by eluting the rare earths from the anion-exchange column with concentrated hydrochloric acid that is 1 *N* in nitric acid. In the absence of nitric acid, it had been found that the plutonium was not quantitatively absorbed by the resin and thus contaminated the rare earth eluant.

In the anion-exchange separation with methanol-

nitric acid, refinements were made to provide a better and more reproducible separation of the rare earths from yttrium; these were (1) closer control of the amount and height of resin in the column, (2) closer control of the methanol and nitric acid concentrations when the column is converted to this medium from a dilute nitric acid medium, and (3) reslurrying of the resin after this conversion to insure homogeneity of the column packing.

The modified procedure was tested using two mixtures of rare earths and yttrium. One mixture simulated that which would be produced by uranium-235 fission; the other mixture simulated that which would be produced by plutonium-239 fission. Three rare earth determinations were carried out on each mixture. Recoveries for the ^{235}U mixture were 100.5, 100.5, and 101.0% and for the ^{239}Pu mixture, 99.9, 100.4, and 100.6%.

Because the constituents of stainless steel interfered slightly in previous procedures, the effect of stainless steel was retested using the revised procedure. No interference was observed.

The procedure was evaluated by analyzing two

samples of irradiated UO_2 . One sample was declad prior to the dissolution; the other was not. The rare earth (R.E.) content and the cerium-144 gamma-count rate of each solution were determined. A comparison of the results obtained on the two solutions was made by means of the ratio $(\mu\text{mol R.E.}/\text{ml})/({}^{144}\text{Ce cpm}/\text{ml})$. Ratios of 1.597×10^{-5} and 1.613×10^{-5} were obtained for the declad and clad samples, respectively.

The determined rare earth content of each sample

differed by 6% from the value calculated from pre- and post-irradiation mass-spectrometric uranium analysis and the best available data for rare earth fission yields. Uncertainties in both the mass-spectrometric burnup analysis and the fission yield data could easily account for this difference. The agreement in the analyses of the clad and declad samples is a further substantiation that stainless steel constituents no longer interfere in the analysis.

No further work on this method is planned.

2. X-Ray Spectrometric Determinations of Rare Earth Fission Products (R. V. Schablaske, M. I. Homa)

Measurement of burnup in fast reactor fuels by an X-ray spectrometric assay of the rare earths is under development. The general analytical procedure to be used was described in ANL-7425, p. 194, and preliminary evaluations of the sensitivity and selectivity of the method were reported. In the proposed procedure, terbium (a rare earth not produced in fission) is added to the sample as an internal standard; the rare earth fraction is separated from uranium, plutonium, and high-activity fission products; and the separated rare earths are mounted on a metal plate and assayed by X-ray spectrometry.

Mounting the rare earth fission products as a solid on a metal plate provides the necessary sensitivity; however, a high degree of geometric reproducibility of the sample mount is difficult to achieve. This variability can be overcome by the introduction of an internal standard. The increase in precision achieved by this technique is demonstrated by the following experiment.

Six aluminum plates, each containing a total of 58 μg of inactive fission product rare earths and 8 μg of terbium internal standard, were prepared and assayed by measuring the La $L\alpha 1$, Ce $L\alpha 1$, Pr $L\alpha 1$, Nd $L\alpha 1$, and Tb $L\beta 1$ line intensities. Line-intensity ratios (rare earth/internal standard) were then calculated from the line-intensity data.

A comparison of the precision obtainable from absolute intensity data with the precision obtainable by use of an internal standard is shown in Table VII-2. For simplicity only the neodymium and terbium data are presented. The precisions of the line-intensity ratios for the other rare earths were similar to that shown for neodymium in Table VII-2. Relative standard deviations of the ratios for the $L\alpha 1$ lines were as follows: lanthanum, 4.3%; cerium, 2.9%; praseodymium, 2.8%; neodymium, 2.3%. The poorer precision for lanthanum is the result of a line intensity that

is significantly lower than that of the other rare earths.

In further testing of the internal-standard technique, a calibration curve was prepared using a series

TABLE VII-2. COMPARISON OF ABSOLUTE AND RELATIVE LINE INTENSITY DATA IN X-RAY SPECTROMETRIC RARE EARTH ANALYSIS; Nd = $L\alpha 1$, Tb = $L\beta 1$

	Nd (counts/sec)	Tb (counts/sec)	Nd/Tb
	159.9	61.5	2.60
	172.6	69.7	2.48
	176.8	66.8	2.65
	164.2	65.1	2.52
	125.7	48.9	2.57
	149.9	58.2	2.58
Average	158.2	61.7	2.57
Rel. Std. Dev.	11%	8%	2.3%

TABLE VII-3. RELIABILITY OF THE X-RAY SPECTROMETRIC ANALYSIS FOR COMBINED RARE EARTHS

Amount Present (μg)	Amount Found (μg)	Difference (%)
14.6	14.4	-1.5
	14.7	+0.7
29.2	28.8	-1.3
	29.6	+2.5
43.9	43.4	-1.2
	44.6	+1.6
58.4	58.8	-0.5
	59.2	+1.3
72.9	72.0	-1.3
	73.5	+0.8
87.9	86.6	-1.1
	88.5	+1.0

of 12 plates. Each plate contained 8 μg of terbium and a total of 15 to 90 μg of the principal fission product rare earths: lanthanum, cerium, praseodymium and neodymium. (The amounts of individual rare earths were based on their respective fission yields.) The La $L\alpha_1$, Ce $L\alpha_1$, Pr $L\alpha_1$, Nd $L\beta_1$, and Tb $L\beta_1$ line intensities were measured, and line-intensity ratios (rare earth to internal standard) were calculated from the line-intensity data. Calibration curves (line ratio *vs.* composition) were then derived from a least-squares analysis of the data.

To evaluate the calibration curves prepared from this data, the actual concentration of each rare earth on each plate was compared with that calculated using the measured line intensity and the calibration curve. When the total weight of the rare earth mixture was 30 to 90 μg , the average relative error calculated for each rare earth was as follows: lanthanum, 1.9%; cerium, 1.6%; praseodymium, 1.1%; and neodymium, 1.1%. When the total weight of the mixture was <30 μg , the errors were somewhat larger due to low line intensities.

Typical results were as follows:

Rare Earth	Amount (μg)	
	Present	Found
Lanthanum	11.6	11.8
Cerium	21.5	21.9
Praseodymium	9.7	9.8
Neodymium	37.8	37.9

A further evaluation of the data obtained in the calibration study showed that summing the four individual rare earths provides a more sensitive method of analysis with no decrease in precision. The data shown in Table VII-3 demonstrate that in the range

from 15 to 90 μg of combined rare earths, a precision of 1 to 2% is obtained. It is anticipated that the lower limit could be extended to 5 μg by increasing the counting time in the X-ray spectrometer from 1 to 3 hr.

Attention is now being given to the development of a simple separation procedure which will isolate the rare earths in a form suitable for X-ray spectrometry. A successful separation must meet at least two criteria: (1) the separated rare earths must be free of other elements that emit X-rays in the region of the L-spectra of the rare earths, and (2) the separated rare earths must be free of such bulk constituents as uranium, plutonium, and cladding. The latter criterion is necessary because the L-spectra of the rare earths consist of very soft X-rays which are easily absorbed by other solids.

Anion exchange in hydrochloric acid is being considered as a means of separating the rare earths from the bulk constituents of the fuel and cladding. This separation, which is one step in the rare earth photometric titration described above, is expected to be well suited to the X-ray spectrometric analysis, provided that the reagents do not introduce solids onto the X-ray plates.

In preliminary tests of the anion-exchange procedure, only the terbium internal standard and a simulated mixture of fission product rare earths were used. X-ray analysis of the "separated" rare earths showed no change in the individual rare earth-to-terbium ratios. However, the intensities of the "separated" rare earths were significantly lower than those of directly plated standards.

It is believed that this decrease in intensities resulted from small amounts of solids on the "separated" rare earth plates. Investigation of the source of the solids will be necessary before proceeding with testing of the anion-exchange separation.