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SUMMARY

Chemical Engineering Division Semiannual Report

I. Compact Pyrochemical Processes (pages 21 to 60)

Development work has continued on compact pyrochemical processes for the recovery of uranium and plutonium from fast breeder reactor fuels. The basic separations in present process concepts are accomplished through differences in the partition behavior of the fuel constituents between liquid metal and salt solvents. These processes have applicability to oxide, carbide, and metal reactor cores and blanket material.

New Pyrochemical Processes. Exploratory experiments have been performed to test the feasibility of uranium-plutonium-fission product separations by the selective transfer of solutes between two liquid metal alloys in mutual contact with a molten salt. The first two experiments, which were conducted in a divided tantalum crucible, showed selective transfer of plutonium (97.5 and >99%) from a Cu-33 w/o Mg alloy to a Zn-5 w/o Mg alloy, both alloys being in mutual contact with a 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl salt. In similar experiments, 83 and 92% uranium transfers were observed, using Cu-8 w/o Mg and Zn-5 w/o Mg alloys. Zirconium, also present in the Cu-Mg alloy, showed no transfer. These preliminary experiments are very encouraging and with improved equipment and techniques, high (99%) uranium recoveries should be achievable. The salt transport concept is highly attractive in that it offers the potential advantages of versatility, small process volumes, and high recoveries of fissionable and fertile elements. The flowsheet is readily adaptable to oxide, carbide, or metallic fuels and to core or blanket materials.

A conceptual flowsheet has been developed which makes use of fluid-bed and pyrochemical processes for the purification and reconversion of a carbide fuel (ThC_2 and UC_2). In order to determine the feasibility of the pyrochemical steps, a run consisting of three batch extractions was made: (1) uranium, thorium, and cerium (representative of the rare earths) were first oxidized by CdCl_2 from a Cd-3 w/o Zn solution containing thorium, uranium, cerium, and molybdenum (representative of the noble elements), (2) uranium and thorium were subsequently separated from cerium

in two batch extractions by selectively transferring the uranium and thorium from a salt phase to a Cd-50 w/o Mg solution. The results of this run indicated that (1) selective oxidation of uranium and thorium from metal solutions and transfer to a salt solution can be accomplished smoothly, thereby providing an excellent separation from noble metal fission products, which remain in the metal phase, and (2) distribution coefficients for uranium, thorium, and cerium are such that high recovery of uranium and thorium, and excellent separation from rare earths, alkali, and alkaline earth elements, can be achieved in a relatively small number of extraction stages.

Supporting Chemical Studies of Pyrochemical Processes. Supporting chemical studies of liquid metal and molten salt systems have been continued in order to provide data of process importance and to elucidate the chemical aspects of various process steps. These studies included the determination of distribution coefficients in order to estimate the difficulty to be expected in any separation and the determination of the solubilities of various substances in liquid metal and molten salt solutions in order to estimate process volumes, to evaluate corrosion results, and to develop separations based upon precipitation procedures.

Further determinations of the distribution coefficients of uranium, plutonium, praseodymium, and zirconium between various liquid cadmium-magnesium alloys and 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl were made. These determinations indicate that (1) the distribution coefficients are favorable for a separation of praseodymium¹ from uranium and plutonium at 600°C in a Cd-Mg alloy, (2) a separation of zirconium from uranium and plutonium is feasible because the separation factor is large, but would require abnormally large salt-to-metal ratios, and (3) separation of plutonium from uranium in this system would be difficult because there is little difference in their

¹Praseodymium is a key rare earth element because it is the one that is most difficult to separate from uranium or plutonium by pyrochemical methods.

distribution coefficients. However, uranium and plutonium can be processed together (as is desired for core fuel) and can be highly purified from fission products by selective extraction procedures using the cadmium alloy-halide flux systems.

In another distribution experiment, the effect of substituting bromide for chloride as the anion in the salt phase was investigated. With the Cd-Mg alloy, it was found that, although the separation factors at 600°C for uranium, plutonium, and praseodymium are smaller with the bromide salt than with the chloride salt, the distribution coefficients are larger with the bromide salt. The result is that more favorable salt/metal ratios could be used for multistage extractions with the bromide system, but more stages would be required.

The solubilities of iron, zirconium, and chromium in liquid Zn-Mg alloys as a function of magnesium concentration at 800°C, the solubility of iron in various Cu-Mg alloys over the temperature range 600 to 850°C were determined during this reporting period.

Another supporting study involved the determination of the solubility of various intermetallic compounds in molten salts. During the past reporting period the solubilities of two magnesium intermetallic compounds and of magnesium metal in magnesium chloride were determined. The solubility of magnesium in magnesium chloride at 800°C was found to be 0.22 ± 0.02 m/o when determined in closed apparatus and 0.13 ± 0.01 m/o when determined in open apparatus in a high-purity helium atmosphere. In open apparatus the solubility of Mg_2Sn in MgCl_2 was determined to be 0.03 ± 0.015 m/o at 800°C, and the solubility of Mg_3Bi_2 in MgCl_2 varied from 0.12 m/o at 731°C to 0.23 m/o at 851°C. At 886°C the solubility of the Mg_3Bi_2 dropped to 0.14 m/o.

Interactions of CdCl_2 in a molten salt with cadmium metal to form a lower cadmium chloride occur in a conceptual process employing cadmium as a liquid metal solvent for the recovery of uranium and plutonium from irradiated nuclear fuels. Accordingly, a supporting chemical study has been made to determine the nature of the subhalide species described by the equation

Spectrophotometric measurements of the colored cadmium (I) species in LiCl, 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl, and 59 m/o LiCl-41 m/o KCl eutectic, made at temperatures of 500 and 650°C, indicate that within experimental error, x has a value of 2 for all three salts. An equilibrium constant for the reaction was also determined in each of the salt systems at each of the temperatures studied.

Supporting Engineering Studies of Advanced Pyrochemical Processes. The development of engineering technology required for the separation of plutonium and uranium from fission products by multistage extractions between molten metal and molten salt phases was continued. One initial objective of this program is the demonstration of countercurrent, liquid-liquid extraction between a liquid cadmium-base metal and a liquid chloride salt. Such extraction was demonstrated in a 1-in. OD quartz tube, the middle six inches of which were packed with 1/4-in. lengths of 1/4-in. OD tantalum tubing. In these transient experiments a Cd-Zn-Mg alloy containing cerium (representative of the rare earths) was countercurrently contacted with a mixed chloride salt at temperatures varying between 490 and 620°C. The overall average mass transfer coefficient for cerium and uranium (studied earlier) was estimated to be 0.008 sec^{-1} . This gives a height equivalent to a theoretical stage of about two feet for an extraction column in which uranium or plutonium is separated from rare earths.

A total of 130 kg (20 to 40 kg per batch) of MgCl_2 -base salt has been purified for use in engineering scale experiments. The procedure used was to contact the molten salt with cadmium-30 w/o magnesium alloy at 600°C and thereby reduce the oxidizing constituents of the salt. Residual oxygen content of the purified salt was about 5000 ppm. This residual oxygen, thought to be present as finely divided insoluble magnesium oxide, has caused no difficulty in engineering experiments.

Materials testing is an important adjunct to the development of advanced pyrochemical processes. Corrosion tests of various conventional materials of construction to determine their suitability for use in flowsheets utilizing both cadmium-base and copper-magnesium solvent metal/salt systems are in progress. In one test, type 430 stainless steel was exposed at 600°C for 400 hr to the corroding phases (metal, salt-metal interface, salt and vapor) that exist in a 83 w/o Cd-11 w/o Zn-6 w/o Mg/50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl system. The type 430 stainless steel was corroded at an excessive rate in this system (4.5 mils/400 hr was observed in the metal phase sample). This high corrosion rate indicates that a lower concentration of zinc (the most corrosive constituent of the metal alloy) will have to be used to reduce the corrosion rate to an acceptable value.

In other tests the corrosion resistance of four ferrous alloys (mild steel, 1% Cr alloy steel, type 304 stainless steel, and type 405 stainless steel) to copper-magnesium/chloride salt systems was determined at 600 and 800°C in 200-hr tests. The metal composition varied from 50 to 90 w/o copper in magnesium. The

Results show that at 600°C there was less than 1 mil corrosion of any of the alloys tested. Corrosion rates increased with temperature and with copper concentration (up to nearly 2 mils/200 hr at 800°C for a copper concentration of 90 w/o). In nearly all mixtures, the principal mode of attack appeared to be uniform surface dissolution in the molten metal/salt mixture. The solubility of iron in various Cu-Mg alloys containing from 9 to 50 w/o Mg was found to be ~0.1 w/o at 800°C. Additional forms of attack, such as intermetallic compound formation, surface reaction, or spalling may also be occurring.

Vitreous carbon, which in a previous test was not wet by a Zn-Mg-10 w/o U/chloride salt solution after 24 hr of exposure at 800°C, was tested further by exposure to a zinc-2 w/o uranium/chloride salt system and a zinc-5 w/o magnesium-2 w/o uranium/chloride salt system for 200 hr at 800°C. In both cases the metal phase did not wet the small crucibles tested and the salt phase only slightly wet the crucibles. These results are indicative that corrosion of vitreous carbon by these solutions will be negligible up to 800°C.

At the present time, pressed-and-sintered tungsten crucibles are used in the skull reclamation process. Efforts to procure less expensive, longer-lived, impermeable crucibles for this process are continuing. One approach consists in the addition of 0.1 w/o nickel to pressed-and-sintered tungsten. At this concentration a solid solution of nickel in tungsten is reportedly formed during sintering. This should result in a higher density pressed product. After exposure of an agitator blade of nickel-impregnated tungsten to a zinc/47.5 m/o MgCl₂-47.5 m/o CaCl₂-5 m/o MgF₂ system at 800°C for 200 hr, no deterioration of the blade was evident. Thus, the addition of a small amount of nickel seems to have little effect on the corrosion-resistance properties of tungsten.

A tungsten crucible (4-in. OD by 6 in. high by 1/4-in. wall), which was fabricated by plasma-spraying on a sacrificial mandrel and sintering of the plasma-sprayed body at 2500°C, failed after a total of over 1000 hr service at 600 to 850°C. Failure occurred upon inadvertent solidification, caused by a power failure, of a cadmium-magnesium-zinc/chloride flux system in the crucible. Failure was most probably caused by physical or thermal shock acting upon residual stresses left in the crucible after fabrication.

Metallwerk Plansee (Austria) has successfully completed shear-forming a tungsten crucible 18.1 in. high by 11.1-in. OD by 0.18-in. wall. This is probably the largest tungsten crucible ever fabricated by this technique. This crucible has been received and, after thermal cycling, will be tested for containment of molten zinc-magnesium/salt systems.

Purification of Argon from Nitrogen with Titanium Sponge. Work on the removal of nitrogen from argon by gettering the nitrogen on hot titanium sponge has been completed. Although this method has general utility for purifying argon for such applications as glovebox atmospheres, the major incentive for its development has been a possible future need to remove nitrogen from the atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility. The kinetics of the nitrogen-titanium sponge reaction have been determined at nitrogen concentrations of 100, 300, 1000, 5000, and 50,000 ppm in argon. A single experimental relation has been developed and found to agree well with the experimental data:

$$\frac{0.242 - W}{W} = 6.82p^{-0.18}t^{-0.62}$$

where

W = mg nitrogen absorbed per cm² of titanium surface area

p = partial pressure of nitrogen in argon, mm Hg

t = time, hr.

In most reacted sponge particles, three phases were identifiable by X-ray diffraction techniques: TiN_x, ε-TiN, and a solid solution of nitrogen in alpha titanium.

The 10-cfm pilot plant, designed to obtain overall performance data for the continuous removal of nitrogen from argon by reaction with titanium sponge, was shut down after 1800 hr of operation. It was found that to insure satisfactory operation, care must be taken to minimize contamination of the inert atmosphere by oxygen and water vapor and a satisfactory gas circulating blower must be provided. The process appears feasible from both an operational and cost standpoint.

Preparation of EBR-II Fuel Alloy. The Chemical Engineering Division was requested to prepare fuel alloy for fabrication of EBR-II fuel pins. Two fuel alloys of different uranium-235 enrichment values were prepared in an existing melt refining furnace. About 200 kg were produced of one alloy in which the required uranium-235 portion of the uranium was 52.5 ± 1.2 a/o; about 27 kg were prepared of the other alloy in which the required uranium-235 content of the uranium was 70 a/o.

Skull Reclamation Process. Work was continued on the skull reclamation process, which is to be used in the EBR-II Fuel Cycle Facility for the recovery and purification of uranium contained in melt refining crucible residues (skulls). In the current reporting period, the skull reclamation process was greatly simplified (Figure I-9). With the modified flowsheet, only three steps are now required to accomplish reduction

of uranium oxides to uranium metal and purification of the uranium. In addition to having fewer steps, the new flowsheet also has the advantages (as compared to the previous flowsheet) of (1) a substantially shorter processing time per batch, (2) higher uranium recovery, (3) smaller consumption of raw materials, (4) smaller waste volumes, and (5) greater equipment operating life. Fission product removals are substantially unchanged. Conditions and performance of the new flowsheet have been established in pilot plant runs. Testing of plant-scale equipment is now under way.

The plant equipment to be used in the Fuel Cycle Facility is sized for batch-operation with about 6 kg of skull oxide (about 5 kg of uranium oxide), which is formed by the controlled oxidation of melt refining crucible residues (skulls). Three major equipment items are required in the skull reclamation process: (1) a skull oxidation furnace, which is already in operation in the Fuel Cycle Facility, (2) a reduction furnace in which the skull oxides are reduced and the uranium is partially purified in a large (14-in. ID by 24½-in. inside height) tungsten crucible, and (3) a retorting furnace in which uranium metal is isolated for return to the main fuel stream by evaporating magnesium and zinc solvent metals away from the uranium. The latter two furnaces are currently being tested and, where necessary, modified for later installation in the Fuel Cycle Facility. Testing of the two furnaces is being conducted in a large argon-atmosphere enclosure (volume, ~4000 cu ft); operation of the furnaces within the enclosure simulates that planned for the Fuel Cycle Facility.

Ten nonradioactive runs have been made in the reduction furnace using the simplified skull reclamation flowsheet (Figure I-9); oxidized uranium-fissium alloy was used as the feed material. The primary purpose of this series of runs was to evaluate the mechanical performance and reliability of the equipment. In addition, information was obtained on the effect of varying the process and operating conditions on uranium recovery and fission product removal. To simulate plant conditions, successive runs were made without cleaning the tungsten process crucible between runs.

Mechanically, the operation of the reduction furnace was very satisfactory. No difficulties were encountered during charging of materials, heating, mixing, sampling, and transferring molten metals and fluxes from the furnace to exterior receivers.

Two problems, neither of which is considered major, and their proposed solutions are as follows:

(1) Insufficient mixing intensity. Increasing mixing intensity will be achieved by adding another impeller

to the mixer shaft and by incorporating baffles into the process crucible.

(2) Control of metal and salt fumes. Fuming of metal and salt vapors was observed during opening of the reduction furnace at operating temperatures for charging reagents. To overcome this problem, an exhaust manifold, which is attached to the furnace charging port, was developed. It has performed very well in preliminary tests. To a lesser extent fuming also occurs at the transfer receiver during and following transfers of metal and salt solutions from the furnace. These fumes will be controlled by an exhaust-filter assembly.

The following general observations can be made on the three reduction furnace runs for which analytical data are complete:

(1) Overall uranium recoveries in the product solutions transferred from the furnace ranged from 82 to 95.5% of the uranium charged. Losses in the waste streams amounted to 2 to 7%. The bulk of the uranium loss occurred in the waste flux and is attributed to insufficient mixing intensity in the reduction step. On the assumption that improved mixing conditions will improve uranium reduction, uranium losses in the waste streams are expected to be reducible to about 3%.

(2) Overall removals of cerium, a representative rare earth, were very satisfactory, ranging from 89 to 96%.

(3) Although occasional satisfactory removals of ruthenium and molybdenum were achieved, the removals of these elements were generally poor and erratic. These poor removals should also be corrected by the steps that are being taken to improve the mixing intensity.

The final step in the skull reclamation process consists of retorting, or solvent evaporation, to recover the product uranium from the uranium solution produced in the dissolution step. This product solution has the nominal composition Zn-12 w/o Mg-12 w/o U, weighs about 36 kg (volume, 8 liters), and contains approximately 4 kg of uranium. Plant retorting equipment is being developed to recover the uranium from the product solution in a form suitable for use as make-up feed material for the melt refining process. Four retorting runs have been completed using beryllia crucibles and Zn-Mg-U ingots; the ingots were the product of reduction furnace runs. A thixotropically cast beryllia crucible was in good condition after two runs; in both runs, the uranium product ingot could be easily removed from the crucible. Additional retorting runs with this crucible are planned to determine its useful life. An isostatically pressed beryllia crucible showed hairline cracks after two runs; after the second

run, the uranium product ingot adhered tenaciously to the crucible and could not be removed. No additional retorting runs with this crucible are planned. The retorting assembly operated very satisfactorily and effectively contained the zinc-magnesium vapors.

Fuel Cycle Facility Operations. Additional irradiated fuel subassemblies with burnup levels of up to 1.2 a/o have been received from the EBR-II Reactor and processed in the Fuel Cycle Facility. Refabricated fuel has been returned and charged to the reactor. Pouring yields in melt refining irradiated fuel with burnup levels between 0.3 and 0.9 a/o averaged about 93 w/o.

Early melt refining runs with irradiated fuel investigated the effect of small variations in the liquation period on pouring yield and on decontamination from fission products and plutonium. No correlation was found between the pouring yield and the liquation time. However, the gross pouring yield (not corrected for fission product removal) was observed to decrease slightly with increasing burnup (average) of heavy atoms in the fuel pin. The slope of the curve correlating the pouring yield and the average burnup indicates a 2.6% decrease in the pouring yield for a 1 a/o burnup. A significant fraction of this decrease, however, represents volatile fission products and fission products that were removed in the melt refining operation. This fraction does not represent a decrease in the uranium yield. Removals of iodine, barium-lanthanum, cerium, and cesium obtained in the normal (2 or 3 hr) liquation period were quite adequate (more than 99%). Except for zirconium, the noble metals did not show a partitioning from uranium. Although the plutonium concentration levels were very low (<0.1%), the plutonium data, also obtained in the normal liquation period, indicated that it was effectively retained in the melt refined ingot at these concentrations.

The induction coils of the two melt refining furnaces failed when a 1½-in. section of the copper coil melted. This appeared to be the result of a crack in the furnace insulation which allowed the susceptor, which operates at 1600 to 1800°C, to radiate heat to the coil, thereby causing it to melt. The crack in the insulation resulted from its compaction. A replacement coil unit has been installed in one of the two furnaces in the Argon Cell and the furnace is operating satisfactorily. The high-frequency feed-throughs for the melt refining furnaces failed because of arcing having occurred as a result of what appeared to be moisture penetration. The feed-throughs have been repaired, new sealants applied, and the feed-throughs reinstalled.

On-site burial of sealed cans of high-level-activity

wastes has started. The cans are placed in 12-ft deep, steel-lined holes, covered with gravel, and a cap is then welded on the steel liner. At present, 140 holes are available; several thousand of these holes are planned. Cans containing about 2100 kg of waste material and an estimated 395,000 curies of radioactivity have been buried in thirty of the holes. After the gravel backfill was added to the hole, radiation readings of less than 1 mR/hr at 6 in. from the top of the hole were observed.

The surveillance program to determine the condition of the EBR-II Mark I fuel at progressively increasing burnup levels has continued. Discharged fuel assemblies with burnup levels up to 1.2 a/o have been examined in the Fuel Cycle Facility. Data obtained in these examinations along with information developed by the Metallurgy Division, Argonne, Illinois and an assumption that the fuel cladding does not deform under stress have provided the basis for establishing a tentative maximum burnup limit of 1.2 a/o for the Mark I fuel. This maximum burnup may be increased as information is obtained in the future. A new EBR-II fuel element (designated as Mark I-A) which should permit greater burnup is being provided for the reactor. The design of the fuel element provides for greater void space above the fuel pin and thus allows for greater fuel pin expansion.

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (pages 61 to 106)

Laboratory-Scale Investigations. Development studies are being performed in a 2-in. dia. fluidized-bed reactor to determine optimum conditions for fluorinating $\text{UO}_2\text{-PuO}_2$ pellets containing fission products. Specific emphasis concerns establishing those conditions that would achieve the most rapid fluorination of plutonium and would result in a minimum retention of uranium and plutonium by the fluidized bed of alumina. The pellets are reacted in a sequence consisting of a two-zone oxidation-fluorination (450°C) followed by a single-zone fluorination (450°C) and recycle fluorination at 450, 500, and 550°C. The pellets used in the initial series of runs (designated Type I pellets) were prepared from solid solution $\text{UO}_2\text{-PuO}_2$ powder and fission product oxides and sintered to 94% theoretical density in 6 v/o hydrogen in nitrogen at 1600°C for 2 hr. In subsequent runs, the pellets used (Type II) were fabricated by blending a powdered mixture of UO_2 , PuO_2 , and fission product oxides and sinter-

ing the mixture to 88% theoretical density in 6 v/o hydrogen in nitrogen at 1700°C for 6 to 8 hr. Both Type I and Type II pellets contained, nominally, 0.4 w/o plutonium (as PuO_2) and 86 w/o uranium (as UO_2). However, the concentration of fission products in the Type II pellets was lower than in Type I pellets by approximately a factor of 2.

Samples of the final alumina bed from one run (Pure-2) were used to determine the distribution of the residual uranium and plutonium in the alumina bed after fluorination as a function of the alumina particle size. It was found that although the concentrations of both uranium and plutonium in smaller sized alumina particles (-170 mesh) were approximately 6 times the concentrations in larger particles, the bulk of uranium and plutonium was associated with the larger sized particles.

Changes in the plutonium concentration of the fluidized alumina bed during recycle-fluorination in four runs (Pure-1, Pure-2, Pure-3, and Pure-4) indicated that the highest rates of plutonium removal occurred during the first few hours of recycle-fluorination at a given temperature and that the overall recycle-fluorination time could be reduced without adversely affecting the final plutonium retention on the alumina. Subsequently, in runs Pure-5 and Pure-6 the total recycle fluorination time was reduced from 20 hr to 13 and 12 hr, respectively. In both runs, the final uranium and plutonium concentrations in the alumina bed, 0.004 and 0.007 w/o, respectively, were similar to those obtained in runs in which the recycle-fluorination period was 20 hr. In all runs with Type I pellets (Pure-1 through Pure-6), uranium removal from the alumina was greater than 99.99% and plutonium removal was 97% for a single use of the alumina bed. (Previous work has indicated that plutonium removal may be increased by reusing the alumina bed.)

Since cesium has not been present in any of the pellets used thus far, cesium fluoride was added to the alumina beds for runs Pure-7, -8, and -9 in proportion to the quantity of pellets charged and in the amount expected from fission product cesium. In these runs, which utilized the Type II pellets, higher retention of uranium and plutonium on the alumina bed has been observed. Uranium removal in these runs averaged 99.95%, whereas plutonium removal for total recycle fluorination times of 8.5, 12, and 20 hr was 93, 94, and 91%, respectively. At present it is not possible to separate the effects of the added cesium fluoride and the use of pellets with different characteristics; runs are in progress to evaluate these effects. However, incomplete results from recent work indicate that higher plutonium removals are achieved by different fluorination procedures which use lower initial fluorination temperatures.

Studies are continuing on the use of BrF_5 as a selective fluorinating agent for the separation of uranium and plutonium compounds. Since BrF_5 converts uranium compounds to volatile UF_6 while plutonium compounds are converted to nonvolatile PuF_4 , separation between uranium and plutonium can be achieved in a single fluorination step through the use of BrF_5 . The BrF_5 fluorination step is being considered as an alternative processing scheme for reprocessing low enrichment nuclear power reactor fuels. Experimental results are reported for reactions of BrF_5 with uranium compounds and mixtures of uranium and plutonium compounds.

A series of experiments was performed in which solid mixtures containing U_3O_8 , alumina, and a number of fission product element compounds were reacted with a gas phase containing 26 v/o BrF_5 and 74 v/o nitrogen. These experiments showed that greater than 99% of the uranium was converted to UF_6 in 1 hr at a temperature of 400°C. These conditions were then used for experiments to determine if plutonium is volatilized from mixtures containing U_3O_8 , PuO_2 , alumina, and fission products and from mixtures containing only PuO_2 and alumina by reaction of the mixtures with BrF_5 . Plutonium was not volatilized during BrF_5 fluorination. Analyses of a soda lime trap for the collection of UF_6 and BrF_3 reaction products and excess BrF_5 failed to detect the presence of plutonium. In a subsequent fluorination of the alumina residue at 500°C, 99% of the plutonium was converted to PuF_6 in a reaction time of 8 hr.

Kinetics are reported for the U_3O_8 - BrF_5 reaction over the temperature range 250–400°C using a gas phase composed of 26 v/o BrF_5 in nitrogen. The results showed an increase in reaction rate (volatilization of UF_6) with time at reaction temperatures of 300°C or higher. This phenomenon is attributed to the occurrence of a concomitant reaction between U_3O_8 and UF_6 producing solid UO_2F_2 and UF_4 . A change in rate results when accumulation of UO_2F_2 on the U_3O_8 hinders the reaction between UF_6 and U_3O_8 , thereby allowing greater volatilization of UF_6 . Reaction rate constants for the initial period varied from 0.0051 min^{-1} at 250°C to 0.0266 min^{-1} at 400°C. For the second period, the reaction rate constants varied from 0.0192 min^{-1} at 300°C to 0.0396 min^{-1} at 400°C. An activation energy of about 6 kcal/mole was derived for the U_3O_8 - BrF_5 reaction as compared to a value of 8 kcal/mole previously obtained for the UO_2F_2 - BrF_5 reaction.

Preliminary experiments were performed at 300°C for the UO_3 - BrF_5 and UO_2 - BrF_5 reactions. These experiments showed a change in the reaction rate with reaction time similar to that observed for the U_3O_8 - BrF_5 reaction. The reaction rates for both the UO_3 -

BrF_5 and $\text{UO}_2\text{-BrF}_5$ reactions were higher than the rates found for the $\text{U}_3\text{O}_8\text{-BrF}_5$ reaction.

Experiments were performed to determine the effect of BrF_5 partial pressure on the $\text{U}_3\text{O}_8\text{-BrF}_5$ reaction at 250°C . The gas phase containing BrF_5 and nitrogen was varied to contain 26, 46, and 66 v/o BrF_5 , corresponding to BrF_5 partial pressures of 198, 250, and 502 mm, respectively. The reaction rate constants obtained from these experiments were 0.0051, 0.0131, and 0.0235 min^{-1} for BrF_5 concentrations of 26, 46, and 66 v/o, respectively.

The kinetics of the fluorination of neptunium tetrafluoride by elemental fluorine have been studied in the temperature range 250 to 400°C . The data were treated according to the "diminishing sphere" model for gas-solid reactions, and an activation energy of 20 kcal/mole was calculated.

Vapor-liquid equilibrium data on the system $\text{PuF}_6\text{-UF}_6$ will be useful in the design of a fractional distillation column for the separation of PuF_6 and UF_6 produced in the fluid-bed fluoride volatility process. Fourteen determinations of such equilibria have been made on UF_6 -rich mixtures of $\text{PuF}_6\text{-UF}_6$ at 73, 81, and 89°C . Activity coefficients calculated from the results are close to 1.0, thereby indicating that the $\text{PuF}_6\text{-UF}_6$ mixture is close to ideal in its vapor-liquid behavior. A continuous fractional distillation column can therefore be designed assuming ideal behavior for $\text{PuF}_6\text{-UF}_6$ mixtures in the UF_6 -rich region. There appears to be little fundamental interest in a system of similar compounds, such as PuF_6 and UF_6 , exhibiting ideal vapor-liquid behavior. Since the purposes of the investigation have been substantially realized and the use of increasing quantities of PuF_6 results in operational difficulties, the determinations will not be extended into PuF_6 -rich mixtures.

An investigation has been initiated to determine the rates of corrosion of nickel-200, Monel, and Inconel coupons by some of the volatile fission product fluorides, namely, GeF_4 , AsF_5 , SeF_6 , MoF_6 , and TeF_6 , either individually or in the presence of fluorine. Data were obtained at 500°C for exposures up to 29.5 hr. The corrosion rates of nickel, Monel, and Inconel when exposed to the above fluorides, either alone or in the presence of fluorine, excluding TeF_6 , were low (<0.008 mil/hr) for Monel and nickel, while Inconel exhibited corrosion rates up to 0.284 mil/hr. The corrosion of nickel and Monel by TeF_6 at 500°C appears to be quite rapid; rates up to 0.608 mil/hr were observed. The rate of corrosion of Inconel by TeF_6 was 0.030 mil/hr.

Two experiments investigating the corrosion of nickel-200 coupons suspended in a 2-in. dia. fluid-bed reactor during fluorination of UO_2 and $\text{UO}_2\text{-PuO}_2$ -fission product mixtures have been carried out. For ex-

posures up to 68 hr in process environments, corrosion rates of less than 36 mils/yr were generally observed. Intergranular penetration was less than 3.5 mils.

Two 1½-in. dia. fluid-bed reactors, which had been exposed to UF_6 , PuF_6 , and fluorine for periods of 442 hr and 658 hr and at temperatures up to 550°C , have been sectioned at various locations and the total amount of intergranular penetration measured.

Engineering-Scale Investigations. Engineering-scale development work is in progress on a fluid-bed fluoride volatility process for the recovery of uranium and plutonium from spent uranium dioxide fuels. The process scheme under current investigation includes the following basic steps: decladding, fluorination of the $\text{UO}_2\text{-PuO}_2$ fuel to the corresponding hexafluorides, distillation of $\text{UF}_6\text{-PuF}_6$ mixtures, and conversion of the mixed hexafluorides to dense particles of $\text{UO}_2\text{-PuO}_2$. In addition, thermal decomposition of PuF_6 provides a means of separating the plutonium as PuF_4 from $\text{UF}_6\text{-PuF}_6$ mixtures. Process steps are to be demonstrated with nonirradiated uranium-plutonium materials in three pilot-scale units—a fluorinator, a distillation column, and a converter—installed in an engineering-scale alpha facility. The thermal decomposition studies are being made in the converter. The facility comprises two large alpha boxes; the larger box contains the main process equipment, and the smaller box houses auxiliary equipment.

The fluorinator and converter systems recently underwent final shakedown tests in the facility. The facility is now fully operational, and the initial experiment with plutonium-bearing materials in a combined fluorination-thermal decomposition operation was also completed. The distillation column has been erected in a mock-up area for preliminary testing. The unit will be installed in the large alpha box upon completion of these tests.

Batches of UO_2 pellets weighing 8.8 kg (12-in. depth) were processed in the two final shakedown experiments in the fluorinator. A similar batch, consisting of 7.0 kg of 0.5 w/o $\text{PuO}_2\text{-UO}_2$ pellets (containing inactive fission product oxides) and 1.8 kg of UO_2 pellets, made up the charge for the initial experiment with plutonium materials. The pellets were processed by the two-zone oxidation-fluorination scheme in a fluidized bed of alumina. The total alumina charge was 6 to 7 kg of Alcoa Tabular 61, which was of a nominal 48 to 100 mesh. This charge produced a bed extending about 2 ft above the pellet bed.

The run sequence consisted of a two-zone reaction period, a one-zone fluorination reaction period, and finally a cleanup period; the cleanup period was characterized by total gas recycle, high fluorine concentrations (to 90 v/o), and higher temperatures (to 550°C) than that (450°C) used in the previous two

periods, in which the bulk of the uranium was converted to UF_6 . In the two-zone period, oxygen concentrations to 25 v/o (in nitrogen) have been used to effect the oxidative pulverization of the fuel pellets; fluorine concentrations to 15 v/o were fed to the zone above the pellets. In the intermediate (one-zone) period the gas was recycled or used on a once-through basis depending on fluorine utilization efficiency. The durations of the three periods, in hours, for the three current experiments were:

	2-Zone Period	1-Zone Period	Cleanup Period
Shakedown run 3	15.0	8.0	4.0
Shakedown run 4	20.5	5.3	10.0
Run Pu-1	8.0	4.2	8.3

The run with plutonium-containing fuel was the best to date in terms of sustained periods of high hexafluoride production and was of relatively short overall duration. The average rate for the bulk hexafluoride collection period was about 1.0 kg/hr. Fluorine efficiency in this period was about 50%. Uranium and plutonium levels in the final alumina bed sample were 0.018 and 0.025 w/o, respectively, for this single use of the bed. The bed is to be reused for two additional experiments.

Final shakedown experiments on the converter and auxiliary equipment were performed simulating (1) the separation of plutonium from uranium by the thermal decomposition of PuF_6 and (2) the conversion of uranium hexafluoride to uranium dioxide by high-temperature reduction with hydrogen in the presence of steam. In simulating the separation step, UF_6 alone was used. A thermal decomposition experiment with a UF_6 - PuF_6 feed was also completed.

In the conversion experiment, about 5.5 kg of UF_6 was converted to dense oxide particles in a 15-hr period. Uranium hexafluoride was fed at rates to 18 g/min to the UO_2 bed, which was maintained at 650°C. The material produced had a particle density similar to that of the starting material, about 8.4 g/cc. Effectiveness of size reduction by an oxidation-reduction sequence was demonstrated in two separate periods in which 0.13 and 0.27 equivalents of oxygen ($3\text{UO}_2 + \text{O}_2 \rightarrow \text{U}_3\text{O}_8$) were fed at 400°C; the average bed particle size was reduced from 366 μ to 344 μ and from 392 μ to 140 μ .

The UF_6 - PuF_6 product of the fluorination experiment was processed in the converter to evaluate the fluid-bed thermal decomposition step. Conditions were: bed temperature of 350°C, static bed depth of sintered alumina of 18 in., superficial fluidizing gas velocity of 0.15 ft/sec, hexafluoride feed rate of 22 g/min, and

feed gas composition of 40% hexafluoride in nitrogen. A total of 10.6 kg of feed were processed. Operation of the equipment was completely satisfactory.

Although hydrochlorination of uranium-Zircaloy-2 alloy fuels has been extensively investigated both at bench-scale level and pilot-scale level, to date no work has been done on the decladding of Zircaloy-2-clad low-enriched uranium dioxide fuels. It has been assumed that decladding of the low-enriched fuels by reaction with HCl would proceed similarly to that of the alloy fuels. Since the pilot-scale development of the fluid-bed fluoride volatility process for alloy fuels has been completed, studies have been initiated in the same pilot-scale equipment to study the progress of decladding Zircaloy-2-clad UO_2 fuel bundles by reaction with HCl. This equipment consists of a 6-in. dia. halogenation reactor, a 9-in. dia. packed-bed filter, and a 6-in. dia. pyrohydrolysis reactor.

Zircaloy-2-clad UO_2 rods, assembled in the form of 28-in. long fuel bundles simulating those used in the Dresden reactor, or, alternatively, unclad UO_2 pellets were hydrochlorinated in fluid beds of alumina in seven runs. The operating conditions employed were, in general, similar to those used in the hydrochlorination of alloy fuels. In all of the runs, the halogenation reactor, the packed-bed filter, and the pyrohydrolysis reactor operated smoothly during the entire period of decladding. In the hydrochlorination step, the fuel bundle reacted gradually with HCl, the reaction starting at the bottom of the bundle and progressing to the top as the cladding was consumed. The bundle moved downward in the reactor as the reaction progressed. The average hydrochlorination rate (0.9 kg Zr/hr) during decladding of the UO_2 fuel bundle was similar to that, about 1 kg/hr, observed during processing of uranium-Zircaloy-2 alloy fuel elements. The uranium loss by transport in the gas stream from the packed-bed filter was less than 0.04% of the uranium charged to the halogenation reactor. It was observed that the presence of up to 2.5 v/o oxygen in the reactant gas mixture did not result in significant reaction of the UO_2 pellets. Less than 5% of the UO_2 charged to the fluid bed was converted to U_3O_8 fines, which were effectively filtered from the off-gas stream. The uranium loss by transport of U_3O_8 fines through the packed-bed filter was less than 0.002% of the UO_2 charged. Experimental work is continuing to study the effect of fluid-bed height on the hydrochlorination of fuel bundles longer than those used in the current work.

Processing of the declad pellets either by the two-step oxidation-fluorination process or by an oxidation-hydrofluorination-fluorination process has been studied in a 3-in. dia. pilot-scale fluid-bed reactor to establish:

(a) the feasibility of sampling the fluid bed after oxidation (the oxidation disintegrates the pellets to fines) for accountability purposes, (b) the feasibility of processing large quantities of fines in fluid beds, and (c) the optimum processing conditions for each processing scheme, with particular emphasis on the behavior of the fine particles. Four runs were conducted; three runs were performed using the two-step oxidation-fluorination scheme and one run demonstrated the three-step oxidation-hydrofluorination-fluorination scheme. Two runs were made in which UO_2 pellets of different ^{235}U contents were placed in separate layers in order to obtain a measure of the homogeneity of the bed after oxidation and thus determine whether samples of the oxidized bed would be sufficiently representative for plutonium accountability purposes. Bed samples taken at the end of oxidation from sampling points at three heights from the bottom of the bed established that a fluid bed of alumina containing large quantities of fines can be sampled representatively for accountability purposes. Experimental work is continuing in order to optimize the process conditions of the various reactions.

Modifications to the 1½-in. dia. bench-scale fluid-bed unit are being made to accommodate the use of BrF_5 as a selective fluorinating agent for uranium.

Studies on the cleanup of cell exhaust air contaminated with PuF_6 were continued. In previous studies in which pure PuF_6 , in quantities up to 25 mg, was released into moist air, the fraction of the plutonium penetrating the first two AEC filter media discs in series ranged from 10^{-6} to 10^{-9} . In an attempt to define the uniformity of the properties of filter media in relation to the scatter in the data, equipment was constructed to measure DOP [di(2-ethylhexyl)-phthalate] aerosol penetrations of filter media discs (10-cm dia.). The penetrations of these filter discs taken from widely spaced positions on a sheet of media varied by less than a factor of two.

Experimental work related to bench-scale fluid-bed volatility process studies with irradiated alloy fuel materials has been completed. Four experiments were performed with highly enriched uranium-aluminum alloy fuel which had been cooled 3 months or 7 months. The results of this work show:

(1) The retention of uranium in the reactor bed and filter bed following the processing of irradiated uranium-Zircaloy or uranium-aluminum alloy was similar to that found in processing nonirradiated fuel alloys. It can be concluded that the results obtained for removal and recovery of uranium in bench-scale and pilot-plant work with nonirradiated uranium-alloy fuel materials can be validly applied to irradiated fuels.

(2) The uranium decontamination levels achieved were such that the preponderant gamma activity in the uranium product was due to the uranium isotope ^{237}U .

(3) Iodine was found to volatilize almost completely during the hydrochlorination step of the process. A caustic scrubber was successful in effecting the removal of iodine from the process off-gas stream.

(4) Tellurium was completely removed from the process off-gas during the fluorination step by the use of an activated alumina trap.

Basic Fluidization Studies. In the fluoride volatility process for the recovery of uranium and plutonium from ceramic oxide fuels, several operations are performed in fluid-bed equipment wherein fine particles are produced. Knowledge of the behavior of fluid beds containing large quantities of fines is required in the selection of conditions for processing uranium and plutonium oxide fines generated in the fluoride volatility process. Basic studies were performed in a 3-in. dia. fluid-bed column with alumina fluid beds containing nickel fines to simulate oxide fines. The results of these studies indicated that the average particle diameter of the elutriated fines increased with time and that the fraction of the initial fines which elutriated decreased with an increase in the initial concentration of fine particles in the fluidized bed. A mathematical model was derived for determining the average concentration of fines in the fluid bed as a function of the blowback interval (during blowback, fine particles are returned to the fluid bed from sintered metal filters). This model predicts that blowback frequencies of one every 4 and 8 min result in average concentrations of 96 and 87% of the original amount of fines in the bed, respectively. The particles which are not returned to the bed remain on the filters and in the gas phase above the bed.

In continuing studies on measurement of the particle residence times at surfaces of a gas-fluidized bed, an autocorrelation technique for measuring the particle residence times was established to be sufficiently accurate (by computer simulation) for prediction of heat transfer coefficients. Experimental equipment is being constructed to determine, at the same surface, both the residence times (by the autocorrelation method) and the heat transfer coefficients.

III. Studies and Evaluations (pages 107 to 118)

Studies and evaluations are continuing to estimate cost differentials among alternative cases in the proc-

essing of reactor fuels in conceptual facilities to be operated in about 1980.

Estimates were made of the cost of close-coupled processing of the core and blanket fuel discharged from a hypothetical 1000 Mw(e) oxide-fueled fast breeder reactor. Cost estimates were made of three types of close-coupled plants: (1) an aqueous-solvent extraction plant, (2) a fluid-bed fluoride volatility plant, and (3) a compact pyrochemical plant. The plant specifications were based on reference process flowsheets selected for this study and presented in this report. Conceptual designs for process plant and waste disposal plant based on these flowsheets were used in making detailed estimates of investment costs and processing costs and, ultimately, net unit fuel cycle costs. For the portion of the fuel cycle comprising chemical processing, waste disposal, out-of-reactor fuel inventory, and processing losses, values of the total net unit costs were 0.58, 0.67, and 0.87 mill/kw(e)-hr, respectively, for the volatility, pyrochemical, and aqueous plants.

These three cases are selected from a larger study in progress on the comparative economics of fast reactor fuel processing in which each of the above three types of processes is adapted to three fuel types, metal, oxide, and carbide. The complete study will show the effect of plant size in the range of reactor powers of 1000 to 10,000 Mw(e).

IV. Materials Chemistry and Thermodynamics (pages 119 to 149)

High Temperature Materials Development. This program is directed toward the ultimate development of nuclear reactor materials for use at high temperatures (1500 to 3000°C). Its objective is to amass a fund of basic data which may be drawn on for guidance in materials selection. The studies are concerned with the vaporization and chemical stability of potential fuels, i.e., the oxides, carbides, phosphides, sulfides, arsenides, and nitrides of uranium, plutonium, and thorium, and their solid solutions; and with the reactions of these materials with supporting structural materials and coolant fluids. Experimentation is being done to yield quantitative thermodynamic and phase-diagram information. Each selected system, comprising fuel, structural material, and coolant, is being studied in an integrated way, using several methods of investigation that are mutually supporting. Progress in the application of these methods to the study of the uranium-uranium system follows.

An updated phase diagram of the uranium-uranium system is reported. At the monotectic temperature,

2470 ± 25°C, the compositions in O/U atom ratio unit of the three condensed phases in mutual equilibrium are: liquid uranium, 0.05 ± 0.01; monotectic liquid, 1.30 ± 0.10; and hypostoichiometric urania, 1.61 ± 0.02. The least squares equations representing the liquidus and solidus data below the monotectic temperature are:

Liquidus, (1790 to 2436°C)

$$\log X_o = 6.267 - 2.820 \\ \times 10^4/T + 0.2021 \times 10^8/T^2;$$

Solidus, (1600 to 2470°C)

$$\log X_v = 1.335 - 5608/T;$$

where

X_o = mole fraction of oxygen in oxygen-saturated liquid uranium,

X_v = mole fraction of uranium dissolved in UO_2 at saturation, and

T = temperature in degrees Kelvin.

Exploratory tests indicate that the liquid miscibility gap, which characterizes the uranium-uranium system at elevated temperatures, extends into the uranium-uranium-tungsten system. The solubility of tungsten in solid hypostoichiometric urania appears to be quite small, probably less than 1% up to 2500°C.

Transpiration measurements of the partial pressure of oxygen and of the total pressure of uranium-bearing gaseous species over solid hypostoichiometric urania have been made using H_2 - H_2O buffering carrier gas mixtures. The (calculated) monatomic oxygen partial pressures vary considerably between 2185 and 2600°K. For example, at the solid composition O/U atom ratio = 1.97, the monatomic oxygen pressure (in atm) is 9.1×10^{-11} at 2185°K, 8.5×10^{-10} at 2290°K, 4.1×10^{-9} at 2390°K, 3.2×10^{-8} at 2495°K, and 3.0×10^{-7} at 2600°K. These partial pressures increase rapidly as the oxygen content of the solid increases, particularly near the stoichiometric composition. The total pressure of uranium-bearing gaseous species increases 2.5- to 3.5-fold as UO_2 is reduced to the hypostoichiometric phase boundary in the temperature range 2290 to 2600°K.

Knudsen effusion measurements of the total vapor pressure of uranium-bearing species over the uranium-uranium two-phase system have been completed and a topical report (ANL-7048) on the work has been prepared. The results may be expressed by the equation,

$$(1300 \text{ to } 2000^\circ\text{C}) \log P (\text{atm}) = (7.25 \pm 0.14) - \\ (27,024 \pm 255)/T,$$

where P is the total pressure of uranium-bearing gaseous species.

A study to determine the congruently vaporizing composition of urania has been initiated. The ultrahigh vacuum system set up for this study was found to yield low enough residual gas pressures at high temperatures so that the composition of congruently effusing urania phases will not be affected by the oxidation potential of the vacuum environment.

The mass spectrometric, effusion measurements of the partial pressures of uranium-bearing species over the uranium-urania two-phase system have, in the past, yielded nonreproducible heats of vaporization. Originally it was felt that temperature gradients within the effusion cells were responsible for the discrepancy, and considerable effort was directed toward eliminating such gradients. Recently, however, it was discovered that erroneous temperature readings caused by a defective tungsten lamp in our optical pyrometer were responsible for the nonreproducible heats of vaporization. This defect has been corrected and the mass spectrometric, effusion studies can now be resumed.

Preparation of Reactor Materials. Various fluidized-bed processes are currently under study for synthesizing fast reactor ceramic fuels. At the present time, emphasis is being placed on developing a fluidized-bed process for carburization of hydrided U-Pu alloy with methane-hydrogen gas mixtures to form (U,Pu)C. Thermodynamic calculations and experimental results indicate that the reaction can be limited to formation of the monocarbide by using the proper methane-to-hydrogen ratio. At atmospheric pressure, the production rate would be seriously limited by the rate of addition of methane if the methane concentration was kept low enough to avoid formation of the sesquicarbide. However, it is calculated that by operating at 10 atm total pressure and at 800°C, (U,Pu)C could be produced at a rate of about 10 kg/hr in an 8-in. dia. reactor.

Thermobalance experiments on the reaction of U-20 w/o Pu with methane-hydrogen gas mixtures indicated that at 750°C, atmospheric pressure, and a methane concentration of 1 v/o, the equilibrium solid phase is the sesquicarbide. Based on this result, the free energy change for the reaction, $(U, 20 \text{ w/o Pu})C + C \rightleftharpoons (U, 20 \text{ w/o Pu})_2C_3$, was calculated to be more negative than -4 kcal/mole. Further experiments will define this free energy change more exactly.

Installation of a 2½-in. dia. fluid-bed reactor for the production of stoichiometric UC on a kilogram scale has just been completed. The reactor was designed for operation under the conditions (700–900°C, 5–10 atm pressure, 2–10 v/o methane in hydrogen) that appear most likely to yield stoichiometric carbides at

high production rates. A 1½-in. dia. fluid-bed reactor has produced a 200-g batch of stoichiometric UC with an oxygen content of less than 0.1 w/o.

A microprobe analysis of pressed and sintered pellets prepared from (U, 20 w/o Pu)C which was synthesized in the above thermobalance experiments indicated that the uranium and plutonium were uniformly dispersed throughout the pellets and that the carbon was probably also evenly dispersed.

The corrosiveness of paste blanket fuels toward type 304 stainless steel was investigated in 1000-hr static tests. In each test, a 5-mil thick coupon of type 304 stainless steel and the paste of interest were enclosed in a capsule (also of type 304 stainless steel) and held at a temperature of 760°C for the duration of the test. A paste of hyperstoichiometric UC and sodium caused severe carburization of the coupon, as determined by metallographic observation, chemical analysis, and electron probe microanalysis. A sodium-UO₂ paste caused little change in the coupon except the normal carbide precipitation expected on heating 304 stainless steel for extended periods. A sodium-UN paste caused slight nitriding of the coupon. However, no significant redistribution of iron, chromium, or nickel occurred in the coupon, as determined by electron probe microanalysis, nor was there any evidence of physical deterioration.

Calorimetry. A comparison of certain enthalpy-of-formation data for fluorides determined in this laboratory by fluorine bomb calorimetry with values determined elsewhere by solution calorimetry clearly indicates that the accepted value for the enthalpy of formation of aqueous HF is too positive by ~0.5 kcal. Direct determination of this value is subject to various uncertainties. It is planned to obtain $\Delta H_f^\circ(\text{HF}, \text{aq})$ from cycles involving the enthalpies of formation and solution of some of the alkali metal fluorides. A by-product of the research will be the direct determination of the enthalpy of formation of the alkali metal fluorides.

A redetermination by fluorine bomb calorimetry of the enthalpy of formation of boron trifluoride, $\Delta H_f^\circ(\text{BF}_3, \text{g}) = -271.6 \pm 0.2 \text{ kcal mol}^{-1}$, has led us to revise our previously reported data for boron compounds. Revised values of ΔH_f° (in kcal mol⁻¹) are -59.97 ± 0.3 , -77.8 ± 1.5 , -78.9 ± 2.5 , -59.0 ± 1.8 and -44.5 ± 1.7 for BN(c), ZrB_{1.996±0.006}(c), HfB_{2.009±0.007}(c), NbB_{1.880±0.007}(c), and TaB_{1.925±0.006}(c), respectively.

Despite considerable modern investigation by various methods, there still remains an uncertainty in the enthalpy of formation of carbon tetrafluoride (tetrafluoromethane). A direct determination of this important datum by means of fluorine bomb calorimetry has been undertaken. Highly purified samples of natural

graphite and of pyrolytic graphite are being prepared. Nearly complete (>99.8%) combustions of the pyrolytic graphite have been achieved.

The enthalpies of formation of two pnictogen pentafluorides have been determined. The values obtained (in kcal mol⁻¹) are $\Delta H_{f298}^{\circ}(\text{PF}_5, \text{g}) = -380.71 \pm 0.31$ and $\Delta H_{f298}^{\circ}(\text{AsF}_5, \text{g}) = -295.59 \pm 0.19$. In addition to the standard white phosphorus, two modifications of red phosphorus were also burned. This led to the following enthalpy-of-transition values:

kcal mol⁻¹

The enthalpies of formation of three chalcogen hexafluorides have been determined. The values obtained for ΔH_{f298}° are -291.77 ± 0.24 , -266.95 ± 0.14 , and -327.25 ± 0.56 kcal mol⁻¹ for the gaseous hexafluorides of sulfur, selenium, and tellurium, respectively. The corresponding average bond dissociation energies are 78.5, 71.5, and 81.2 kcal mol⁻¹. This interesting non-monotonic variation appears to result from the operation of two opposing effects as one proceeds from sulfur to tellurium: bond weakening owing to decreasing *d*-orbital overlap, and bond strengthening owing to increasing amounts of double-bond character.

The calorimetric combustion of nickel in fluorine, one of the most difficult fluorine bomb calorimetric studies carried out so far, has led to the value $\Delta H_{f298}^{\circ}(\text{NiF}_2, \text{c}) = -157.3$ kcal mol⁻¹. Work on the determination of the enthalpy of formation of thorium tetrafluoride is also in progress. The construction of a flow calorimetric system for use with fluorine-sensitive substances is continuing.

The 1500°C drop calorimeter is being used for determination of the enthalpy increments of uranium monophosphide. Construction of an electron-bombardment-furnace calorimeter for making measurements to 2500°C is continuing.

Liquid Sodium Coolant Chemistry. The nature of carbon in liquid sodium is under study. Mass spectrometric investigation indicated that the high molecular weight, presumably organic, compounds which volatilize from heated sodium are characteristic of sodium that is cast in oil-coated molds. Reactor-grade sodium, which is dry cast, did not give rise to heavy, volatile, organic compounds; neither did heated graphite electrodes of the type used in the electrolytic manufacture of sodium. The reactions of liquid sodium with common carbon-containing materials, e.g., Na_2CO_3 , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, lamp-

black, and graphite, were investigated in a preliminary manner in order to gain experience with analytical techniques for identification of the reaction products. The results obtained by gas chromatographic analyses were in agreement with those of previous investigators. Ultrapurification of sodium, with respect to carbon-containing impurities, was attempted using the techniques of electromigration, thermoelectrodiffusion, electrodiffusion, and directional freezing; only the first of these gave evidence that carbon had been removed. The analytical procedure for the determination of total carbon in sodium was shown to be satisfactory for elemental carbon.

Chemistry of Liquid Metals. The partial pressure of monatomic sodium over liquid sodium was determined at about 140°C by the atomic absorption spectrophotometric method. After allowance is made for the profile of the resonance line emitted by the hollow cathode lamp and for the broadening of the absorption line by Doppler and nuclear hyperfine splitting effects, the measured pressures and extrapolated literature values are in good agreement. The effects of these corrections on the measured activity of sodium and potassium in Na-K alloys is minor.

The decomposition pressures of CeCd and PrCd have been determined by the Knudsen effusion method to complete the series of measurements on rare earth-cadmium compounds of the CsCl structure. From these measurements, the standard free energies of formation of CeCd and PrCd at 450°C were found to be -14.3 and -14.4 kcal/mole, respectively.

The activity coefficient of plutonium present in dilute solution in liquid magnesium has been obtained by two distinctly different methods. In the first method, $\gamma_{\text{Pu}(\text{Mg})}$ was calculated from observations of the distribution of plutonium between liquid Mg-Zn alloys and fused MgCl_2 -NaCl-KCl salt mixtures. In the second method, $\gamma_{\text{Pu}(\text{Mg})}$ was calculated from the data on the mutual solubility of liquid plutonium and liquid magnesium. Typically, values of 11.5 and 11.0, respectively, were found for $\gamma_{\text{Pu}(\text{Mg})}$ at 700°C and low ($<10^{-3}$ atom fraction) plutonium concentrations.

Final results on the phase-diagram and thermodynamic studies of the cadmium-rich portion of the Pu-Cd system are reported. The high-temperature galvanic-cell method was employed.

The measurement of the magnetic susceptibility of a series of US-ThS solid solutions was completed. With dilution the ferromagnetic transition temperature of US is lowered. At US contents below 37%, magnetic ordering disappears. The results seem best interpreted in terms of a 5f¹ state of the uranium ion in both concentrated and dilute solutions.

V. Reactor Safety (pages 150 to 199)

Metal-Water Reactions. The experimental program to determine rates of reaction of molten fuel and cladding metals with water is continuing. In general, it has been necessary to study the reaction of each metal of interest by several methods. One of these techniques utilizes a high pressure furnace which was designed especially for isothermal studies of the reaction of steam with molten stainless steel. Measurements of the rate of this reaction were made at 1400°C. At this temperature the sample undergoes rapid swelling and foaming which prevents a simple interpretation of the rate data as a reaction rate law expressed in terms of original sample surface area. It is likely that the reaction rate will have to be expressed as a function of sample size and shape. Samples $\frac{3}{4}$ in. in dia. and $\frac{1}{4}$ in. long (weight, ~ 13 g) were approximately one-third reacted in 15 min. The results also showed that the reaction rate was not affected by steam pressure over the range 1 to 12 atm.

Small samples of stainless steel were reacted to completion at 1500°C. These samples released 0.51 liter (STP) of H_2 per gram of stainless steel. The oxide formed was composed of spinel compounds, such as Fe_3O_4 , $FeCr_2O_4$, $NiCr_2O_4$, and $NiFe_2O_4$. The heat of the reaction of molten stainless steel to form the molten oxide mixture was calculated to be 155 cal/g steel.

The high pressure furnace apparatus was also used for experiments designed to simulate the environment of the fuel of a water-cooled power reactor following a loss-of-coolant accident. In these experiments, simulated fuel rods consisting of several UO_2 pellets sealed in an 8-in. length of either type 304 stainless steel or Zircaloy-2 tubing were exposed to rapidly flowing steam at temperatures which increased to a maximum of about 1600°C during a period of 8 min. The fuel rods were then maintained at the maximum temperature for 2 min and rapidly withdrawn. The upper one-third of the stainless steel cladding appeared to react completely, forming the characteristic foamed oxide. The overall extent of stainless steel reaction was about 35% and was independent of flow rate and pressure. The Zircaloy-2 cladding was about 50% reacted at the top (hottest) end of the fuel rod while the overall reaction was about 20%. The Zircaloy-2 reaction was also independent of the steam pressure. The extent of reaction of a Zircaloy-2-clad fuel rod was within 15% of the value calculated from integration of the parabolic rate law for zirconium over the measured temperature-time history of the cladding.

A calculational study and an experimental study of

the UO_2 -steam reaction were performed in order to evaluate a previous finding of an apparent UO_2 -water reaction occurring during an excursion test in the Transient Reactor Test Facility (TREAT). Comparison of the reported partial pressure of O_2 in equilibrium with UO_{2+x} with that in equilibrium with pure steam indicated that significant reaction would occur. The equilibrium compositions of UO_{2+x} in the presence of excess steam were calculated to be $x = 0.27$ at 1000°C, $x = 0.21$ at 1200°C, and $x = 0.17$ at 1500°C. An extrapolation to 2727°C (3000°K) indicated that x would be about 0.12 at this temperature. The reaction of UO_2 with steam to form $UO_{2.25}$ was calculated to be endothermic by about 20 cal/g UO_2 at temperatures in the range 850 to 1100°C and proportionately less for a lesser extent of oxidation.

An experimental study of the reaction of pressed and sintered UO_2 pellets with steam was performed at 1500°C and 1 atm pressure. The experiments were performed in the high pressure furnace using a procedure which avoided contact between UO_2 and air above room temperature. The experiments showed that the reaction followed an apparent parabolic rate law for about 70 min, reaching a composition of $UO_{2.14}$, and then more gradually approached a limiting composition of $UO_{2.17}$ after 240 min.

Another general method of studying metal-water reactions involves nuclear heating of typical reactor fuel materials submerged in water. A series of experiments was performed in TREAT with aluminum- U_3O_8 cermet fuel plates [High Flux Isotope Reactor (HFIR) fuel]. Experiments were performed over a range of fission energy input from 133 to 1062 cal/g in 30°C, 120°C, and 285°C water. The samples retained their plate-like shape at fission energy inputs as high as 440 cal/g, even though an energy of 230 cal/g was sufficient to melt the aluminum cladding and the aluminum in the matrix of the fuel. The extent of reaction for the fuel samples that received 440 cal/g or less of energy was $< 2.5\%$, with the exception of one sample in 285°C water which reacted to the extent of 11.8%. Samples subjected to energies greater than about 500 cal/g lost their resemblance to plates. In this energy range, two samples irradiated in 30°C water fragmented and reacted to the extent of 28.4 and 74.6%, respectively; samples irradiated in 120 and 285°C water formed single large globules and reacted from 91 to 94%. Results with the HFIR fuel were generally similar to those from previous studies with aluminum-uranium alloy fuel except that the cermet fuel retained a plate-like shape at energies up to 440 cal/g. The results indicated that the aluminum- U_3O_8

thermite reaction may not be an important energy source in the transient meltdown of the cermet fuel.

Experiments in TREAT using the scale-up autoclave were continued. Four experiments were performed: two with stainless steel-clad and two with Zircaloy-2-clad, UO_2 -core fuel elements. In each experiment, 9 fuel elements, $5\frac{5}{8}$ in. long in a square array, were submerged in water and exposed to a transient burst of neutrons. The fission energy input in one of the experiments with Zircaloy-2-clad fuel elements was sufficient to heat the UO_2 , adiabatically, to the melting point and melt about one-half of it. The Zircaloy-2 cladding showed only a partial failure near the top of the elements. An analysis of the energy dispositions within the autoclave and the pressure-time history of the experiment suggest that the top of the elements had become uncovered (of water) during the transient, a condition which allowed greater zirconium-steam reaction over that portion of the elements. The overall extent of reaction of the zirconium was 4%. In a more energetic experiment with Zircaloy-2-clad elements, complete fragmentation and a 24% metal-water reaction occurred. Complete fragmentation also occurred in the two experiments with stainless steel-clad elements; the extents of reaction were 23 and 24%, respectively. The extents of reaction achieved in all of the experiments were consistent with the reaction observed in previous TREAT experiments with single fuel pins.

Additional results are reported on the studies of metal-water reactions performed in conjunction with the destructive test of the Kiwi-TNT reactor on January 12, 1965. As part of these studies, six autoclaves containing samples of metallic uranium fuel were arranged at distances from 8 in. to 6 ft from the periphery of the reactor. The residues from the irradiated samples have now been analyzed and it has been determined that the extent of uranium-water reaction varied from 3.4 to 77% for the six samples. The results of the extent of uranium-water reaction compared favorably with previous results of similar studies in TREAT and with laboratory studies by the condenser discharge method.

The combined results of the three methods of study were used to define a region of the probable extent of uranium-water reaction that would occur during the course of a nuclear excursion accident. The principal parameters that determine the extent of reaction are the temperature reached by the uranium, the water temperature, and the degree of fragmentation produced by the rapid heating. The degree of fragmentation, as judged by the average particle size of the residue, was

greater for very rapid heating (Kiwi and condenser discharge) than for slower heating (TREAT).

The calculational study to demonstrate the application of metal-water reaction data to the analysis of a loss-of-coolant accident in a reactor was continued. A previous analysis had been made using as a model the proposed Loss of Fluid Test (LOFT) reactor with the assumption that UO_2 fuel was clad with 25-mil thick zirconium. The present analysis was performed for the fuel originally proposed in the LOFT design: UO_2 clad with 15-mil thick stainless steel. The analysis was performed for two different initial conditions: (A) the core blowdown following the pipe break completely removed the stored energy in the fuel, i.e., initial temperature of the core was that of the coolant (285°C); and (B) the energy stored in the UO_2 was fully retained by the fuel elements, i.e., only the cladding is cooled to the coolant temperature (285°C). Calculations were performed for four cases of steam availability: unlimited steam available for reaction, steam flow rate of 1000 lb/hr, steam flow rate of 100 lb/hr, and no steam available for reaction. The assumption was made that the stainless steel cladding did not react until it had reached a temperature of 1400°C (melting point, $\sim 1370^\circ\text{C}$).

Above 1400°C , the stainless steel reaction rate was assumed to be limited only by the steam availability. Although the results of the calculations closely paralleled the corresponding case for the zirconium-clad core, the extent of reaction for the stainless steel cladding was somewhat less than that for the zirconium cladding under all conditions at comparable times after blowdown. The principal difference between the two cladding metals was the difference in the heat of reaction. Because of the very low heat of the stainless steel-steam reaction, the timing of core collapse was not greatly affected by the extent of reaction. In the case of zirconium cladding, the estimated time of collapse was greatly shortened because of the large amount of energy released by the zirconium-steam reaction.

Fast Reactor Safety Studies. The program of studies of potential problems in the field of fast reactor safety has continued. As part of this program, studies were made of the interaction of fuel and cladding materials with molten sodium. The experimental method consisted to heating samples (~ 0.3 cc in volume) to temperatures as high as 2400°C and then dropping them into a container of liquid sodium. Studies with molten cladding metals showed that extensive fragmentation of the samples occurred, resulting in violent expulsion of some of the fragmented material along with a portion of the sodium. Molten stain-

Stainless steel at temperatures above 1600°C fragmented when dropped into sodium at 250°C. The degree of fragmentation increased with increasing sodium temperature up to 800°C; at this temperature the steel residue was a finely divided gray powder. Uranium metal fragmented at drop temperatures above 1700°C; however, a filamentary network was formed instead of individual particles. Uranium dioxide pellets dropped at 2100°C cracked extensively and absorbed sodium into the body of the ceramic.

In an attempt to determine the cause of the observed fragmentation phenomenon, experiments were performed to compare the effects of dropping hot molten metals into sodium and into water. Molten silver did not fragment when dropped into water, but did fragment when dropped into liquid sodium; this suggests that the difference in behavior was not associated with the formation of oxide films in water, since silver does not form a significant oxide film under these conditions. Therefore, the difference in behavior was attributed to differences in the boiling behavior of water and sodium. Presently, the hypothesis is that the breakup results from the violent formation and collapse of vapor bubbles in the nucleate and transition boiling regimes. Cladding metals are in a molten state in the violent boiling regime for sodium (900–2300°C) and thus fragment; however, they are not in a molten state in the violent boiling regime for water (100–373°C) and, therefore, do not fragment in that medium. This hypothesis is supported by the observation that a series of low melting metals, tin, bismuth, and lead, do indeed fragment when dropped into water. Also, fragmentation of molten stainless steel occurred in liquid lithium and potassium as well as in sodium. More detailed understanding of the various boiling regimes with liquid metals is necessary to improve significantly the postulated theory of the mechanism of fragmentation.

Studies of transient boiling heat transfer are continuing. The research is directed toward obtaining the information necessary to predict the magnitude of explosive pressures generated when hot fuel materials are suddenly dispersed into liquid coolant. Both water and liquid sodium coolants are of interest; however, the initial work has been limited to water systems. Experiments have been performed with a swinging arm apparatus in which a heated nickel ball is passed rapidly through a pool of water. The temperature drop of the ball as it passes through the water is recorded as a function of initial ball temperature, water temperature, ball velocity, path length, and immersion time. These data are fed to a computer along with appropriate physical properties, and calculations are made

which result in values of heat flux, heat transfer coefficient, and an average temperature of the ball surface. Experiments have been completed with a ¼-in. nickel ball moving through water at 12 ft/sec. Initial temperatures of the ball ranged from 150 to 1000°C, path lengths from 12 to 26 in., and immersion times from 74 to 176 msec. Water temperatures of 30, 60, and 94°C were employed. Computed results have yielded a consistent set of heat flux values and heat transfer coefficients. Additional results with other ball materials and with other experimental conditions are required before an overall correlation of the results can be attempted. Apparatus for conducting similar experiments in liquid sodium is being developed.

Studies have continued of the high temperature physical properties of materials that are important in the field of reactor safety. Experiments to measure the specific heat of molten UO_2 are progressing. In these experiments, induction heating is now being used instead of electron beam heating. Sealed tungsten crucibles containing UO_2 have been heated to as high as 3150°C; however, molten UO_2 leaked from one crucible at this temperature. Microscopic examination of the crucible suggested that a crack was responsible for the failure; there was no evidence of a general attack of the tungsten by the UO_2 . Work is continuing with tungsten crucibles from various manufacturers. Apparatus is also being prepared in which to perform the calorimetric measurements.

Two other research programs concerning fast reactor safety are under way. One is the determination of the extent of fuel migration and segregation in mixed uranium-plutonium fuels. A significant degree of segregation could seriously inhibit the effectiveness of Doppler broadening as a shutdown mechanism in an operating reactor. Tests of a gradient furnace for the migration studies are in progress. The other research program, which is in the planning stage, is an experimental study of the transient pressure and the aerosol produced by the liquid sodium-air reaction in simulated spray-type accidents.

VI. Energy Conversion (pages 200 to 236)

Regenerative Emf Cells—Physical-Chemical Laboratory Studies. Investigations on regenerative electrochemical systems for the conversion of heat into electrical energy have been continued. The program is divided between physical-chemical laboratory studies and engineering considerations. This report is a comprehensive summary of all the work completed to

date and contains references to all the published work of the group.

The physical-chemical laboratory studies include three major projects: (1) lithium hydride cell studies, (2) intermetallic cell studies, and (3) liquid-vapor equilibrium studies on intermetallic systems.

The lithium hydride cell studies were the first initiated at this laboratory. A review is given of our studies of the hydrogen diffusion diaphragms of pure iron, iron-molybdenum alloys, niobium, and pure vanadium and their application in the lithium hydride cell as the cathode.

Extensive studies on electrolytes for a lithium hydride cell have been made. The binary systems LiCl-LiH , LiBr-LiH , LiI-LiH have been studied by thermal analysis and the liquidus surfaces of the ternary system LiH-LiF-LiCl have been determined.

Thermodynamic studies of lithium hydride by an emf method have been made on cells with pure liquid lithium anodes, electrolytes of fused lithium halides saturated with lithium hydride, and with one atmosphere hydrogen gas pressure in the cathode. These cells contain the two reactants and the cell product in their standard states and measure E° directly. The cell emf measurements are shown to be consistent with calorimetric measurements of the enthalpy of lithium hydride. In addition, these measurements provide the first direct measurement of the free energy of formation of lithium hydride.

Kinetic studies have been made which establish the mechanistic features controlling the equilibrium potential at the hydrogen-hydride electrode. The rate determining step in this mechanism is the rate of diffusion of hydrogen through the metal electrode lattice. The low rate at which hydrogen saturates the metal also controls the rate at which the equilibrium cell potential is established. Further, voltammetric and chronopotentiometric studies have established that the overall hydrogen-hydride oxidation process at an iron electrode surface was considerably faster than that at a tungsten electrode surface.

Data are presented on the hydrogen equilibrium pressure at regeneration temperature for a variety of electrolyte compositions. These studies indicate that the best cell electrolyte will be one in which pure solid lithium hydride can be separated from the system. By regenerating nearly pure lithium hydride, the maximum equilibrium pressure will result. Recommendations are made pertaining to equipment design for a regeneration system.

In the intermetallic studies, the emf-temperature-composition characteristics of the sodium-bismuth bimetallic concentration cell have been determined

using several cells with a solid NaCl electrolyte and one cell with a liquid NaI-NaCl-NaF electrolyte. The observed potentials versus a pure sodium anode for cells with solid electrolytes ranged from 0.40 to 0.74 volt at temperatures between 540 and 1040°K and for cathode compositions between 10 and 50 a/o sodium in bismuth. The cell with a pure liquid sodium anode, a fused mixture of sodium halides as the electrolyte, and a liquid metal cathode with an initial composition of 30 a/o sodium in bismuth was operated at a constant temperature of 817°K for a period of 143 hr. (Thermal gradients within the cell were minimized by enclosing the cell in a copper block.) As the run progressed, the open-circuit cell potential decreased steadily from an extrapolated initial value of 0.6084 volt, as sodium was irreversibly transferred from the anode to the cathode alloy by diffusing through the electrolyte as a soluble species. The rate of irreversible transfer in this cell was estimated to be 0.002 g/(hr)(cm^2), or 0.6 ma/ cm^2 , thereby indicating the low rate of irreversible transfer which may be attained for a cell in the absence of thermal convective mixing of the liquid phases.

A theoretical discussion of a cell with ionic and electronic conductivity is given. It is shown that a cell with such an electrolyte will not yield a "true thermodynamic" potential even at open circuit. However, the apparent decrease in power output of a cell with a drop in the open circuit potential as the electronic conductivity increases may be more than compensated for by an increase in the total cell conductivity; this results in an increased power output of the cell.

The results of thermodynamic studies of lithium-bismuth and lithium-tin concentration cells are evaluated for possible use of these cells in a regenerative system. Both show reasonable cell voltages for open circuit conditions, but have very low temperature coefficients of cell potential, indicating that they can be thermally regenerated only at temperatures which are not readily attained. It is shown that the sodium-bismuth cell has somewhat lower cell potentials, but may be regenerated, probably by either thermal or electrothermal means. A theoretical discussion of the latter is given which indicates its practical use in avoiding certain solid-vapor regions of the phase diagram.

In order to regenerate a cell electrothermally at a reasonably attained temperature, the cell should have a large, negative temperature coefficient of cell potential. This indicates that bimetallic concentration cells should utilize strongly interacting metals.

The free energy of formation of solid Li_2Te has been determined as -77.9 ± 0.4 kcal/mole at 798°K. This value was determined using a reference electrode con-

sisting of liquid bismuth saturated with solid Li_3Bi , a liquid molten salt electrolyte of LiCl-LiF , and a cathode alloy of lithium and tellurium.

Studies of vapor-liquid equilibria of intermetallic systems have shown that, in order to avoid plugging the regenerator of a bimetallic regenerative cell with solid compound, it is necessary to operate the cell at a pressure which is high enough so that the liquid-vapor loop does not overlap the solid-liquid region of the temperature-composition phase diagram of the system. Measurements have been made which permit calculation of the information necessary for such operation. These measurements are total pressure determinations and vapor composition determinations. The total pressure measurements have been made by the quasi-static and boiling-point techniques while the vapor compositions have been determined by the transpiration technique. The principle of the quasi-static method is discussed, and the apparatus is described.

Measurement of vapor compositions above sodium-bismuth alloys showed that sodium exhibits negative deviations from ideality. From the vapor composition data, values were calculated for the activity coefficient of sodium, γ_{Na} . In 20 a/o sodium-80 a/o bismuth at 900°C , $\gamma_{\text{Na}} = 5.7 \times 10^{-3}$; in 40 a/o sodium-60 a/o bismuth at 900°C , $\gamma_{\text{Na}} = 1.7 \times 10^{-2}$. For bismuth, the corresponding activity coefficients are 0.67 and 0.52.

From the total pressure and vapor composition data, a pressure-composition diagram for the sodium-bismuth system at 900°C was constructed.

The presence, location, and direction of breaks in the total pressure curves for some compositions are explained in terms of a sequence of phase diagrams which come into play as pressure is lowered. The location of the break depends on the initial liquid composition in the total pressure measurement, whereas the direction of the break depends on whether the initial composition is to the left or to the right of the point of tangency of the liquid-vapor loop and the solid-liquid region. The temperature of the break corresponds to the temperature on the solid-liquid solubility curve for the composition of liquid under consideration. This fact enables one to derive information for the solid-liquid phase diagram from vapor pressure measurements. The literature value (775°C) for the melting point of Na_3Bi was found to be in error. In the liquid-vapor equilibrium studies, it was found to be 842°C . This value is in good agreement with subsequent cooling curve measurements which showed it to be at least 838°C .

The pressure-composition diagram was interpreted to show that, for likely cathode compositions in a

sodium-bismuth regenerative cell, the regeneration temperature would be about 1200 to 1300°C .

Considering the effect of the solidus discussed above, the bimetallic systems for a regenerative galvanic system were again surveyed to find likely candidates. On the basis of melting points of components and of compounds, and on the basis of the phase diagram considerations discussed earlier, many systems were eliminated. Still others were eliminated because of corrosion problems. The systems that are proposed for future study are sodium-lead, sodium-thallium, and potassium-thallium, in that order of preference.

Regenerative Emf Cells—Engineering Studies. Work on the engineering development of thermally regenerative emf cell systems of the bimetallic type has been continued.

The density, viscosity, and surface tension of the NaF-NaCl-NaI molten salt eutectic, used as an electrolyte for cells with sodium anodes, were measured at temperatures up to 800°C . The densities of liquid sodium-bismuth and sodium-lead alloys at sodium concentrations up to 50 m/o were also measured at temperatures up to 800°C . In addition, the surface tension of sodium-bismuth alloys containing 30 to 50 m/o sodium was measured.

An experimental sodium-bismuth closed cell apparatus without a thermal regenerator has been operated as a battery by charging and discharging it electrically. It has been at an operating temperature of from 535 to 650°C for one year (as of December 9, 1965).

An experimental sodium-lead cell apparatus with attached thermal regenerator has been constructed and operated. The cell and regenerator are constructed of stainless steel. The cell has a frozen electrolyte-silicone rubber combination electrical insulator and pressure seal. The sodium is regenerated from the lead-sodium cathode metal by distillation in the regenerator. To date, nine runs for a total operating time of $36\frac{1}{2}$ hr have been made with this apparatus. The cell has provided open-circuit voltages up to 0.41 volt, maximum (short circuit) currents up to 7.5 amperes, and a current of 2.5 amperes at 0.28 volt.

A theoretical equation was developed for non-faradaic or irreversible sodium transfer in a bimetallic cell. This equation indicates that the irreversible sodium transfer should decrease as the cell current is increased as has been experimentally observed. This work indicates that most of the irreversible transfer is caused by electronic conduction and that the direct diffusion of sodium atoms contributes only to a small extent.

Corrosion studies of materials of construction of bimetallic cells and regenerators by lead, bismuth, and

tin as well as by sodium-lead and sodium-bismuth alloys are being continued. The tests include both static and dynamic (thermal circulation) corrosion studies of steel, stainless steel, and refractory metals. The results of corrosion tests with stainless steels and low-carbon steel show that they may be suitable as construction materials for the low-temperature operating section of a bismuth cell.

VII. Nuclear Constants (pages 237 to 240)

Measurements of neutron cross sections of materials important to the fast reactor program are being continued. Radiative capture cross sections of ^{141}Pr , ^{175}Lu , ^{139}La , and ^{176}Yb have been measured for monoenergetic neutrons in the fast reactor energy region. Samples of uranium and plutonium isotopes are undergoing irradiation in EBR-II in experiments designed to measure the ratio of the capture and fission cross sections of these isotopes. A lithium drifted germanium gamma-ray detector is being developed by the Elec-

tronics Division; this should serve to improve the accuracy of neutron inelastic scattering measurements.

VIII. Analytical Research and Development (pages 241 to 243)

A program for the development of analytical methods for the determination of burnup of fast reactor fuels and for the measurement of fast fission yields is being carried out. The determination of total rare earths is being considered as a means of measuring burnup. Using a compleximetric titration with ethylenediaminetetraacetic acid, 500 μg of rare earths have been determined with an accuracy of $\pm 0.5\%$. At the 50- μg level, the accuracy is $\pm 2\%$.

The use of neutron activation for the determination of the fast fission yield of praseodymium-141 and other stable fission nuclides is also being investigated. Preliminary results would indicate that this measurement can be made with an accuracy of $\pm 1\%$.

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I

Compact Pyrochemical Processes¹

Compact pyrochemical processes are nonaqueous processes for the recovery and purification of partially burned reactor fuels. They possess utility for the recovery of ceramic fuels (such as oxides or carbides) as well as metallic fuels, and may be used in small plants serving one or several reactors. In general, these processes utilize molten metal and salt systems as processing media. The metal solvent systems consist principally of various alloys (usually binary) of zinc, cadmium, magnesium, and copper. The salt systems are halide salts of alkali and alkaline earth metals. The present indications are that both core fuel containing about 10 to 20 w/o plutonium, and blanket material containing 5 w/o or less plutonium could be handled in the same process with little or no change in the sequence of operations.

The objectives of pyrochemical processing are to remove the bulk of the fission products, to extract bred plutonium from the blanket, to re-enrich the core with plutonium, and to repair irradiation damage. To achieve these objectives, separations of cladding

material, uranium, plutonium, and fission products from one another are required. Remote operation of all steps is anticipated because, even if complete fission product removal were achieved, the buildup of radioactive isotopes of uranium and plutonium in extensively recycled fuel would preclude direct refabrication.

These processes have continued to be intensively developed for the recovery and purification of fuel materials discharged from power reactors. They possess features which should be economically beneficial, particularly in fast reactor fuel cycles. Among these features are: (1) the ability to process short-cooled high-burnup fuels of both ceramic and metallic types with consequent reductions in fuel inventory, (2) the decrease in criticality problems because of the absence of aqueous solutions, (3) the recovery of expensive alloying agents for recycle, (4) the direct production of concentrated fission product wastes, and (5) in some of these processes, the retention of valuable alloying elements in the fuel.

A. LABORATORY-SCALE INVESTIGATIONS (R. K. STEUNENBERG, L. BURRIS, JR., G. A. BENNETT)

1. New Pyrochemical Processes for Future Reactor Fuels (R. K. STEUNENBERG, R. D. PIERCE)

a. LIQUID METAL-MOLTEN SALT TRANSPORT PROCESSES (J. B. KNIGHTON, W. KNOCH,² K. R. TOBIAS, J. D. SCHILB)

Pyrochemical separations based upon the selective transfer of solutes between two liquid metal alloys in mutual contact with a molten salt have been described by Chiotti and Klepfer.³ This concept has been extended as a potential method for processing uranium-plutonium fuels. On the basis of distribu-

tion data reported earlier for various binary alloys of magnesium and MgCl_2 -bearing salts (ANL-6925, pp. 36, 37), a Cu-Mg alloy containing uranium and plutonium and a Zn-Mg alloy in mutual contact with 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl were selected for an experimental investigation. In this system a plutonium-uranium separation is possible through preferential and continuous oxidation of plutonium in a Cu-Mg-Pu-U alloy by MgCl_2 and subsequent reduction of the resulting PuCl_3 in the salt by a Zn-Mg alloy. The low solubility of uranium in the Cu-Mg alloy, combined with a low distribution coefficient, provides a means of minimizing the amount of uranium transferred with the plutonium.

Several preliminary experiments have been per-

¹ A summary of this section is given on pages 1 to 5.

² On leave from the University of Braunschweig, Germany.

³ P. Chiotti and J. S. Klepfer, Ind. Eng. Chem., Process Design Develop., 4, 232 (1965).

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FIG. I-1. Conceptual Salt Transport Process for $\text{UO}_2\text{-PuO}_2$ Fuel.

formed on the uranium-plutonium separation. The first two experiments, which were conducted in divided tantalum crucibles, showed selective transfer of plutonium from a Cu-33 w/o Mg alloy to a Zn-5 w/o Mg alloy. The amounts of plutonium transferred were 97.5 and >99%, while the amount of uranium transferred was negligible. Some copper was found in the Zn-Mg alloy, probably as a result either of splashing over the divider or of an electrolytic concentration cell effect, since the two alloys were not electrically insulated from each other.

By selecting the experimental conditions so as to provide suitable solubility and distribution coefficient relationships in the two alloys, uranium also can be transferred from a Cu-Mg alloy to a Zn-Mg alloy, leaving noble and refractory metal fission product elements behind in the Cu-Mg alloy. In another experiment, a uranium transfer of 83% was obtained, using Cu-8 w/o Mg and Zn-5 w/o Mg alloys. Zirconium, which was also present in the Cu-Mg alloy, showed no transfer. In the last experiment, 92% uranium transfer was observed in a system of this type.

The concept of fuel purification by transport through salt is highly attractive in that it offers the potential advantages of versatility, small process volumes, and high recoveries. A conceptual process flowsheet, shown for oxide fuels, but also readily adaptable to carbide or metallic fuels, is outlined in Figure I-1. Oxidative decladding is employed, followed by a reduction of the oxides by Cu-Mg alloy in the presence of a molten salt. The Group I and II and lanthanon fission prod-

ucts remain in the salt, which also contains the MgO formed as a by-product of the reduction. Another molten salt is then simultaneously contacted with the Cu-Mg alloy, a Zn-3 w/o Mg alloy, and a Zn-80 w/o Mg alloy. Under these conditions the distribution coefficients and solubilities are such that uranium transfers to the Zn-80 w/o Mg alloy and plutonium to the Zn-3 w/o Mg alloy, while the noble and refractory metal fission products remain in the Cu-Mg alloy. The product streams are separately retorted to remove zinc and magnesium, and the resulting metallic products are oxidized to regenerate UO_2 and PuO_2 . A process of this type should be equally applicable to core or blanket material, although in the case of core material the process might be simplified by recovering the uranium and plutonium together.

b. PYROCHEMICAL PROCESSES FOR THORIUM-BASE FUELS (R. D. PIERCE, I. O. WINSCH, K. NISHIO, T. CANNON, P. MACK)

A conceptual flowsheet, developed primarily to illustrate the utility of pyrochemical process steps for recovery and decontamination of a thorium-base fuel (ThC_2 and UC_2), such as that prepared for the High Temperature Gas Cooled Reactor (HTGR), is being investigated. The flowsheet (Figure I-2) was developed using existing or partially developed technology. For example, conversion of oxides to carbides has been studied at Atomics International. Fluidized-bed reactions of the types shown in the oxidation and chlorination steps are under study at Argonne and should

be adaptable to the oxidation, chlorination, and the final fuel refabrication steps.

The pyrochemical steps of the process consist of selective reduction by cadmium, zinc, or cadmium-zinc alloys, of the chlorides of elements more noble than uranium and thorium. The chlorides of uranium, thorium and the more reactive fission products remain in solution in a 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl salt. The relatively noble fission products (Mo, Ru, Pd) would be extracted into the metal phase, and this phase would be discarded to waste.

Subsequently, the uranium and thorium chlorides would be reduced by contacting with a reducing solution such as magnesium-cadmium. The bulk of the rare earth elements would remain in the salt phase while most of the uranium and thorium would transfer to the metal phase. Although the separation factors for this step are high, high recovery of the uranium and thorium in conjunction with high removal of the fission product elements would require a countercurrent extraction operation.

The uranium-thorium-protactinium product solution would then be retorted to vaporize the solvent metals, and the resulting Th-U-Pa sponge could be processed by the sequence of steps shown in the flow-sheet to prepare HTGR fuel. Alternatively, the sponge might be dissolved in nitric acid, and then processed by the ORNL Sol-Gel process to produce HTGR fuel.⁴

In order to determine the feasibility of the pyrochemical steps, a run was made in which batch extractions were employed. The manner in which the steps were performed differed in several respects from those outlined in the flowsheet of Figure I-2. As an example, the flowsheet shows the reduction of the relatively noble elements from a salt solution. In simulating this step, uranium, thorium, and cerium were oxidized by CdCl_2 from a cadmium-3 w/o zinc solution containing thorium, uranium, cerium, and molybdenum. Cerium was used as representative of the rare earth elements and molybdenum as representative of the noble elements. Whether this step is evaluated by oxidizing thorium, uranium, and cerium or by reducing noble metals such as molybdenum, the results should be the same.

The second major difference in the demonstration run was the use of two successive batch extractions instead of continuous countercurrent or batch countercurrent extractions. Batch extractions can be used to indicate whether the expected distribution coefficients are realized and whether the desired result could have been achieved in a countercurrent operation.

⁴ D. E. Ferguson, E. D. Arnold, W. S. Ernst, Jr., O. C. Dean, Preparation and Fabrication of ThO_2 Fuels, ORNL-3225, Oak Ridge National Laboratory, June 19, 1962.

*Cd-3 w/o Zn used in demonstration run (see text).

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FIG. I-2. Conceptual Process for HTGR Core Fuel.

The results of these operations are as follows:

(1) *Removal of Noble Fission Product Elements.*

In this step, uranium and thorium present in solution in the metal phase were oxidized by CdCl_2 and transferred to the flux phase, leaving behind the noble metal fission product. To perform the step, 4.76 kg of thorium, 0.40 kg of uranium, 0.17 kg of cerium, and 0.16 kg of molybdenum were dissolved in 40.2 kg of a cadmium-3 w/o zinc alloy at 600°C. About 8 kg of a 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl flux was used. The oxidation of the uranium, thorium, and cerium by cadmium chloride at 600°C proceeded smoothly, but inadvertently only enough CdCl_2 was added to carry the oxidation to about 85% completion. However, the extent of oxidation agreed within 2% of the amount of CdCl_2 added. No significant loss of

TABLE I-1. URANIUM, THORIUM, AND CERIUM DISTRIBUTION AFTER BATCH EXTRACTIONS SIMULATING PROCESSING OF HTGR FUEL

Liquid metal phase: Cd-36 w/o Mg-~13 w/o Th^a (wt, ~24 kg)
Salt phase: 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl (wt, ~8 kg)

Temperature: 600°C

	Distribution Coefficients (w/o in salt)/(w/o in Metal)			Separation Factors ^b		Material Balance ^c	
	Thorium	Uranium	Cerium	Ce from Th	Ce from U	Thorium	Cerium
First extraction	0.28	0.62	9.8	35	15.8	101	98
Second extraction	0.0066	0.5	7.1	1070	14.2	98	97

^a Besides thorium, about 0.3 kg of uranium and 0.1 kg of cerium were present as distributing solutes.

^b Ratio of distribution factors.

^c Uranium material balance not shown because of uranium precipitation from solution. The magnesium-cadmium composition could be adjusted to provide solubility for uranium.

uranium and thorium in the metal phase would be expected.

In this experiment, the behavior of noble metal fission products (molybdenum, ruthenium, palladium, and technetium) was determined by observing the behavior of molybdenum. That the separation of molybdenum was good in the noble metal extraction step is shown by the fact that in the subsequent extraction step only 10% of the initial amount of molybdenum was present with uranium and thorium. This is equivalent to the percentage of the noble metal extract remaining in the crucible as a heel after the bulk had been transferred out. This result is consistent with a considerable amount of past experience on the behavior of noble metal fission products.

(2) *Uranium and Thorium Extraction.* Two successive batch extractions were performed. In the first, the flux containing the uranium, thorium, and cerium chlorides was contacted at 600°C with about 24 kg of 50 w/o Mg-Cd alloy. After reduction of the uranium and thorium chlorides, the magnesium concentration was 36 w/o. The flux, containing the bulk of the cerium, was discarded. A fresh batch of flux was added

and the extraction repeated. The distribution coefficients for uranium, thorium, and cerium are shown in Table I-1.

The separation factors for cerium from both uranium and thorium indicate that high recovery of thorium and uranium, together with high removal of cerium as well as other rare earth and alkaline earth elements, could be obtained in a few stages of countercurrent extraction. The distribution coefficients for uranium, cerium, and thorium in the second extraction step are in good agreement with laboratory data (ANL-6925, pp. 36-37). However, the thorium distribution coefficients are in poor agreement, the value for the first extraction being 40 times greater than that in the second extraction. Although the thorium distribution coefficient for the first extraction step is still satisfactory, the high value is puzzling.

A possible explanation is that some thorium oxide was produced in the flux as a result of reaction with impurities in the flux. Since procedures and equipment for pretreating flux are still under development, it is not unusual to encounter treated fluxes with oxygen content as high as 0.5 w/o, presumably as MgO (see section on salt purification, in this report). Even oxygen present as MgO would be harmful because the reaction:

is thermodynamically feasible. The presence of a small amount of thorium oxide in flux samples (which were not filtered) could cause a substantial error in the apparent equilibrium thorium content of the fluxes.

From the results of this run, the following conclusions can be made:

(1) Selective oxidation of uranium and thorium from metal solutions and transfer to a salt solution can be accomplished smoothly. The alternative reduction of noble metal chlorides into a metal phase would be expected to go equally well. Excellent separation of uranium and thorium from noble metals is possible.

(2) Distribution coefficients for uranium, thorium, and cerium are such that high recovery of uranium and thorium, and excellent separation from rare earths and alkaline earth elements, can be achieved in a relatively small number of extraction stages.

(3) The pyrochemical steps should be easy to perform by either batch or continuous operations.

2. Supporting Chemical Investigations (R. K. STEUNENBERG)

Supporting chemical studies of liquid metal and molten salt systems are conducted in order to provide data of process importance and to elucidate the chemical aspects of various process steps. During this

reporting period, this effort has included investigations of (1) the distribution of various elements between liquid metals and molten salts, (2) the solubilities of various solute elements in liquid metal alloys of proc-

ess interest, (3) the consolidation of lanthanon fission products in aluminum-magnesium alloys, (4) the chemistry of intermetallic compounds in molten salt solutions, and (5) the chemistry of cadmium subchloride species that are formed in liquid metal-molten salt systems.

a. DISTRIBUTION OF ELEMENTS BETWEEN LIQUID METALS AND MOLTEN SALTS

In the pyrochemical processes currently under investigation, the basic separations of uranium, plutonium, and fission products are effected by differences in the distribution behavior of these elements between liquid metals and molten salts. Pertinent distribution coefficient measurements are therefore an essential part of the process development effort.

(1) Codistribution of Uranium and Plutonium Between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Cd-Mg Alloys (J. B. KNIGHTON, J. D. SCHILB, K. R. TOBIAS)

A conceptual process for the separation of uranium and plutonium from fission products employs liquid Cd-Mg alloy and molten 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl salt mixture as solvents. The process, which was described previously in ANL-7055, p. 40, utilizes a multistage extraction procedure for the separation of uranium and plutonium from the fission products. To provide additional information on this step, the codistribution behavior of uranium and plutonium in this system has been determined at temperatures of 425, 500, and 600°C.

The results obtained at 600°C are presented in Figure I-3, together with previously determined data for praseodymium, a representative lanthanon fission product, and zirconium. The zirconium results are given in greater detail later in this section of this report.

These data indicate that the distribution coefficients are favorable for a separation of praseodymium from uranium and plutonium, but that a uranium-plutonium separation would be difficult at a low magnesium concentration (2 to 4 w/o) in the Cd-Mg alloy. A low magnesium concentration is necessary for the solubility of uranium to be high enough for process use.

(2) Codistribution of Uranium, Plutonium, and Praseodymium Between 50 m/o MgBr_2 -30 m/o NaBr -20 m/o KBr and Cd-Mg Alloys (J. B. KNIGHTON, J. D. SCHILB, K. R. TOBIAS)

The effect of substituting bromide for chloride as the anion in the salt phase was investigated in a codistribution experiment with uranium, plutonium, and praseodymium at 600°C, with Cd-10 w/o Mg alloy

FIG. I-3. Distribution of Praseodymium, Plutonium, Uranium, and Zirconium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl Salt and Cadmium-Magnesium Alloy at 600°C.

Atmosphere: Argon
Crucible: Tantalum

serving as the metal phase. To allow comparison of these data for the MgBr_2 - NaBr - KBr salt with earlier results obtained for the MgCl_2 - NaCl - KCl salt under similar conditions, distribution coefficients and separation factors at 600°C for uranium, plutonium, and praseodymium in the two salt mixtures are shown in Table I-2.

Although the separation factors obtained with the bromide salt mixture are smaller than those for the chloride salt mixture, the distribution coefficients are larger. The result is that more favorable salt/metal ratios could be used for multistage extractions in the bromide system, but more stages would be required.

To decrease process volumes, a high uranium solubility is desirable. Since uranium exhibits retrograde solubility down to about 440°C in Cd-2 w/o Mg alloy, operation in the vicinity of 440°C would provide the maximum uranium solubility for this alloy, which is

TABLE I-2. DISTRIBUTION OF URANIUM, PLUTONIUM, AND PRASEODYMIUM BETWEEN CHLORIDE OR BROMIDE SALTS AND Cd-10 w/o Mg ALLOY AT 600°C

Element	Distribution Coefficient ^a	
	MgCl ₂ -NaCl-KCl ^b	MgBr ₂ -NaBr-KBr ^b
U	0.0105	0.035
Pu	0.065	0.15
Pr	1.35	2.05
Separation Factor ^c		
	MgCl ₂ -NaCl-KCl	MgBr ₂ -NaBr-KBr
$\frac{\text{Pu}}{\text{U}}$	6.2	4.28
$\frac{\text{Pr}}{\text{U}}$	128	58.7
$\frac{\text{Pr}}{\text{Pu}}$	20.7	13.7

^a Distribution Coefficient, K_d

$$= \frac{\text{Concentration of element in salt, w/o}}{\text{Concentration of element in metal, w/o}}$$

^b Atomic ratio of $\text{Mg}^{++}:\text{Na}^+:\text{K}^+ = 0.5:0.3:0.2$.^c Separation factor for elements A and B = $K_d(A)/K_d(B)$.

about 1.5 w/o. The data available to date also indicate that small amounts of zinc can be added to a Cd-Mg alloy containing 2 to 4 w/o Mg to increase the solubility of uranium without adverse effects on the process.

At the present time, the most favorable conditions for a separation of lanthanon fission products from uranium and plutonium appear to be (1) a salt consisting of 50 m/o MgBr_2 -30 m/o NaBr -20 m/o KBr , (2) a Cd-Mg alloy containing 2 to 4 w/o Mg, and (3) temperatures between about 425°C and 600°C.

(3) Distribution of Zirconium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Cd-Mg Alloys (J. B. KNIGHTON, G. E. KOVALL,⁵ J. D. SCHILB)

The distribution of zirconium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Cd-Mg alloys was determined at temperatures from about 425 to 600°C in order to evaluate the feasibility of separating fission product zirconium from uranium and plutonium in the system. The results, shown in Table I-3 and Figure I-4, indicate that zirconium distributes strongly to the metal phase with a minimum value of about 5×10^{-5} in the distribution coefficient curve at a magnesium concentration of approximately 10 w/o in the Cd-Mg alloy. The data show considerable scatter

because of analytical difficulties associated with the very low zirconium concentrations in the salt phase. The distribution coefficients show no significant temperature dependence.

In general, the distribution coefficients for zirconium lie about two orders of magnitude below those for uranium and plutonium (see Figure I-3). Thus, a separation of uranium and plutonium from zirconium by selective extraction of the uranium and plutonium into the molten salt phase appears feasible. In this experiment, the zirconium concentrations in the Cd-Mg alloy probably represent the solubility limit.

b. SOLUBILITY DETERMINATIONS

The solubilities of various substances in liquid metal and molten salt solutions are of importance in determining process volumes, evaluating corrosion results, and developing separations based upon precipitation procedures.

(1) Solubilities of Iron, Zirconium, and Chromium in Liquid Zn-Mg Alloys at 800°C (J. B. KNIGHTON, J. D. SCHILB, J. W. WALSH)

The solubilities of iron, zirconium, and chromium in liquid Zn-Mg alloys were individually determined as a function of magnesium concentration in the alloy at a temperature of 800°C. The results are summarized in Figure I-5.

TABLE I-3. DISTRIBUTION OF ZIRCONIUM BETWEEN MOLTEN CHLORIDE SALT AND Cd-Mg ALLOY

Metal phase: Cd-Mg Alloy, Mg concentration as indicated
Salt phase: 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl
Atmosphere: Argon
Crucible: Tantalum

Temperature (°C)	Mg Conc. in Metal Phase (w/o)	Zr Conc. in Metal Phase (w/o)	Zr Conc. in Salt Phase (w/o)	$K_d = \frac{\text{w/o Zr in Salt}}{\text{w/o Zr in Metal}}$
592	1.69	0.439	2.64×10^{-4}	6.02×10^{-4}
502	1.44	0.308	1.24×10^{-4}	4.03×10^{-4}
426	1.42	0.134	6.7×10^{-5}	5.0×10^{-4}
600	1.84 ^a	0.400	2.37×10^{-5}	5.93×10^{-5}
499	4.08	0.238	8.5×10^{-5}	3.57×10^{-4}
426	4.17	0.199	1.28×10^{-4}	6.43×10^{-4}
599	6.13 ^a	0.426	2.37×10^{-5}	5.57×10^{-5}
498	8.88	0.416	2.77×10^{-5}	6.67×10^{-5}
425	9.68	0.289	3.84×10^{-5}	1.33×10^{-4}
600	14.8 ^a	0.444	3.6×10^{-5}	8.1×10^{-5}
498	19.4	0.433	4.90×10^{-5}	1.13×10^{-4}
602	22.4 ^a	0.388	6.61×10^{-5}	1.7×10^{-4}
504	28.4	0.358	2.0×10^{-6}	5.58×10^{-5}
473	27.0	0.128	3.4×10^{-5}	2.65×10^{-4}

^a Magnesium was added to melt prior to sampling of metal phase. Low magnesium analysis indicates incomplete alloying of added magnesium with Cd-Mg-Zr alloy.

⁵ Co-op student, Illinois Institute of Technology.

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FIG. I-4. Distribution of Zirconium between 30 m/o NaCl-20 m/o KCl-50 m/o MgCl₂ and Cd-Mg Alloy.

Atmosphere: Argon

Crucible: Tantalum

The observed solubility of iron in the Zn-Mg alloys at 800°C is consistent with the data reported by Truesdale et al⁶ and by Seibel⁷ for the solubilities of iron in pure zinc and pure magnesium, respectively. The solubility of zirconium is in agreement with an extrapolation of the data of Martin et al⁸ on the solubility of zirconium in zinc, and the data of Schaum and Burnett⁹ on the solubility of zirconium in magnesium. The solubility of chromium in zinc is about 1.5 w/o at 800°C, and decreases to an extrapolated value of approximately 0.045 w/o in magnesium. Lihl and Jenitschek¹⁰ report a value of 0.98 w/o for the solubility of chromium in zinc at 463°C.

(2) Solubility of Iron in Cu-Mg Alloys (J. B. KNIGHTON, G. E. KOVALL⁵)

Recent corrosion tests have indicated that various steels may be suitable for the containment of liquid Cu-Mg alloys (see Supporting Engineering Studies,

⁶ E. C. Truesdale, R. L. Wilcox, and J. L. Rodda, Trans. AIME **122**, 192 (1963).

⁷ G. Seibel, Z. Metallkunde **39**, 22 (1948).

⁸ A. E. Martin, J. B. Knighton, and H. M. Feder, J. Chem. Eng. Data **6**(4), 596 (1961).

⁹ J. H. Schaum and H. C. Burnett, J. Research Nat. Bur. Standards **49**, 155 (1952).

¹⁰ F. Lihl and P. Jenitschek, Z. Metallkunde **45**, 686 (1954).

this report). The small amount of corrosion that did occur apparently resulted primarily from the simple dissolution of iron in the liquid alloy. Therefore, a

FIG. I-5. Solubilities of Iron, Zirconium, and Chromium in Zn-Mg Alloys at 800°C.

TABLE I-4. SOLUBILITY OF IRON IN Cu-Mg ALLOY

Temperature (°C)	Magnesium Concentration (w/o)	Iron Solubility (w/o)
850	8.96	0.144
748	8.78	0.082
800	8.61	0.100
850	30.3	0.092
748	29.8	0.049
646	30.4	0.018
597	33.5	0.012
700	30.3	0.034
802	29.6	0.086
855	51.8	0.122
751	51.8	0.054
646	51.6	0.019
601	51.7	0.013
700	51.0	0.034
803	51.2	0.074

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Fig. I-6. Solubility of Iron in Cu-Mg Alloys.

brief investigation was conducted on the solubility of iron in copper-magnesium alloys.

A crucible of 1020 mild steel was used for containment, as well as a source of iron, for the solubility determinations. Filtered samples were taken from Cu-Mg alloys containing nominally 30 or 50 w/o magnesium over a temperature range of 600 to 850°C and from a Cu-9 w/o Mg alloy from 750 to 850°C. The results are presented in Table I-4 and Figure I-6.

The solubility values range from a minimum of 0.0115 w/o in Cu-30 w/o Mg alloy at 600°C to a maximum of 0.14 w/o in Cu-9 w/o Mg at 850°C. The solubility of iron showed little variation between the alloys containing 30 and 50 w/o magnesium, but was somewhat higher in the Cu-9 w/o Mg alloy than in the 30 and 50 w/o magnesium alloys.

c. CONSOLIDATION OF LANTHANON FISSION PRODUCTS IN AL-Mg ALLOYS (J. B. KNIGHTON, R. A. MANCINI,¹¹ K. R. TOBIAS)

The extraction of lanthanon fission products from molten chloride salts by liquid Al-Mg alloys to produce a metallic ingot suitable for disposal was reported in part in ANL-7055, pp. 38-40. This procedure appears attractive as a means of purifying process

¹¹ Co-op Student, University of Detroit.

salts for recycle. Distribution coefficients of yttrium, lanthanum, cerium, and praseodymium between 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl and liquid Al-Mg alloys were reported, along with the solubilities of these elements in Al-Mg alloys. These results indicated that effective removal of lanthanon fission products from the salt could be achieved in a single-stage extraction with the Al-Mg alloy.

An additional experiment has been performed, in which an ingot having the approximate composition, 10 w/o Ce-20 w/o Mg-70 w/o Al was prepared for metallographic and autoradiographic examination. Inactive cerium was used in the preparation of the ingot, which was then sectioned. One section was neutron-irradiated to produce ¹⁴¹Ce (*t*_{1/2} = 32.5 days). The autoradiograph of the cross section of the ingot is reproduced in Figure I-7. The cerium is visible as relatively well-dispersed, needle-like deposits of a cerium-aluminum intermetallic compound. This observation suggests that high loadings of lanthanon fission

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FIG. I-7. Autoradiograph of a Cerium-Magnesium-Aluminum Ingot. (An ingot of 10 w/o Ce-20 w/o Mg-70 w/o Al was prepared and a slice was irradiated to form ¹⁴¹Ce. Radioactive deposits of cerium-aluminum intermetallic are visible as needle-shaped areas in the autoradiograph.)

products in Al-Mg alloys could be used to produce ingots in which the temperature resulting from fission product decay heat would be fairly uniform because of the dispersion of the heat source and the high thermal conductivity of the alloy.

d. CHEMICAL STUDIES OF INTERMETALLIC COMPOUNDS IN MOLTEN SALTS (J. FISCHER, J. J. HEIBERGER)

Certain intermetallic compounds are soluble in molten salts, sometimes to a greater extent than the individual component metals of the intermetallic compound. Since magnesium alloys are used in liquid metal-molten salt processes, the solubilities of magnesium metal and of two magnesium intermetallic compounds in molten chloride salts have been investigated.

(1) Solubility of Magnesium in MgCl_2

Experimental data on the solubility of magnesium in molten MgCl_2 at 800°C , determined by equilibration of the salt and metal phases, are summarized in Table I-5, along with a result reported by Rogers et al.¹² It is apparent that the solubility values obtained with a closed system are higher than those obtained with an open system. In the closed system, it was necessary to take solid samples from the quenched salt; in the open system (open to a high-purity helium atmosphere), liquid samples were taken at the equilibration temperature. In the closed system, because of the quenching, the exact equilibrium temperature is uncertain; some vaporization of magnesium was noted in the open system. Both methods are therefore subject to some question, although the data are believed to be in the correct general range.

(2) Solubility of Mg_2Sn in MgCl_2

The average value for the solubility of Mg_2Sn in MgCl_2 , also given in Table I-5, is 0.03 ± 0.015 m/o at 800°C . The large standard deviation of this result is attributed to difficulties in obtaining satisfactory tin analyses because of the low tin concentration in the salt.

(3) Solubility of Mg_3Bi_2 in MgCl_2

In order to determine the solubility of Mg_3Bi_2 in an open system, two separate equilibrations were made, and replicate samples of the equilibrated system were taken at various temperatures. One sample from each set was analyzed for bismuth by the titration method and a replicate sample was analyzed by gas chroma-

¹² P. S. Rogers, J. W. Tomlinson, and T. D. Richardson, *Physical Chemistry of Process Metallurgy*, Interscience Publishers, Inc., New York, 1961, p. 909.

TABLE I-5. SOLUBILITY OF MAGNESIUM AND Mg_2Sn IN MgCl_2 AT 800°C ^a

Type of System	Solubility of Mg in MgCl_2 (m/o Mg)
Closed ^b	0.22 ± 0.02
Open ^c	0.13 ± 0.01
Closed (Rogers et al. ¹²)	0.30
	Solubility of Mg_2Sn in MgCl_2 (m/o Mg_2Sn)
Open ^c	0.03 ± 0.015

^a Temperature held to $\pm 5^\circ\text{C}$.

^b Quenched samples, contained in closed tantalum vessels.

^c Liquid samples taken from molten salt equilibrated in tantalum vessels at 800°C ; system open to high-purity helium atmosphere.

TABLE I-6. SOLUBILITY OF Mg_3Bi_2 IN MgCl_2
Open system—unless otherwise noted

Temperature ($^\circ\text{C}$) ($\pm 2.5^\circ\text{C}$)	Solubility of Mg_3Bi_2 (m/o)
886	0.14
851	0.23
826	0.16
815	0.18
805	0.20
752	0.18
728	0.14
Quenched from 731°C ^b	0.12

^a Melting point of Mg_3Bi_2 : 820°C .

^b Closed tantalum capsule.

tography. The hydrolysate from each hydrolysis was also analyzed for bismuth. The three different analyses usually agreed within 5%.¹³ Average values for the solubility of Mg_3Bi_2 in MgCl_2 are summarized in Table I-6.

During the experiments in which Mg_3Bi_2 was equili-

¹³ In order to determine if hydrolysis and gas chromatography could be used as an analytical method for Mg_3Bi_2 , 45.3 mg of Mg_3Bi_2 was hydrolyzed in 20 ml of 1 N HCl and a sample of the resulting gas was examined by gas chromatography. The result indicated that 46.6 mg of Mg_3Bi_2 had been hydrolyzed, assuming that 3 moles of hydrogen were evolved for each mole of Mg_3Bi_2 . The hydrolysis can be represented by any of the three reactions: $\text{Mg}^0 \rightarrow \text{Mg}^{+2}$, $\text{Mg}^+ \rightarrow \text{Mg}^{+2}$, or $\text{Bi}^0 \rightarrow \text{Bi}^3$. In any case, the amount of hydrogen evolved is proportional to the quantity of Mg_3Bi_2 originally present. After hydrolysis in 1 N HCl, the bismuth remained in the hydrolysate in the form of a flocculent precipitate which was soluble in 2 N HNO_3 . After the addition of HNO_3 to dissolve the bismuth, the hydrolysate was analyzed for bismuth by EDTA titration. The titration indicated 38.1 mg of bismuth compared to the known amount of 38.6 mg present as Mg_3Bi_2 . Thus two different analytical methods were used to determine Mg_3Bi_2 in MgCl_2 .

brated with MgCl_2 , a red color was observed in the salt phase. The color was more intense than that which was observed when magnesium alone was equilibrated with MgCl_2 .

(4) Melting Points of MgCl_2 and Mg_3Bi_2 ; Eutectic Point of $\text{Mg}_3\text{Bi}_2\text{-MgCl}_2$ System

In addition to the solubility measurements, thermal analysis was used to obtain the melting points of the pure components and the eutectic point of the $\text{Mg}_3\text{Bi}_2\text{-MgCl}_2$ system. Thermal analysis curves were also obtained for several other compositions in the system.

The melting point of the MgCl_2 used was 716°C , as compared with the generally accepted literature value of 714°C . Since these experiments were performed in a system that was open to the helium atmosphere of the dry box, the melting point could be determined by visual observation as well as by the thermal halt. When determining the freezing point of the MgCl_2 , the point at which the first crystals were observed coincided with the thermal halt.

In order to determine the eutectic temperature of the $\text{Mg}_3\text{Bi}_2\text{-MgCl}_2$ system, the salt that was used was taken from the salt layer of a mixture of 84 g of MgCl_2 and 20 g of Mg_3Bi_2 that had been equilibrated at 850°C and then slowly cooled until it had solidified. The melting point of this salt, which should be the eutectic temperature of the $\text{Mg}_3\text{Bi}_2\text{-MgCl}_2$ system, was determined to be 715.3°C .

The melting point of the Mg_3Bi_2 used in these experiments was 820°C , as compared with the literature value of 823°C .¹⁴ Since the liquidus curve in the magnesium-bismuth phase diagram comes to a very sharp point at Mg_3Bi_2 , a small deviation from the stoichiometric composition of Mg_3Bi_2 could account for the discrepancy in melting points.

A thermal curve was obtained for a composition approximately at the midpoint of the $\text{Mg}_3\text{Bi}_2\text{-MgCl}_2$ system. A mixture containing 51.6 m/o MgCl_2 was equilibrated at about 830°C and then cooled slowly. A thermal change was observed at 818°C , followed by a second thermal change at 718°C , where visual observation showed the first crystals forming in the salt. A third thermal change corresponding to the $\beta \rightarrow \alpha$ phase transition of Mg_3Bi_2 was observed at 702°C .

e. CADMIUM (I) CHLORIDE STUDIES (D. A. WENZ, R. D. WOLSON)

A conceptual process employing cadmium as a liquid metal solvent for the recovery of uranium and plutonium from irradiated nuclear fuels was described in ANL-7055, pp. 40-41. In this process uranium, plu-

tonium, and the electropositive fission products are separated from the refractory and noble metal fission products through selective oxidation by CdCl_2 in a molten salt solvent to form the chlorides of the oxidized elements and cadmium metal. The CdCl_2 may be regenerated by chlorination of the metallic cadmium produced in this step. Interactions of CdCl_2 in the molten salt with cadmium metal to form a lower cadmium chloride are therefore of process interest.

Although solutions resulting from the interaction of cadmium metal with CdCl_2 are highly colored and diamagnetic¹⁵ and although the reduction of the resulting cadmium (I) species has been shown to be a two-electron process¹⁶ (suggesting Cd_2^{++}), the exact nature of the subhalide species had not been determined. The reaction has been described by the equation

in which various investigators have suggested that x may have a value of 1, 2, or 3.^{17, 18}

In an effort to resolve the uncertainty concerning the nature of the cadmium (I) species, the reaction between cadmium metal and CdCl_2 in various molten chloride solvents has been investigated by equilibrating molten CdCl_2 in chloride solution with liquid cadmium metal at 500°C and 650°C and then making spectrophotometric measurements of the colored cadmium (I) species. The cadmium (I) species was assumed to obey Beer's law:

$$A = \epsilon l [\text{Cd}(\text{CdCl}_2)_x] \quad (2)$$

where A is the optical absorbance, ϵ is the molar absorptivity of the absorbing species in liter cm^{-1} mole $^{-1}$, l is the path length of the cell in cm, and $[\text{Cd}(\text{CdCl}_2)_x]$ is the molar concentration of the colored cadmium (I) species in the molten salt.

The mole fraction equilibrium constant expression for reaction 1 can be converted into one in terms of molarities, since the number of moles of $\text{Cd}(\text{CdCl}_2)_x$ was small compared to the number of moles of CdCl_2 and solvent under the experimental conditions employed. The concentration of cadmium metal can be regarded as constant, since it was always present as an immiscible liquid phase, and in the following equation it is included in the equilibrium constant, K :

$$K = \frac{[\text{Cd}(\text{CdCl}_2)_x]}{[\text{CdCl}_2]^x} ([\text{CdCl}_2] + [\text{solvent}])^{x-1} \quad (3)$$

¹⁵ J. Farquharson and E. Heymann, *Trans. Faraday Soc.* **31**, 1004 (1935).

¹⁶ L. E. Topol, *J. Phys. Chem.* **67**, 2222 (1963).

¹⁷ L. E. Topol and A. L. Landis, *J. Am. Chem. Soc.* **82**, 6291 (1960).

¹⁸ M. Fiorani and G. G. Bombi, *Nature* **207**, 289 (1965).

¹⁴ M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill Book Co., New York (1958).

where the brackets denote molarities. When this equation is solved for $[\text{Cd}(\text{CdCl}_2)_x]$ and the result is substituted in Equation 2, the following expression is obtained:

$$A = \epsilon l K [\text{CdCl}_2]^x ([\text{CdCl}_2] + [\text{solvent}])^{1-x} \quad (4)$$

or,

$$\log A = \log \epsilon l K + \log ([\text{CdCl}_2] + [\text{solvent}]) + x \log \frac{[\text{CdCl}_2]}{[\text{CdCl}_2] + [\text{solvent}]} \quad (5)$$

Equation 5 is linear in the two unknowns, x and $\log \epsilon l K$. Therefore the values of x and $\epsilon l K$ can be obtained from the dependence of the absorbance, A , upon the CdCl_2 concentration. This was done by measuring absorbance at several CdCl_2 concentrations in each of several molten chloride solvents. At each CdCl_2 concentration, values for $\log \epsilon l K$ were calculated for several assumed values of x and a curve was plotted of $-\log$

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FIG. I-8. Graphical Determination of x for the Compound $\text{Cd}(\text{CdCl}_2)_x$.

Temperature: 650°C
Wavelength: 5000 Å
Solvent: LiCl

TABLE I-7. ABSORPTION MAXIMA OF SOLUTIONS RESULTING FROM THE REACTION OF CADMIUM METAL WITH CADMIUM CHLORIDE IN MOLTEN CHLORIDE SOLVENTS

Solvent	Temperature (°C)	λ_{max} (mμ)
59 m/o LiCl-41 m/o KCl	500	300
LiCl	650	305
CdCl ₂	575	340*
59 m/o LiCl-41 m/o KCl	650	340
50 m/o MgCl ₂ -30 m/o NaCl-20 m/o KCl	500	340
50 m/o MgCl ₂ -30 m/o NaCl-20 m/o KCl	650	365

* J. Bookless and J. Egan, Nuclear Engineering Department Progress Report, September 1-December 13, 1963, Brookhaven National Laboratory, BNL-841.

TABLE I-8. STOICHIOMETRY OF THE ABSORBING SPECIES FROM THE REACTION OF CADMIUM METAL WITH CADMIUM CHLORIDE IN MOLTEN CHLORIDE SOLVENTS

Solvent	Temperature (°C)	x
50 m/o MgCl ₂ -30 m/o NaCl-20 m/o KCl	650	1.9
50 m/o MgCl ₂ -30 m/o NaCl-20 m/o KCl	500	2.3
LiCl	650	2.0
59 m/o LiCl-41 m/o KCl	650	2.2
59 m/o LiCl-41 m/o KCl	500	2.4

$\epsilon l K$ versus x . The intersection of the curves obtained at different CdCl_2 concentrations in the same chloride solvent represents a graphical solution to all the pairs of simultaneous equations. A typical plot of results for LiCl solvent at 650°C and absorbance measurements at 5000 Å is shown in Figure I-8. Ideally, all of the lines should cross at the same point, but the experimental error causes some scatter of the intersections.

Table I-7 lists the absorption maxima of the colored cadmium (I) species in several solvents at various temperatures. The molar absorptivities of these maxima are estimated to be about 10^4 liter mole⁻¹ cm⁻¹. The spectral observations were made at 4700, 5000, and 5300 Å because this was the region of optimum absorbance measurements under the experimental conditions (10-50 w/o CdCl_2 in the molten salt solvent). None of the other components of the mixtures used has a significant absorbance at these wavelengths. The values obtained for x are given in Table I-8. The uncertainty in x is approximately $\pm 20\%$. It is apparent that the value of x is close to 2 in all solvents.

B. ENGINEERING-SCALE INVESTIGATIONS (R. D. PIERCE, L. BURRIS, JR., G. A. BENNETT)

The Chemical Engineering Division at Argonne, Illinois, is continuing to develop equipment for pyrochemical processes which will be operated in the EBR-II Fuel Cycle Facility in Idaho. One such process is the skull reclamation process developed for

recovery of uranium from melt refining crucible residues (skulls). Final pilot plant studies of this process are reported. Development of plant equipment for use in the Fuel Cycle Facility is reported in Section IC.

1. Pilot Plant Studies of the Skull Reclamation Process (I. O. WINSCH, T. F. CANNON, P. MACK, K. L. NISHIO, K. R. TOBIAS, W. H. SPICER, L. KIRKEL)

Operation of the pilot plant to study and demonstrate the skull reclamation process on an engineering scale was discontinued after the completion of 36 process runs. These process demonstration runs have established process procedures and the mechanical reliability of the equipment. Reliable engineering techniques have been developed and these are now being further engineered in the EBR-II plant-scale experiments described in the following section. In the pilot plant, about 2 kg of skull oxide is processed in each run; in the full (EBR-II) scale runs, about 5 kg of skull oxide is processed. Uranium recovery and fission product removal during the various steps of the process have been studied.

In the previous semiannual report, it was stated that uranium losses were often somewhat high as a result of entrainment in the intermetallic compound precipi-

tation step of the process (see flowsheet ANL-7055, Fig. I-3, p. 30). The use of a strainer-weir on transfer lines (ANL-7055, Fig. I-5) has since proved helpful in reducing uranium losses in the waste solution; however, before an optimum design for the strainer-weirs could be developed, a modification to simplify the process was successfully tried. This modification, which completely eliminated the troublesome step, has proved so attractive that work on the intermetallic compound precipitation step was discontinued.

The simplified skull reclamation process is represented in Figure I-9. The major feature of the flowsheet modification is the complete elimination of the intermetallic compound precipitation step. With this elimination, it was possible to combine the reduction step with the uranium-zinc intermetallic compound decomposition step. (In the latter step, the uranium

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FIG. I-9. Simplified EBR-II Liquid Metal Process for Reclamation of Melt Refining Skulls. (For a charge of 2 kg of skull oxide, the following charges of other materials are required: salt flux, 7 kg; zinc, 35 kg; ZnCl_2 , 0.5 kg; 60 w/o Mg-Zn alloy, 18 kg; and zinc + magnesium for product dissolution, 11 kg.)

intermetallic precipitate was converted to a uranium metal precipitate.) This was done by reducing the uranium oxide directly with a magnesium-rich alloy and allowing uranium metal to precipitate as it is formed. Thus, the simplified flowsheet is shorter by two steps than its predecessor. A further simplification possible in the new flowsheet is the elimination of the three very time-consuming cooling and heating cycles (between 800°C and 450 or 500°C) that were used in the original flowsheet (ANL-7055, Fig. I-3, p. 30). This has made it possible to process a batch of skull oxide (once the equipment has been brought up to operating temperature) within 8 hr as compared with about 18 hr for the previous flowsheet. Other advantages of the new flowsheet as compared to the previous flowsheet are reduced material consumption and a consequently smaller volume of waste, and increased uranium recovery. An uncertainty in the new flowsheet is the adequacy of zirconium removal since the intermetallic precipitation step had provided the major zirconium removal; other than this, fission product removals should not be adversely affected.

Elimination of the heating and cooling cycles in the new flowsheet was achieved by:

(1) Developing proficiency in the transfer of the waste zinc phase from beneath a liquid salt phase rather than from beneath a solidified salt layer. This also eliminated the need for the high-melting salt previously used to accommodate the high-temperature solidification of the salt, and so a change was subsequently made to a lower melting salt (from a 47.5 m/o CaCl_2 -47.5 m/o MgCl_2 -5.0 m/o CaF_2 salt melting at about 600°C to a 47 m/o MgCl_2 -27.7 m/o NaCl -18.6 m/o KCl -6.7 m/o NaF salt melting at about 495°C).

(2) Eliminating the uranium-zinc intermetallic compound precipitation step, which was mentioned above.

(3) Decreasing the uranium solubility in the supernatant metal solution of the reduction step by increasing the magnesium concentration in the metal solution from 50 w/o to 60 w/o, which made it unnecessary to cool the solution. Previously, the uranium solubility in 50 w/o Mg-Zn solution had been reduced from 0.44 w/o at 800°C to 0.07 w/o by cooling to 450°C. By using a 60 w/o Mg-Zn solution and operating at 750°C, a sufficiently low uranium solubility of 0.15 w/o was achieved without further cooling. The uranium loss in the supernatant solution was further reduced by using a minimum weight of reducing alloy (33% less than the weight of the 50 w/o Mg-Zn alloy). While the uranium loss in the waste alloy stream is not yet as low as was previously possible, it is acceptable in view of the elimination of the uranium loss associated with the intermetallic precipitation step.

TABLE I-9. RECOMMENDED INITIAL OPERATING CONDITIONS FOR MODIFIED SKULL RECLAMATION PROCESS IN PLANT-SCALE EQUIPMENT

Step	Temperature (°C)	Time (hr)	Degree of Agitation		Expected U Loss in Waste Stream (% of total U)
			Qualitative	Mixer rpm in Pilot Plant ^a	
Noble metal extraction Reduction	750	1	Very vigorous	800-1000	<0.5
	750	2	Vigorous	600	Waste flux, ~1 Supernatant metal waste, 1.4 to 2.5 Total, <4 U recovery, ~96%
Product dissolution	810	1	Vigorous	600	

^a The pilot plant crucible is equipped with mixing baffles. Because mixer size and location and the nature of the mixing baffles are very important, different mixing speeds will undoubtedly be required in the plant equipment to produce agitation intensities equivalent to those realized in the pilot plant.

Seven runs were made using the new flowsheet. Because of the change to a low-melting salt flux, it became possible to consider operating temperatures within the range of 650°C to 800°C. Other variables investigated were reaction time, agitation intensity, and charge size. As would be expected, reaction time (for uranium oxide reduction or extraction of noble metals) and temperature are closely connected; the higher the temperature, the shorter the reaction time. A reaction temperature of 750°C is somewhat arbitrarily recommended as one which provides reasonably rapid reactions (complete within 1 to 2 hours) without incurring excessive vaporization of metal and salt phase constituents. Good agitation intensity is also necessary to effect the reactions within a short period of time.

In one run a double charge of oxide and salt was used. The quantity of oxide was so great that when the flux was not being stirred (e.g., when the zinc and flux phases were allowed to separate), a large amount of the oxide, which accumulates at the interface, settled into the zinc phase and was transferred out in the zinc waste, thereby leading to a high uranium loss. The use of larger charges in a run, which would have resulted in fewer skull reclamation runs, appears impractical because of the above difficulty.

The conditions recommended for initial operation of the plant-scale equipment are given in Table I-9.

As pointed out in previous reports, a uranium recovery of 96% is ample because less than 10% of the total EBR-II fuel will probably be cycled through the skull reclamation process. A uranium recovery of 95%

in the skull reclamation process would provide an overall uranium recovery of greater than 99.5%. Achievement of a high uranium recovery in the skull reclamation process requires that the following conditions be met in the noble metal extraction step and the reduction step:

Noble Metal Extraction Step. Sufficient oxidizing power must be available to oxidize (1) uranium (and consequently the magnesium) present in the recycle product solution heel of the previous run and (2) any unoxidized uranium metal in the skull oxide charge so that all of the uranium will transfer to the flux phase. Considerable oxidizing power is available through reactions such as:

If experience shows that the available oxidizing power is insufficient, an additional quantity of oxidant, such as ZnCl_2 , must be added. ZnCl_2 was usually employed in the pilot plant runs. The use of an oxidant is recommended for plant operations as a safety precaution. Since the volatility of ZnCl_2 can be a problem, ZnO may be a more convenient reagent for the plant. In the pilot plant runs, uranium loss in the noble metal extract was no problem, being generally well under 0.5%.

Reduction Step. Uranium losses in the waste flux have averaged about 1%. Achievement of a low loss is a matter of providing sufficient agitation intensity and enough time (about 2 hours) for the reduction to go to completion. The minimum attainable uranium loss in the flux, which is that due to the equilibrium concentration in the flux phase, is about 0.6%.

The minimum attainable loss of uranium in the supernatant 60 w/o Mg-Zn metal phase, which is determined by the solubility of uranium, is about 1.4%. Loss of uranium in excess of this value results from the entrainment of the uranium metal precipitate. The minimum loss was achieved in runs in which moderate care was taken to allow the uranium to settle (0.5 hr) and to avoid its resuspension. In two runs made to determine whether the uranium was, in fact, easily suspended, the supernatant solution was stirred at 400 rpm during removal. Most of the uranium was entrained in the supernatant metal. However, routine precautions should be sufficient to avoid uranium entrainment.

Fission Product Removal. Fission product removals were not significantly affected by the change to the

new flowsheet. These may be summarized as follows:

Cerium (a stand-in for all rare earth elements)—greater than 90%

Ruthenium —~90%

Molybdenum—~40–70%. Because molybdenum is insoluble in the product solution, there is opportunity to achieve additional molybdenum removal by allowing it to settle prior to transfer of the product solution. By utilizing this procedure, apparent molybdenum removals of over 90% have been achieved.

Zirconium —50–70%. Because the intermetallic compound precipitation step has been eliminated, zirconium removal in the new flowsheet had been uncertain. However, it has been found that the zirconium removal is not substantially different from that achieved in the old, more complicated flowsheet. Zirconium removal in the new flowsheet occurs by two mechanisms: (1) unreduced zirconium oxide is removed in the waste flux, and (2) zirconium is removed in the 60 w/o Mg-Zn supernatant waste as a result of a slight solubility in the solution. The latter is the predominant mechanism.

Performance of Pilot Plant Equipment. The pilot plant equipment, described in ANL-6687, p. 37, was operated in a glovebox containing a dry (<150 ppm H_2O) nitrogen-argon atmosphere to eliminate moisture pickup by the hygroscopic salts. All process steps up to the retorting step were performed in a 9½-in. ID pressed and sintered tungsten crucible. The crucible is inductively heated in a bell jar furnace, which allows performance of the process steps in an inert atmosphere and permits pressurization of the system for transfer of molten metals or salts through a transfer line to a container outside the bell jar.

Waste and product streams are removed from the process crucible by pressure transfer through the same molybdenum-30 w/o tungsten transfer line. Operation of the transfer line has been completely reliable in the last series of runs. Transfers of at least 90% are desired since the efficiency of fission product removal is limited by the transfer efficiency for the waste phases. In the latest runs, the noble metal extract transfers (made above the melting point of the flux) have been deliberately held to about 90%, as determined by weighing the material as it was collected in the receiver, so as to avoid transfer of any of the salt-uranium oxide slurry. The transfer efficiencies for

the 60 w/o Mg-Zn supernatant and the waste flux have ranged from 85 to 96% and 82 to 100%, respectively. Transfer efficiencies ranging from 87 to 97% have been experienced with the uranium product solutions.

The pressed and sintered tungsten crucible used in the process has shown no sign of deterioration, and the repaired pressed and sintered tungsten crucible (originally a manufacturing reject, ANL-6925, p. 32) continued to perform well for resampling of waste ingots.

2. Supporting Engineering Studies (R. D. PIERCE)

Large fast reactors will require high-capacity fuel processing plants capable of recovering plutonium as well as uranium. Investigations are being directed toward equipment and procedures for continuous and batch pyrochemical processes that are capable of high processing rates and that can recover both plutonium and uranium from ceramic and metallic fuels.

Continuous processes generally require less space and less direct manipulation than batch processes. These advantages may be especially important in shielded facilities where space is expensive and any handling of the equipment must be done remotely. Batch processes, on the other hand, may be advantageous where few processing steps are required and the volumes of solutions to be handled are small. Because the advanced flowsheets are not clearly defined at this time, the objective of the engineering program is to develop equipment which is generally applicable to pyrochemical processes. One initial objective is the demonstration of countercurrent, liquid-liquid extraction between a liquid cadmium-base metal and a liquid chloride salt. This unit operation is proposed in several advanced core processes to separate plutonium and uranium from rare earths and, in another step, to extract rare earths from a liquid salt into a liquid metal solution for long-term storage. Several support studies are being made. These include estimation of the mass transfer rates of actinides and rare earths between a liquid metal and a liquid salt; the development of a salt purification process and equipment; an investigation of the corrosion resistance of promising materials of construction toward the process solutions; and an investigation of the removal of nitrogen from argon with titanium sponge.

a. MEASUREMENT OF MASS TRANSFER RATES —TRANSIENT COLUMNS (T. R. JOHNSON, W. J. WALSH, F. G. TEATS, K. R. TOBIAS, T. F. CANNON)

Additional experiments have been made to estimate the mass transfer rates in countercurrent liquid metal-liquid salt extraction columns. These runs were es-

sentially identical to those described in ANL-7055, pp. 44-45. The principal difference in the later runs was the use of cerium rather than uranium as the distributing component. To simulate a packed extraction column, the middle six inches of a quartz tube (1-in. OD, 17 in. long) was packed with 1/4-in. lengths of 1/4-in. OD tantalum tubing. The quartz tube was filled to a level above the packed section with a molten salt (50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl). The metal alloy (Cd-11 w/o Zn-5 w/o Mg-0.5 or 1.9 w/o Ce) was allowed to flow through the column of static salt. The run was terminated by plunging the column into a bath of low-melting metal alloy at 100°C, thereby freezing the contents of the tube. In the earlier report, it was shown that, with certain assumptions which apply approximately to these experiments with cerium, the mass transfer coefficient based on the salt phase was:

$$k_s a \sim \left(\frac{S}{\rho_s V} \right) \frac{1}{T} \ln \left(\frac{1}{1 - \alpha} \right)$$

where:

$S/\rho_s V$ = void volume fraction of packed column (~ 1)

T = time of contact

α = fraction of equilibrium cerium concentration reached in the salt in the active section of the column.

The experimental results of the latest runs are summarized in Table I-10 where the previously published results (ANL-7055, p. 44) of runs with uranium are also presented. If a mass transfer coefficient of 0.008 sec^{-1} for actinides and rare earths is assumed, the height of a theoretical stage would be about two feet in an extraction column in which uranium or plutonium is separated from rare earths.

b. SALT PURIFICATION (T. R. JOHNSON, F. G. TEATS)

Equipment has been assembled to purify relatively large quantities (up to 80 kg per batch) of MgCl_2 -base salts for use in engineering-scale experiments. Oxidiz-

TABLE I-10. DYNAMIC EXTRACTIONS OF URANIUM AND CERIUM FROM MOLTEN CADMIUM ALLOYS TO CHLORIDE SALT. EXPERIMENTAL CONDITIONS AND RESULTS

<i>U-Metal Alloy</i>	Initial composition: Cd-3.6 w/o Mg-U	
	Charge to column: 210 g	
<i>Ce-Metal Alloy</i>	Initial composition: Cd-11 w/o Zn-5 w/o Mg-Ce	
	Charge to column: 130 g	
<i>Salt</i>	Initial composition: 50 m/o MgCl ₂ -30 m/o NaCl-20 m/o KCl	
	Charge to column: ~100 g	
<i>Column</i>	(quartz tube): 7/8-in. ID, 6-in. packed height	
<i>Packing</i>	1/4-in. length, 1/4-in. OD Ta tubing	

Temp (°C)	Contact Time ^a (sec)	Initial Conc. in Metal	Final Conc. in salt ^b ($x_f \times 10^2$)	Conc. in Salt at Equil. (cal- culated) ($x_e \times 10^2$)	Overall Average Mass Transfer Coefficient ^c $k_a a$ (sec ⁻¹)	Height Equivalent to a Theo- retical Stage (ft)
Uranium						} 2 ^h
490	<300 ^d	0.240 ^e	0.49	0.64 ^f	>0.005	
610	60	0.244 ^e	0.92	2.6 ^f	0.0074	
560	110	0.206 ^e	0.82	1.4 ^f	0.0079	
Cerium						
620	40	0.477	0.20	0.63 ^g	0.0096	
540	150	1.90	0.67	2.66 ^g	0.002	

^a Time from start of metal flow to start of salt freezing.

^b Transfer to the salt assumed to occur only in packed section.

$$^c \text{ Calculated from: } k_s a = (1/T) \ln \left(\frac{1}{1 - \frac{x_f}{x_e}} \right)$$

^d Contact time uncertain.

^e Final uranium concentration in metal approximately equal to initial concentration.

^f See ANL-7055, p. 45.

^g Salt in equilibrium with average cerium concentration in metal. Distribution coefficient for cerium estimated from that for praseodymium reported in ANL-7020, p. 42.

^h Calculated for a countercurrent column assuming $k_s a = 0.008 \text{ sec}^{-1}$.

ing constituents of the salt are reduced by contacting the molten salt with cadmium-30 w/o magnesium alloy at 600°C. Insoluble materials are removed by passing the salt through a stainless steel filter which has a pore size of about 20 μ . Untreated MgCl₂ salts are extremely corrosive toward all steels and contain large quantities of insolubles and of substances that react with UCl₃ to form UO₂Cl₂ and UO₂.

Earlier small-scale experiments have shown this method of treatment to be effective in producing a

salt that is noncorrosive toward stainless steels and that contains negligible amounts of oxygen and insolubles. The residual oxygen content of the purified salt has been in the range of 200 to 2000 ppm and is thought to be present as finely divided insoluble magnesium oxide, which has caused no difficulties in engineering experiments.

Five runs (batch size, 20 to 40 kg) have been successfully completed and a total of 130 kg of usable salt has been prepared. The equipment operated satisfactorily and, based on preliminary analyses, the product salt appeared to be of good quality. A diagram of the equipment is shown in Figure I-10. The receiver tank presently being used can be moved to other locations to supply liquid salt directly to experiments, or the tank can be connected to an argon-filled dry box where the salt may be cast in molds under a dry inert atmosphere.

c. MATERIALS TESTING (M. L. KYLE, J. ARNTZEN, A. RASHINSKAS)

(1) Corrosion of Iron-Chromium Alloys by Cadmium-Base Alloy/Salt System

One of the processes currently under development for advanced reactor fuels utilizes cadmium containing smaller amounts of zinc and magnesium as a solvent metal and a solution of MgCl₂-NaCl-KCl as a solvent salt. Results of previous tests (see ANL-7055, p. 50) showed type 405 stainless steel to possess adequate corrosion resistance to this system. Because of success in the use of this chromium steel as a containment medium for this system, three other iron-chromium alloys were investigated. The three alloys, type 430 stainless steel, type 1-JR steel (type 410 stainless steel with 3% aluminum addition), and type 329 stainless steel, were tested for corrosion resistance in a run conducted at 650°C for 24 hr in an 81 w/o Cd-11 w/o Zn-6 w/o Mg-2 w/o U/chloride salt¹⁹ system. This metal phase composition was selected for screening tests as being representative of the probable process solvent. Table I-11 presents the approximate corrosion rates obtained. More extensive testing of these alloys is planned to determine if these corrosion rates are representative of the rate that would be obtained in longer term exposures.

An additional test to determine the corrosion resistance of type 430 stainless steel to a system composed of 83 w/o Cd-11 w/o Zn-6 w/o Mg (no uranium) in contact with the chloride salt¹⁹ has been completed. This test was conducted at 600°C for 400 hr and con-

¹⁹ 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl purified by contact with molten cadmium-magnesium to remove oxidizing impurities.

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FIG. I-10. Salt Purification Facility.

sisted of mounting the four test coupons as agitator blades and exposing each blade to a different corroding phase (metal, salt-metal interface, salt, or vapor) contained in a tungsten crucible. Results obtained are presented in Table I-12. Corrosion rates in the salt and vapor phases were significantly less than the corrosion rate of 4.5 mils/400 hr observed in the metal

TABLE I-11. CORROSION OF IRON-CHROMIUM ALLOYS IN CADMIUM SOLUTION/CHLORIDE SALT SYSTEM

Liquid compositions: Metal: 2384 g of an 81 w/o Cd-11 w/o Zn-6 w/o Mg-2 w/o U alloy
Salt: 400 g of a 50 m/o $MgCl_2$ -30 m/o NaCl-20 m/o KCl salt

Time: 24 hr
Temperature: 650°C
Exposure: Metal coupons held upright in a tungsten crucible.
Metal and salt phases mixed by tungsten agitator blade rotating at 200 rpm.

Alloy	Depth of Corrosion ^a (mils)		
	Metal Phase	Salt Phase	Vapor Phase
430 SS	0.2	0.3 ^b	0.5 ^b
1-JR ^c	1.0 ^d	<0.2	0.2 ^e
329 SS	0.2	0.5 ^b	0.5 ^e

^a By metallographic examination.

^b Metal leaching.

^c 410 SS with 3% aluminum addition.

^d Intergranular attack.

^e Pitting.

TABLE I-12. CORROSION OF TYPE 430 STAINLESS STEEL BY Cd-Mg-Zn/CHLORIDE SALT SYSTEMS

Time: 400 hr
Liquid compositions: Metal: 2248 g of an 83 w/o Cd-11 w/o Zn-6 w/o Mg alloy
Salt: 418 g of a 50 m/o $MgCl_2$ -30 m/o NaCl-20 m/o KCl salt (purified by contact with molten Cd-Mg and filtered)

Temperature: 600°C
Method of exposure: Agitator blades ($\frac{1}{4}$ in. by 2 in. by 0.11 in.)
Agitator speed: 200 rpm
Crucible material: Tungsten

Phase	Observed Corrosion	
	Wt. Loss (mg/cm ²)	Depth ^a (mils)
Metal	73.0	4.5
Metal-salt interface	54.3	2.5
Salt	23.8	0.5
Vapor	5.6	0.0

^a By metallographic examination.

phase samples. Inspection of the samples indicates that the mode of corrosion was probably surface dissolution or ablation.

Although the above corrosion rates are excessive, several measures may be taken for reducing them. In these tests, the ratio of containment material surface to liquid metal volume was deliberately kept low in order to avoid saturation of the metal phase with the major alloy constituents such as iron, chromium, and

TABLE I-13. CORROSION OF FERROUS ALLOYS BY Cu-Mg/CHLORIDE SALT SYSTEMS

Metal phase:	Cu-Mg alloy, composition listed (20-55 g, depending on composition)
Salt phase:	~10 g of 50 m/o MgCl ₂ -30 m/o NaCl-20 m/o KCl, dried by contact with Cd-Mg alloy and filtered
Time:	200 hr
Method of exposure:	Ta capsules (7/8 by 1 3/4 by 0.030 in.) rotated end over end
Temperature:	600°C or 800°C, at 30 cycles/hr as listed
Specimen size:	1.5 by 0.5 by 0.018 in. AISI 1020 1.5 by 0.5 by 0.030 in. AISI 4130 1.5 by 0.5 by 0.013 in. 304 SS 1.5 by 0.5 by 0.027 in. 405 SS

Metal Phase	Observed Corrosion (mils)			
	304 SS	405 SS	AISI 4130	AISI 1020
Temperature 600°C				
50 w/o Cu-50 w/o Mg	<0.1	<0.1	<0.1	<0.1
70 w/o Cu-30 w/o Mg	0.1	<0.1	<0.1	<0.1
90 w/o Cu-10 w/o Mg	<0.1	<0.1	0.7	0.1
Temperature 800°C				
50 w/o Cu-50 w/o Mg	<0.1	<0.1	1.0	0.9
70 w/o Cu-30 w/o Mg	0.4	<0.1	0.8	0.7
90 w/o Cu-10 w/o Mg	1.3	1.5	1.7	0.8

nickel. Lower corrosion rates would probably be obtained in packed column type operation since the metal phase would become more highly saturated in these elements, resulting in a lower rate of dissolution. Also, the chosen metal composition is high in zinc, the most corrosive constituent, and low in magnesium, the least corrosive. Adjustment of metal composition might also reduce the corrosion rate.

It is concluded that containment of the salt phase in conventional materials of construction may be feasible; however, additional work is required before containment materials, systems, and conditions can be selected for cadmium-base metal/salt systems.

(2) Corrosion of Ferrous Alloys by Copper-Magnesium/Salt Systems

A program is in progress to determine the corrosion resistance of ferrous alloys to copper-magnesium/chloride salt systems since these systems show potential as a liquid metal solvent in compact pyrochemical processes. In initial screening tests, four alloys (AISI²⁰ type 1020 mild steel, AISI type 4130 1% Cr alloy steel, type 304 stainless steel, and type 405 stainless steel) were tested at 600 and 800°C for 200 hr in three

Cu-Mg/chloride salt²¹ systems containing 50, 70, and 90 w/o Cu. Prior to use, the chloride salt was purified by contact with a molten cadmium-magnesium solution (see Section I.D.2.).

The results of these tests (Table I-13) were obtained by size comparison and metallographic examinations made before and after exposure of the coupons. The data show that at 600°C there was less than 1 mil corrosion of any of the ferrous alloys tested. At 800°C, corrosion rates were higher (up to 2 mils/200 hr) and increased with copper concentration. In nearly all instances, the mode of attack appeared to be uniform surface ablation in the molten metal/salt mixture, indicating possible iron dissolution. If attack is by dissolution of iron, greater corrosion rates might be observed under different circumstances since in these tests the molten metal volume was low (15 to 50 g, depending on mixture) and would rapidly have approached saturation. Conversely, it may be possible to decrease the corrosion rates obtained by deliberate addition of iron to the metal solution. However, based on recent measurements of the iron solubility in these metal systems (see Solubility Determinations, earlier in this report), the corrosion rates observed here are higher than would be expected from simple surface dissolution. This indicates the occurrence of an additional form of attack such as intermetallic compound formation, surface reaction, or spalling.

(3) Testing of Tungsten-0.1 w/o Nickel in Zinc/Chloride Salt Systems

A sample of pressed-and-sintered tungsten containing 0.1 w/o nickel was received from the Union Carbide Corporation. At this concentration of nickel in tungsten a solid solution of nickel in tungsten is reported to be formed during sintering and results in a higher density product than is obtainable with pure tungsten. The sample was exposed as an agitator blade to a zinc/salt²² system at 800°C for 200 hr. The quantity of the metal phase (~2 kg) was sufficient to allow for dissolution of all nickel contained in the agitator blade without saturating the solution with nickel.

The results obtained in this test were very encouraging. Metallographic examination of the agitator blade after exposure indicated no evidence of deterioration of the blade except for a slight surface roughening measured at about 0.1 mil. It is concluded that this small addition of nickel to the tungsten, apparently useful in producing more dense tungsten crucibles, has

²⁰ American Iron and Steel Institute designation.

²¹ 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl.

²² 47.5 m/o MgCl₂-47.5 m/o CaCl₂-5 m/o MgF₂.

little effect on the corrosion resistance properties of tungsten in zinc/salt systems. Additional testing of this alloy is planned.

(4) Testing of Vitreous Carbon with Zn-Mg-U/Salt Systems

A new crucible material, vitreous carbon, is being tested for containment of zinc-magnesium-uranium/salt systems. A previous test (see ANL-7055, p. 51) indicated that the crucible material was not wet by a Zn-12 w/o Mg-10 w/o U/salt²³ solution after 24-hr exposure at 800°C.

Two additional tests have been performed. In these tests small (1 $\frac{3}{8}$ -in. OD by 1 $\frac{3}{8}$ -in. tall by 0.1-in. wall) vitreous carbon crucibles were exposed to (1) a zinc-2 w/o uranium/salt²⁴ system and (2) a zinc-5 w/o magnesium-2 w/o uranium/salt²⁴ system for 200 hr at 800°C. In both cases the metal phase did not wet the crucible and it appeared that the salt phase only slightly wet the crucible.

These results are considered highly encouraging and indicative that corrosion of vitreous carbon by these solutions will be negligible. More extensive testing of these crucibles is continuing.

(5) Failure of Plasma-Sprayed Tungsten Crucible

A tungsten crucible (4-in. OD by 6-in. high by $\frac{1}{4}$ -in. wall), which was fabricated by plasma-spraying on a sacrificial mandrel and sintering of the plasma-sprayed body at 2500°C, failed in September 1965. Before failing, this crucible had been exposed to zinc, zinc-magnesium, and cadmium-magnesium-zinc systems at temperatures between 600 and 850°C for a total exposure time of about 1000 hr. Failure occurred after a power failure which resulted in solidification of a cadmium-magnesium-zinc/chloride flux system in the crucible. After the flux had been removed, several cracks were noticed in the crucible, mostly along the metal/salt interface in the crucible wall. These cracks were only slightly water-permeable but proved permeable to dye penetrant. No detectable amount of either metal or salt leaked from the crucible during the approximately 75 hr that the final run was in progress.

The reason for the occurrence of these cracks is uncertain. It is unlikely that solidification of the melt exerted sufficient stress to break the crucible. Visual observation of the crucible disclosed no evidence of corrosion or deterioration. Failure was most probably caused by physical or thermal shock acting upon re-

sidual stresses left in the crucible after fabrication. The crucible fabricator has stated that failures of this type are not uncommon.

(6) Shear-Formed Tungsten Crucible

Metallwerk Plansee (Austria) has successfully completed shear-forming a tungsten crucible 18.1 in. high by 11.1-in. OD by 0.18-in. wall. The completed crucible is equipped with three full-length tungsten mixing baffles (1 in. wide extending 1.2 in. into the crucible). A photograph of this crucible is shown in Figure I-11.

This crucible has been received. After thermal cycling, it will be tested for containment of molten zinc-magnesium/salt systems.

d. PURIFICATION OF ARGON FROM NITROGEN WITH TITANIUM SPONGE (M. L. KYLE, J. ARNTZEN)

A method for removing nitrogen from argon by gettering the nitrogen with hot titanium metal sponge has been investigated. Although this method has general utility for purifying argon for such applications as glovebox atmospheres, the major incentive for its development has been a possible future need to remove nitrogen from the atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility.

Two sets of experimental equipment were constructed for the nitrogen-removal study: (1) equipment for determining the kinetics of nitrogen removal from argon on hot titanium sponge and (2) a pilot

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FIG. I-11. Shear-Formed Tungsten Crucible and Internal Baffle Assembly. (Crucible dimensions: 11.1-in. OD by 18.1-in. high by 0.18-in. wall.)

²³ 38 m/o MgCl₂-38 m/o CaCl₂-4 m/o CaF₂-20 m/o MgO salt of approximately this composition would result after the reduction step of the skull reclamation process).

²⁴ 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl.

plant for obtaining overall process performance data and information on component reliability. Studies were conducted with argon containing nitrogen in concentrations between 100 and 50,000 ppm.

These projects have been completed and separate reports on the two systems will be issued. This section presents the major conclusions on these projects.

(1) Kinetics of Nitrogen Removal from Argon with Titanium Sponge

A gas-circulating loop was built for a study of the kinetics of nitridation of titanium sponge by argon-nitrogen mixtures. Operating principles of the loop were described in detail in ANL-6800, pp. 54-56. In this loop argon-nitrogen mixtures of carefully controlled composition were continuously circulated (by a diaphragm pump) through a series of eight small test beds, each containing 0.7 to 2 g of titanium sponge. The circulation rate (100 to 800 liters/hr) was such that only a small fraction (usually less than 5%) of the nitrogen reacted with the titanium sponge in a single pass through the series of beds. By this technique, all beds in the stack were exposed to approximately the same nitrogen concentration in the reacting gas and no correction was required for a decreasing nitrogen concentration as the gas moved from bed to bed. The extent of reaction of the titanium sponge metal was determined at time intervals by successively and permanently removing the topmost titanium bed and determining, by a modified Kjeldahl analysis, the amount of nitrogen reacted. Data were obtained at nitrogen concentrations of approximately 100, 300, 1000, 5000, and 50,000 ppm in argon.

Metallographic and X-ray diffraction studies were made in an effort to determine the probable reaction mechanism. It was determined that in most reacted sponge particles three phases were identifiable. These were identified by X-ray diffraction techniques as the TiN_x and $\epsilon\text{-TiN}$ phases as described by Ehrlich²⁵ and Brager²⁶ and the solid solution of nitrogen in alpha titanium. These results are in general agreement with the observations of Wasilewski.²⁷ No attempt was made in this investigation to determine if the films were building by diffusion of nitrogen across the multi-layer structure present or by the counterdiffusion of titanium across this structure. The work of Wasilewski indicates that the mechanism is probably by nitrogen

diffusion, with the controlling mechanism in long time rates being the diffusion through the TiN_x phase.

An attempt was made to determine the value of x in the TiN_x phase. X-ray diffraction measurements yielded a lattice parameter of 4.227 Å. This corresponds to approximately $\text{TiN}_{0.6}$ as per the data of Ehrlich and to $\text{TiN}_{1.1}$ as per the data of Brager. It is believed that neither the phase diagram nor the lattice parameters of this system has been sufficiently well established to permit an accurate determination of all structures present in the reacted particle. At least two surface films, TiN_x and $\epsilon\text{-TiN}$, seem to be present in the reacted particles with the controlling reaction mechanism being a combination of the rate of growth of these two films and the diffusion of nitrogen across the two-film boundary.

Several standard kinetic equations were tested in attempts to correlate these data. These included the parabolic, cubic, logarithmic, and asymptotic equations as outlined by Evans.²⁸ These equations were developed assuming a uniform passage of material through a single film, with the film-forming reaction becoming increasingly slow as the film thickens. None of these equations, with the possible exception of the asymptotic, was found to agree with the experimental data obtained, especially at conversions to the assumed TiN in excess of 40%.²⁹ This result is not considered surprising since, in the suspected two-film diffusion barrier case, the equations would hold only if the diffusion across one film was negligible compared to the other.

A single empirical relation has been developed and found to agree well with the experimental data obtained in the nitrogen concentration range studied (100 to 50,000 ppm nitrogen). This relation

$$\frac{0.242 - W}{W} = 6.82 p^{-0.18} t^{-0.62}$$

where

W = mg nitrogen absorbed per cm^2 of titanium surface area,

p = partial pressure of nitrogen in argon, mm Hg,

t = time, hr.

Figure I-12 presents this correlation.

The above empirical relation adequately describes the rate of reaction of titanium metal sponge with argon that contains nitrogen impurities (concentration range, 100 to 50,000 ppm N_2) at a temperature

²⁵ P. Ehrlich, *Z. anorg. Chem.* **259**, 1 (1949).

²⁶ A. Brager, *Acta Physicochim URSS* **11**, No. 4, 617 (1939).

²⁷ R. J. Wasilewski, *The Diffusion of Hydrogen, Nitrogen and Oxygen in Titanium*, Columbia University Doctoral Dissertation, University Microfilm, Ann Arbor, Michigan, Publication No. 8857, 1954.

²⁸ U. R. Evans, *The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications*, St. Martin's Press Inc., New York, 1960.

²⁹ Conversion computed assuming the following reaction: $\text{Ti} + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN}$.

108-9306

FIG. I-12. Kinetics of Nitrogen Removal from Argon by Titanium Sponge at 900°C.

of 900°C. Although this equation was developed utilizing titanium metal sponge with a surface area of about 800 cm²/g (see ANL-7055, p. 28), a moderate change in surface area should not affect the applicability of the equation. For the equation to be applicable, the gas phase should be relatively free of such impurities as oxygen and carbon dioxide, which would interfere with the reaction. The applicability of this relation in cases of wide variation of conditions of temperature, titanium surface area, and gas phase impurities is unknown.

This empirical relation is of the same general form as the asymptotic kinetic equation but has been found to agree better with the experimental data. The asymptotic maximum value approached, 0.242 mg N₂/cm² Ti, is not considered to be a true asymptote. It represents the approximate amount of nitrogen absorption at the time when nitrogen diffusion across the two-film barrier becomes too low for titanium to have engineering usefulness as a gettering agent. The value of this apparent asymptote is in all probability a function of the temperature of the reaction and of gas

and metal phase impurities, and may be related to the specific surface area of the sponge. The presence of an oxygen impurity in the gas phase would probably tend to reduce the apparent asymptotic value since the oxide film would reduce the rate of nitridation.³⁰

(2) Pilot Plant for the Removal of Nitrogen in Argon

Operation of the pilot plant loop designed to obtain overall process performance data for the continuous removal of nitrogen from argon was terminated after approximately 1800 hr of operation. Shutdown was necessitated by failure of the loop blower. Since it was felt that this unit had fulfilled its design purpose, the decision was made to discontinue operation of the unit.

Operation of this loop has led to the following conclusions:

(1) Titanium metal sponge possesses considerable potential as a gettering agent for the removal of nitrogen impurities in inert atmospheres.

³⁰ Nitridation of Titanium, DMIC-Memo-29, Battelle Memorial Institute, September 1959.

(2) In plant-scale operation, the cost of titanium sponge is estimated to be around \$13 per pound of nitrogen removed if a 40% conversion of the metal to the mononitride can be obtained. A conversion of this magnitude is considered feasible and has been demonstrated.

(3) If the gas stream to be purified of nitrogen contains oxygen, carbon dioxide, or water vapor as additional contaminants, the gas to be purified should be contacted with oxygen and water getters before passing through the titanium gettering system for nitrogen if optimum utilization of the titanium is desired.

(4) The critical component in the purification system is the gas circulating blower. The blower must circulate gas at a reasonable discharge pressure (about 2 psig) because of the pressure required to circulate the gas through the titanium bed. General leak-tightness

of the blower is also required to avoid introducing air and water vapor contaminants into the circulating gas. It is recommended that the system blower be located upstream from the water- and oxygen-removal components of a purification system so that any air contamination introduced into the circulating gas would be removed prior to reaction with titanium sponge.

(5) If an oxygen getter such as copper at 600°C is used, this same vessel can serve as a gas preheater for the desired 900°C gas temperature in the titanium bed.

(6) Periodic reversal of the direction of gas flow through the titanium bed produces the desired effect of permitting a higher average conversion of the sponge before "break-through".

(7) Additional equipment items such as regenerative heat exchangers and gas preheaters are effective, but their capital cost must be compared to the projected heat and titanium savings to determine if such installations are economical.

The process appears feasible from both an operational and cost standpoint.

e. PREPARATION OF FUEL ALLOY FOR EBR-II

(G. BERNSTEIN, J. LENC, W. MILLER, A. CHANDLER, R. PAUL)

During the period May, 1959 to March, 1961, all of the fuel alloy for the first core loading of EBR-II was produced by the Chemical Engineering Division in 132 runs in melt refining equipment.³¹ This Division was recently requested to prepare additional fuel alloy for fabrication of EBR-II fuel pins. The nominal composition of the alloy is as follows: enriched uranium, 95.0 w/o; molybdenum, 2.46 w/o; ruthenium, 1.96 w/o; rhodium, 0.28 w/o; palladium, 0.19 w/o; zirconium, 0.10 w/o; and niobium, 0.01 w/o. The required ²³⁵U portion of the total uranium in the alloy is 52.5 ± 1.2 a/o.

The fuel alloy was prepared in an existing melt-refining furnace. The capacity of this furnace is about twice the capacity of the pin casting furnace in the Metallurgy Division. To reduce the number of alloy melts required, a special graphite mold (see Figure I-13) was designed that permitted casting double ingots weighing about 13 kg. The ingots would be broken in two to give Metallurgy Division the desired size.

One of the double ingots produced is shown in Figure I-14. The procedure used was to pour the molten metal at 1400°C into one cavity of the mold. The molten metal then flowed through the overflow gate into the other half of the mold. Both halves of the

108-9018 A

FIG. I-13. Graphite Mold for Fuel Alloy Double Ingot. (Cavity: $3\frac{3}{4}$ -in. dia. by $7\frac{1}{2}$ -in. depth.)

³¹ D. C. Hampson, Preparation of Alloy for First Core Loading of EBR-II, ANL-6290.

108-9019A

FIG. I-14. Fuel Alloy Double Ingot.

ingot were sampled to establish that segregation of alloying elements did not take place. The samples consisted of protrusions cast on the ingot (see Figure I-14). The sample protrusion is shaped to give a flat plane area for X-ray fluorescence determination of noble element content. Mass spectrographic analyses are being obtained to determine the uranium-235 content.

Fifteen double ingots (a total of ~200 kg) have been cast. The average pour yield for the fifteen castings was 96.2 percent, with a high yield of 97.8 percent and a low yield of 95.2 percent. Casting weights ranged between 13.1 and 13.6 kg and averaged 13.3 kg. Incomplete analyses of the samples indicate that segre-

gation of alloying components has not taken place and that uranium-235 enrichment is very close to the required 52.5 a/o.

Using the same equipment, two additional castings (~27 kg) of a more highly enriched alloy (70 a/o ^{235}U in uranium) have been prepared to complete the special alloy casting program. Aside from the change in uranium-235 content, the required composition of this material is the same as that for the previously prepared material. Analysis of samples is in progress.

Analyses of the ingots are not yet completed, but since there appears to be no compositional problem, additional reporting of this subject will be in a topical report.

C. PROCESS EQUIPMENT DEVELOPMENT—SKULL RECLAMATION PROCESS

(G. J. BERNSTEIN, L. BURRIS, JR., P. FINEMAN)

At the conclusion of the EBR-II melt refining operation, a residue (skull) remains in the processing crucible. A process known as the skull reclamation process is being developed (see Section I.B.1., Pilot Plant Studies of the Skull Reclamation Process) for reclaim-

ing the fuel material from the skull and removing fission products from the recovered fuel material. The skull is initially converted into a free-flowing oxide powder in a skull oxidation furnace, which is now in use in the EBR-II Fuel Cycle Facility (see ANL-

6900, pp. 116, 118–120). Plant-size equipment for processing the skull oxides in the Fuel Cycle Facility is being built and tested by this Division. The equipment to be used in the Fuel Cycle Facility is sized for operation on about 5.8 kg of skull oxide (~5 kg of uranium oxide).

In addition to the skull oxidation furnace, two other furnaces are required for processing skull oxide: (1) a reduction furnace where the skull oxides are reduced and the uranium is purified to the extent necessary for return to the main fuel cycle and (2) a retorting furnace where solvent metals are vaporized from the uranium and where the resulting uranium sponge is melted to consolidate it into an ingot. Molten metal

alloys (composed of zinc and magnesium) and halide salt³² are used as solvent media. These alloys and salt are transferred out of the reduction furnace by gas pressure to appropriate waste containers or product receivers. Important auxiliary equipment for the reduction furnace are (1) a tungsten crucible (14-in. ID by 24½-in. inside height) where the reduction and purification steps are performed, (2) a mixer, (3) a transfer line, (4) receivers for transferred molten materials, and (5) fume control equipment. Testing of the plant-scale processing equipment is being carried out using the simplified skull reclamation flowsheet shown in Figure I-9 of this report.

1. Reduction Furnace Runs (I. WINSCH, D. GROSVENOR, W. MILLER, J. WOLKOFF, R. PAUL, A. CHANDLER, P. MACK, P. KELSHEIMER,³³ W. SPICER, E. JOHNSTON)

A series of ten skull reclamation runs (SRR-1 through SRR-10) has been completed in the plant-scale reduction furnace (see ANL-7055, pp. 63–67) located in a large inert-atmosphere enclosure (see ANL-7055, pp. 59–62). This series of runs was conducted primarily to evaluate the mechanical performance and reliability of the equipment. However, some variations in processing and operating conditions were made during the runs in order to evaluate their effect on uranium recovery and fission product removal.

Run SRR-1 was a preliminary run intended only to test some of the operating procedures and did not follow any specific flowsheet. Details of performance are therefore not reported here. Runs SRR-2 through SRR-10 followed the simplified flowsheet shown in Figure I-9. Oxidized uranium-fission alloy was used as the feed material to provide data on fission product removal.

Operating conditions were tested in which the noble metal extraction and reduction steps were carried out at temperatures of 700 to 750°C for 1 to 2 hr with mixing speeds of 650 rpm.³⁴ The uranium product dissolution step was carried out at 810°C for 0.5 to 2 hr with mixing speeds of 300–400 rpm.³⁴ Overall operating times for completion of runs varied between 10.5 and 12 hr; of these time periods, 4 to 5 hr were required for bringing the furnace from room temperature to the processing temperature (~700°C).

To simulate process plant conditions, successive runs were made with no cleaning of the tungsten crucible or the furnace interior between runs. As a consequence, the precise amount and composition of material recycled in the heels became difficult to judge. This condition, which will be present in plant operation, can obscure the results somewhat, especially in early runs when there is insufficient experience on carry-over of heels to succeeding runs. Uranium and fission product material balances for runs SRR-2, SRR-3, and SRR-4 are presented in Table I-14. These are the only runs of the series for which analytical data are complete.

The following general observations can be made based upon the results of these three runs:

Overall uranium recoveries in the product solutions removed from the furnace have ranged from 82 to 95.5% of the uranium charged in each of the three runs. Losses in the waste streams of runs SRR-2 and SRR-3 were low (less than 2%), whereas the uranium losses in the waste streams of run SRR-4 were significantly higher (~7%). On the assumption that improved uranium reduction can be achieved with better mixing, it is expected that losses of uranium in the waste streams will be reduced to about 3%. The equipment will be modified to provide increased mixing intensity by use of an additional impeller on the mixer shaft and by the addition of baffles in the crucible.

Overall removals of cerium, a representative rare earth, were very satisfactory, ranging from 89% to 96% based on analyses of the final product solutions. The bulk of cerium is removed in the waste flux, while about 20% is removed in the waste magnesium-zinc supernatant following the reduction step.

Removal of ruthenium in run SRR-2 was a satisfactory 80%. However, in runs SRR-3 and SRR-4, ruthenium

³² Salt mixtures of two compositions have been employed: (1) 47.5 m/o MgCl_2 , 47.5 m/o CaCl_2 , and 5 m/o CaF_2 , (2) 50 m/o MgCl_2 , 30 m/o NaCl , 20 m/o KCl .

³³ Design Group, Chemical Engineering Division.

³⁴ The rpm is a qualitative indication of mixing intensity. The mixing speed of 650 rpm was intended to provide vigorous agitation in the noble metal extraction and reduction steps, whereas the mixing speed of 400 rpm was intended to provide moderate mixing in the product dissolution step.

TABLE I-14. URANIUM AND FISSION PRODUCT MATERIAL BALANCES IN PLANT-SIZE (~4.25 kg U)
REDUCTION FURNACE RUNS

These runs were carried out using the simplified skull reclamation flowsheet (108-9303) shown below; also see Figure I-9, of this report

Run No.	Percent of Uranium or Fission Products Charged													% Total Prod. Soln. Transfd	Total Percent of Uranium of Fission Products Accounted for			
	Waste Streams							Uranium Product Solution ^a							U	Mo	Ru	Ce
	Waste Zinc			Reduction Metal Waste		Waste Flux		As Analyzed				Trans- sfd ^b U	Heel ^c U					
	U	Mo	Ru	U	Ce	U	Ce	U	Mo	Ru	Ce							
SRR-2	0.03	33	79	0.8	16	1.0	47	91	30	17	8	86	5	94	92.8	63	96	71
SRR-3	0.5	26	55	1.0	18	0.1	50	90	7	30	11	82	8	92	91.6	33	85	79
SRR-4	1.1	69	48	2.3	22	3.5	58	100	74	56	4	95.5	4.5	95.5	106.9	143	104	84

^a Total product solution is based upon total Zn-Mg-U calculated to be present in crucible before transfer.

^b "Transfd" denotes product solution transferred from crucible.

^c "Heel" denotes the product solution left in the crucible. The uranium present in the heel constitutes part of the total uranium charged to the succeeding run.

ni-um removals were significantly lower, being only about 50%. Ruthenium removal is accomplished only in the noble metal extraction step. No variation in the operating conditions of this step occurred in the three runs to which the change in ruthenium removal can be attributed. It is assumed that agitation was not sufficiently vigorous to produce consistently good ruthenium removal. The steps being taken to improve the mixing intensity should correct the poor ruthenium removals.

Molybdenum concentrations in the product samples of runs SRR-2 and SRR-3 are low. However, material balances for molybdenum in these runs are also low. Molybdenum is removed in the waste zinc of the noble

metal extraction step. It may also be separated from the final product solution by allowing the molybdenum to settle before the product solution is transferred. Apparently, there was a large carryover of molybdenum from run SRR-3 into run SRR-4 because despite the relatively large molybdenum removal in the noble metal extraction step of run SRR-4, the concentration of molybdenum in the product solution was high.

The product solutions from these runs will be retorted in the plant-scale retorting equipment. Analyses of the final uranium products of these runs will provide more realistic fission product removal and uranium recovery data.

2. Mechanical Performance of Reduction Furnace and Auxiliary Equipment

Mechanical operations in runs SRR-2 through SRR-10 were carried out successfully and with a minimum of difficulty. These operations included charging, heating, mixing, sampling, and transferring of waste and product solutions. These operations and other equipment tests are described below.

a. CHARGING

The initial charge to the reduction furnace consists of flux, zinc, and skull oxide. During the recent series of runs, these materials were charged through the charging port of the furnace by use of a charging hopper and charging bucket. The flux was charged as

crushed pieces less than 1 in. in maximum dimension; the zinc was charged as pellets of about 1/4-in. diameter. The skull oxide was charged as powder along with the flux. No loss of skull oxide as dust was observed during the charging operation.

Equipment consisting of a hopper and dumper is being designed to permit charging of the furnace when it is located in the EBR-II Fuel Cycle Facility. Process chemicals to be charged would be brought into the Argon Cell in pails (10 1/4-in. dia. by 24 in. high) which would subsequently be used as containers for the process wastes. A dumper is being designed to permit pouring of skull oxides from their containers directly into the charging hopper. This procedure will eliminate the use of zinc cans for loading skull oxides into the furnace (see ANL-7055, p. 63). It had initially been intended that skull oxides would be charged to the furnace in zinc cans.

Two additional charging operations, to supply zinc and magnesium for the reduction and product dissolution steps, are required in the course of a process run. (The magnesium is charged as beads or irregular particles of approximately 14 to 30 mesh.) Since the furnace is hot ($\sim 750^{\circ}\text{C}$) during these operations, there is a considerable escape of fumes during the charging operation. The steps being taken to control the escape of fumes are discussed in subsection g. below.

b. HEATING

The reduction furnace is heated by a close-fitting resistance heater (~ 26 kw) in the form of a vertically split cylinder (see ANL-7055, p. 63, and Figure I-28). Use of the split heater was based upon the former requirement that the heaters be opened to permit the furnace to cool between the various process steps. This cooling was required to allow the flux to solidify and to permit a phase separation between flux and molten metal. In the current process, the zinc is transferred from beneath molten flux after the noble metal extraction step; the molten flux and 60 w/o Mg-Zn are transferred together after the reduction step. Thus, cooling of the furnace between the process steps is not required, and the heaters have been kept in the closed position during runs SRR-1 through SRR-10.

Following run SRR-1, the heaters and the position of the furnace within the heaters have been changed from that previously shown (see ANL-7055, Figure I-27). In order to increase the rate of heating, new heaters of slightly higher capacity (10 kw *vs.* 8 kw) were installed in the bottom zone of the heater halves. In addition, the furnace body was raised approximately 3 1/2 in. to bring the bottom of the furnace into a higher temperature region. During runs SRR-2 through SRR-10, heat-up time of the furnace and its contents from room temperature to 700°C has been about four hours.

c. MIXING ASSEMBLY

The agitator shaft seal and the 4-bladed impeller are described in ANL-6925, pp. 59-61. The packing used has been changed slightly and now consists of alternate rings of two special asbestos packings made by John Crane Company. One is an Inconel reinforced asbestos packing lubricated with molybdenum disulfide, and the other is a softer all-asbestos packing also lubricated with molybdenum disulfide. Both packings are completely without solvent carriers for the molybdenum disulfide. In the design of the seal assembly a graphite sleeve bearing (National Carbon TS-574) is located below the ball bearing. An annular ring of the same material is located at the bottom of the seal assembly below the packing.

The agitator and shaft seal assembly are being evaluated during runs in the plant-scale equipment. Leakage of furnace fumes through the shaft seal during transfer operations (when the interior of the furnace is pressurized) has not been apparent. Typical operating temperatures within the mixing assembly have been determined by thermocouples to be as follows: top bearing temperature, 200°C ; graphite bearing temperature, 250°C ; packing temperature, 300°C . These temperatures are higher than those found in the mock-up tests (ANL-6925, p. 61). However, no difficulty has been noted in the operation of the assembly.

The cast iron gear mounted on the mixer shaft underwent excessive wear in the first few runs of the series. The steel drive gear on the motor shaft showed less wear. Lubrication of the gears with APL³⁵ grease to which molybdenum disulfide powder was added apparently reduced the wear. To reduce further the extent of gear wear, high quality steel gears have been ordered as replacements for the existing gears. A microphone used to monitor mixer assembly noise has worked well and is an excellent means of determining sudden noise changes in gears or bearings. The maximum power input to the mixer motor is about 0.5 hp and occurs during the noble metal extraction step when mixing at 650 rpm.

As indicated earlier in this report, the generally poor ruthenium decontamination which has been achieved in the reported runs may indicate inadequate mixing. The degree of mixing in the crucible will be increased by adding another impeller to the mixer shaft and by installing baffles in the crucible.

d. SAMPLING

Samples of the molten process solutions in the reduction furnace were taken in tantalum sample tubes attached to steel capillary tubing. The procedure is to

³⁵ A product of Shell Oil Company.

108-9033 A

FIG. I-15. Specimen of Heater Cable Used in Rebuilt Transfer Line. (The scale of the ruler is in inches.)

lower the assembly into the furnace through a ball valve on the cover of the charging port. A sample of the desired solution is drawn into the sample tube by actuating a small rubber bulb connected to the capillary tube. A similar device for remote use in the Fuel Cycle Facility is being designed.

e. TRANSFER LINE

The transfer line initially built for use with the reduction furnace consisted of an inverted J-shaped molybdenum-30 w/o tungsten tube that was heated by seven swaged magnesia-insulated heaters (see ANL-6925, p. 61 and ANL-7055, Figure I-29, p. 66). During run SRR-1, several of the heaters failed.

The transfer line was rebuilt using the same molybdenum-30 w/o tungsten tube. In this line, the swaged insulated heaters were replaced by heater cable insulated with braided silica (see Figure I-15). This cable was fabricated to Argonne specifications by Claud S. Gordon Company, Richmond, Illinois. Specifications for the heater cable are as follows:

Wire:	Chromel P No. 14 braided
Cover:	Spiral wound with flat stainless steel
Insulation:	Double vitreous silica braid
Nominal resistance:	0.1 ohm/ft
Overall diameter:	0.15 in.

The heater cable was wound spirally on the molyb-

108-9272

FIG. I-16. Section of Transfer Line showing Internal Construction and Method of Heater Cable Winding.

108-9035 A

FIG. I-17. Heater Cable Winding in Test Assembly before Covering with Insulation. (The same winding and clamping technique is used on the actual transfer line.)

denum-tungsten tube with a $\frac{1}{4}$ -in. pitch (see Figure I-16). The legs of the transfer line were wound using cable bent double, with the U-bend being at the lower end of the heated section of each leg. Winding in this manner avoided return wires through the insulation and was an easy way of positioning the heaters uniformly on the tube. The heater cables were secured to the tube by several clamp assemblies. Each clamp assembly was made by wrapping Refrasil³⁶ tape around the cable, and covering the tape with stainless steel bands held in place with wire ties (see Figure I-17). Three separate heater cables were used, one for each of the vertical sections and adjacent elbows and one for the horizontal section. Fiberfrax insulation was applied directly over the heaters on the horizontal section and potassium titanate powder was used in the two vertical legs. Thermocouples were built into the vertical sections of the line, and insert tubes for additional thermocouples were placed in the horizontal section. The stainless steel cover was fastened over the assembly using spacer screws. The power leads and the

thermocouple leads passed through the gap in the stainless steel cover. No organic materials were used in the construction of the transfer line since decomposition of such materials at high temperature could cause breakdown in the cable insulation. This type of construction is much simpler than the original all-welded steel construction and is permitted because the transfer line will be used only in an inert atmosphere.

Since being rebuilt, the transfer line has been used successfully for 29 separate transfers in nine runs, SRR-2 through SRR-10. The rates of transfer of the waste metals, supernatants, fluxes, and product solutions have been easy to maintain by controlling the argon pressure in the furnace during transfer operations. Pressures required for transferring the various metals and flux phases are as follows:

Phase	Pressure (psi)
Noble metal extractant (zinc)	9-10
60 w/o magnesium-zinc supernatant	4-5
Waste flux	4-5
Uranium product solution	8-9

The transfer line was heated to about 700 to 750°C for about six to eight hours during a run. An auxiliary coiled insulated heater was used to heat the discharge end of the transfer line for about ten minutes before a transfer was made to eliminate the possibility of plugging of the cooler discharge end of the transfer line. An auxiliary heater of this type will be incorporated in the transfer line now being built for use in the Fuel Cycle Facility.

Since the transfer line is a critical auxiliary component of the reduction furnace the line must necessarily have a long useful life. A separate test has been conducted to obtain information on the performance of the heaters under extended use.

The test assembly duplicated the construction used in making the transfer line, with two exceptions: (1) a 2-ft long piece of stainless steel pipe was used instead of the molybdenum-tungsten tubing, and (2) the stainless steel outside shell was omitted. The manner in which the heating cable (25 ft long) was attached to the pipe is shown on Figure I-17. The assembly was covered with Fiberfrax insulation before the test. The test was conducted in a glovebox with an argon atmosphere containing low levels of oxygen (40 ppm) and water (40 ppm).

During the heating period, the region of maximum temperature in the assembly was found with a thermocouple probe inside the pipe. At a temperature of 950°C, the applied voltage was 35 volts and the current was 10 amp. The heating conditions of the test are given below.

(a) Number of temperature cycles between 600 and 900°C.....	18
---	----

³⁶ A silica insulation product of HITCO, H. I. Thompson Fiber Glass Company, Gardena, California.

- (b) Number of temperature cycles between room temperature and 900°C..... 5
- (c) Number of temperature cycles between room temperature and 950°C..... 10
- (d) Accumulated running time in the temperature range 900–925°C..... 158 hr
- (e) Accumulated running time in the temperature range 950–975°C..... 740 hr

At the end of the test, no evidence of deterioration in the heater cable was found. In the operation of the reduction furnace, the transfer line would be heated to 700 to 750°C for 6 to 8 hr during the processing of each batch. (Localized temperatures are not expected to exceed 825°C.) Since the assembly has been tested under temperature conditions more severe than those expected and for a time-period equivalent to about 100 runs, it is believed that sufficient reliability for this application has been demonstrated. No further testing is planned.

f. TRANSFER RECEIVER

The transfer receiver equipment and its operation have been described in previous semiannual reports (ANL-6925, pp. 61–62 and ANL-7055, Figure I-30). In the simplified flowsheet now being used, purging of the transfer line has been eliminated as a process requirement. Since this eliminated the need for a gas-tight seal around the discharge end of the transfer line, the motorized equipment for raising and sealing the

secondary waste container into position has been removed. The receiver enclosure will still be used during the transfer operation to weigh the transferred material and to control the fumes that are generated at the discharge end. An exhaust-filter assembly will maintain the enclosure under a slight negative pressure until fuming subsides.

During runs SRR-1 through SRR-10, a temporary transfer receiver was in use. This consisted of a steel bucket suspended from a dial scale which was hung from the crane in the inert-atmosphere enclosure. The waste stream or product stream was collected in a steel pail or graphite mold held within the steel bucket. The dial scale allowed the quantity of transferred material to be measured during the transfer operation. When 90% of the zinc has been transferred from beneath the molten flux after the noble metal extraction step, transfer must be terminated to prevent loss of flux containing suspended skull oxide. This has been accomplished quickly and accurately by venting the pressurizing gas from the furnace.

g. FUME CONTROL

During the course of a run, the charging port cover is removed twice to add reagents while the reduction furnace is at operating temperature (~750°C). This results in the escape of considerable zinc fumes from the furnace; the vapor pressure of zinc at 750°C is

FIG. I-18. Operation of the Fume Control Manifold at the Charging Port of the Reduction Furnace.

~150 mm Hg. Fuming also occurs, but to a lesser extent, during and following the transfers of metal and flux solution from the furnace. In the Fuel Cycle Facility, fuming would cause in-cell atmosphere contamination and would create difficulties in viewing through the thick shielding windows.

To overcome this problem, an annular exhaust manifold has been added to the furnace charging port and connected through a flexible metal hose to an exhaust-filter assembly. The most recent design of the manifold is shown in Figure I-18. In Figure I-18A, the charging port cover is shown in place in the freeze seal. This is the normal position during mixing and transfer operations. (During the transfer operation the furnace is pressurized with argon to force liquid out through the transfer line.) In Figure I-18B, the charging port cover is shown removed, leaving the top of the furnace open. (The open condition exists for approximately one-half hour during each charging operation. During this time, the cover is placed on a stand and the charging hopper is picked up from its stand and placed in position at the charging port. After charging, the hopper is placed back on its stand and the cover is picked up and placed back on the charging port.) With the exhaust manifold installed, fumes are

prevented from escaping through the open port because they are mixed with a down draft of cell gas from above the manifold and are carried through duct work to the filter-blower assembly. In Figure I-18C, the charging hopper is shown in place. Fumes rising up through the lower part of the hopper are mixed with a down draft coming through the hopper, and the gases are pulled into the manifold through slots as shown.

The manifold device described above has been successfully tested. Subsequent work in fume control will concentrate on filter and blower problems and on design of duct work and freeze seals so that one blower and one filter will serve to collect fumes from both the furnace and the transfer receiver in the Fuel Cycle Facility.

Summary. Relatively few difficulties have been encountered in preliminary operation of the reduction furnace. The remaining problems, neither of which are major, are:

(1) Increase of the mixing intensity to improve the efficiency of uranium reduction and extraction of noble metals. This will be done by adding another impeller to the mixer shaft and incorporating baffles into the crucible.

(2) Development of fume control devices.

3. Recovery of Uranium Product by Retorting (W. MILLER, J. LENC, M. SLAWECKI,³³ J. WOLKOFF, A. CHANDLER, R. PAUL, P. KELSHEIMER³³)

The final process stream from the reduction furnace is about 8 liters of a Zn-12 w/o Mg-12 w/o U solution weighing approximately 36 kg and containing about 4 kg of uranium. Work is under way to recover the uranium from this solution in a form suitable for use as supplementary feed material for the melt refining process. Retorting equipment is being developed to recover the uranium by distilling off the volatile zinc and magnesium. A drawing of the plant-scale (~4 to 4.5 kg U) retorting equipment, published in the preceding semiannual report, is included here as Figure I-19.

a. SMALL-SCALE RETORTING RUNS

The small-scale retorting and hydriding runs which were in progress at the time of the last report (see ANL-7055, pp. 69-71) were terminated during the current reporting period. This action allowed more concentrated effort to be placed on solving problems associated with the operation of the plant-scale retort. Further work on hydriding will be held in abeyance pending an evaluation of the performance of the plant-scale retort.

b. PLANT-SCALE RETORTING APPARATUS³⁷

Six runs were completed in the plant-scale retorting unit located in the large argon-atmosphere enclosure. Pertinent distillation data for these runs are listed in Table I-15. All six runs were conducted in a beryllia retorting crucible at a nominal pressure of 10 torr. The bulk of the volatile zinc and magnesium metal present in the charge was distilled at temperatures between 650 and 750°C. Vaporization of the remaining volatile material and liquation of the uranium product was achieved by increasing the temperature to about 1150 to 1200°C for a period of 30 to 100 min.

The first two runs (PSR-1 and -2) were blank runs (i.e., no uranium was present) designed to check out the performance and temperature calibration of the retorting unit. Both runs were conducted in the same thixotropically cast beryllia crucible.³⁸ Performance of the equipment was satisfactory. No visible deteriora-

³⁷ The apparatus to be used in the EBR-II Fuel Cycle Facility is sized for operation with the product reclaimed from about 5 kg of U₃O₈.

³⁸ Fabricated by The Brush Beryllium Company of Elmore, Ohio.

108-8736

FIG. I-19. Plant-Scale Apparatus for Retorting Zinc-Magnesium.

tion of the crucible or evidence of liquid metal leakage was found after either run.

In each of the remaining four runs, PSR-3, -4, -5, and -6, the charge consisted of a uranium-bearing ingot which was the product of a plant-scale reduction furnace run. The nominal composition of the charge in each of these runs was Zn-12 w/o Mg-12 w/o U. Two runs (PSR-3 and PSR-6) were conducted in the same thixotropically cast beryllia crucible used in runs PSR-1 and -2. The other two runs (PSR-4 and PSR-5) were conducted in an isostatically pressed beryllia crucible.³⁸

In run PSR-3 the retorted uranium product ingot adhered slightly to the crucible bottom. Gentle mechanical prying was required to free the product ingot from the crucible. The recovered ingot weighed

about 3.8 kg. An additional 0.2 kg of the retorted product adhered to the crucible sidewall, mainly in the form of metallic beads. No attempt was made to recover this latter material from the crucible since such a recovery would be impractical in the EBR-II Fuel Cycle Facility in Idaho where remote operation is required. Instead, the crucible was reused in a second run (PSR-6) with a uranium-bearing charge. The retorted uranium product from this run was loose in the crucible and was easily recovered. The product ingot weighed 3.4 kg. The crucible appeared to be sound and in good condition. Additional runs with this crucible will be made in order to determine its useful life. No difficulty was encountered in disassembling the retorting apparatus.

In a similar series of runs in an isostatically pressed

TABLE I-15. DISTILLATION RUNS CONDUCTED IN PLANT-SCALE RETORTING APPARATUS^a

Nominal pressure: 10 torr

Distillation temperature: 650–750°C, increased to 1150 to 1200°C for final 30 to 100 min.

Retorting Run No.	Retorting Charge from Reduction Furnace Run No.	Weight of Retorting Charge (kg)	Apparent Distillation Time (min)	Apparent Average Distillation Rate (g/min)	Weight of Uranium in Charge ^b (kg)	Weight of Retorted Uranium Product ^c (kg)	Weight of Uranium Product Ingot Removed (kg)
PSR-1	—	39.15 ^d	405	97	None	None	—
PSR-2	—	36.80 ^d	515	71	None	None	—
PSR-3	SRR-4	34.25 ^e	450	67	3.84	4.00	3.80
PSR-4	SRR-5	30.80 ^e	420	65	2.94	3.30	3.20
PSR-5	SRR-7	32.00 ^e	528	54	3.40	3.55	^f
PSR-6	SRR-8	34.20 ^e	560	55	3.28	3.40	3.40

^a Apparatus sized for full-scale (about 4 to 4.5-kg uranium basis) operation in the EBR-II Fuel Cycle Facility in Idaho.^b Based on uranium analysis of the product solution prior to its transfer from the reduction furnace.^c Equals the weight of the BeO retorting crucible plus the retorted product after the run less the weight of the BeO crucible before the run. Product is essentially uranium. Analyses of minor constituents are in progress.^d Nominal composition: Zn-13.5 w/o Mg (no uranium).^e Nominal composition: Zn-12 w/o Mg-12 w/o U.^f Ingot adhered to crucible.

108-9025

FIG. I-20. Isostatically Pressed Beryllia Crucible showing Hairline Cracks after Two Retorting Runs with Uranium-Bearing Charges. (Upper scale of ruler is in inches.)

BeO crucible, the first ingot (from run PSR-4) was loose and easily recovered, but the second ingot (from run PSR-5) adhered tenaciously to the crucible and could not be freed. Visual inspection of the external surface of the crucible revealed hairline cracks in the bottom section and a circumferential crack about halfway up the crucible wall (see Figure I-20). The molten uranium product apparently penetrated the cracks and upon solidification the product ingot was locked to the crucible bottom. Owing to the unsatisfactory performance, no additional runs will be attempted in this crucible.

A composite material balance for the zinc-magnesium vaporized in the four runs (PSR-3, -4, -5, and -6) made with uranium-bearing charges is presented in Table I-16. Containment of metal vapors within the retorting enclosure was satisfactory. Only an average of 0.09 w/o of the metal vaporized was unaccounted for.

TABLE I-16. COMPOSITE MATERIAL BALANCE FOR ZINC-MAGNESIUM VAPORIZED IN RUNS PSR-3, -4, -5, AND -6 CONDUCTED IN PLANT-SCALE RETORTING APPARATUS^a
Total weight of volatile metal in four charges, 117,000 g^b

Location ^c of Volatilized and Condensed Metal	Weight (g)	Percent of Volatile Metal in Charge (w/o)
In graphite distillate collector	109,750	93.80
On graphite condenser	5,900	5.04
On graphite secondary-container cover	50	0.04
On Fiberfrax insulating sleeve	1,200	1.03
Material unaccounted for	100	0.09
TOTALS	117,000	100.00

^a Apparatus sized for full-scale (about 4.0 to 4.5-kg uranium basis) operation in the EBR-II Fuel Cycle Facility in Idaho.

^b Equals the total charge weight (131,250 g) less the total weight of uranium product (14,250 g) for the four runs.

^c See Figure I-19, this report.

4. Performance of Large Inert-Atmosphere Enclosure (L. COLEMAN,³³ J. LUDLOW,³³ M. SLAWECKI,³³ W. MILLER, R. PAUL, P. KELSHEIMER,³³ A. CHANDLER)

The reduction furnace, retorting furnace, and skull oxidation furnace are located in the large inert-atmosphere (argon) enclosure having a volume of about 4000 cubic feet (see ANL-7055, pp. 59-62). This facility has operated satisfactorily throughout the report period.

During this report period following run SRR-1 (when equipment changes were made in the reduction furnace), the atmosphere in the enclosure was re-

verted to air and then returned to argon. The operation was accomplished smoothly and demonstrated that controlled purging of the enclosure with about 5000 cubic feet of argon (125% of enclosure volume) will reduce the oxygen content of the atmosphere below 1000 ppm. The purification equipment then reduced the oxygen and water content to a value below 100 ppm within a total elapsed time of 24 hr.

D. EBR-II FUEL CYCLE FACILITY OPERATIONS (C. E. STEVENSON, M. J. FELDMAN, D. C. HAMPSON)³⁹

The processing of irradiated fuel from the EBR-II reactor has continued at an increased rate in the EBR-II Fuel Cycle Facility and subassemblies containing fuel with a maximum burnup of 1.2 a/o have been processed. Refabricated fuel has been returned and charged to the reactor. Operations throughout the Facility have continued normally, except for minor interruptions for repair of equipment. In melt refining, a slight lowering of the ingot yield has been observed

as burnup of heavy atoms in the pin charge increased. Fission product decontamination generally corresponded to results obtained earlier in small-scale tests. Facilities provided for the burial of high-level-activity solid waste have been placed into operation. Surveillance of fuel subassemblies discharged from the EBR-II reactor has revealed further fuel growth as a result of irradiation and has permitted establishment of a tentative maximum burnup limit for EBR-II fuel of the present composition and configuration.

³⁹ Idaho Division.

1. Melt Refining (R. M. FRYER)³⁹

TABLE I-17. POURING YIELDS IN MELT REFINING RUNS

No. of Runs	Purpose of Run	Average Pour Yield (w/o)
2	Preparation of unirradiated uranium-fissium alloy	89.7
10	Melt refining of irradiated fuel	92.6
25	Scrap consolidation (18 runs with irradiated fuel, 7 runs with unirradiated fuel)	94.4

Thirty-seven melt refining runs, in which 9.0 to 11.5 kg ingots of enriched uranium-fissium alloy were produced, were made during the past reporting period. Twenty-eight of these runs were made with irradiated fuel. Ten of the runs were carried out with fuel that had attained burnup levels of 0.3 to 0.9 a/o to remove fission products and to re-enrich the alloy. Eighteen of the twenty-eight runs were made to consolidate re-fabrication scrap and heels from the irradiated fuel runs. Nine runs were carried out with unirradiated fuel; two of these were made to prepare new fissium alloy, and the remainder were made to carry out scrap consolidation of the new alloy. The average pouring yields obtained in these runs are listed in Table I-17. The pouring yields for the irradiated fuel runs (92.6 w/o) and for the scrap consolidation runs (94.4 w/o) compare favorably with the pouring yields (90 to 97 w/o) obtained in pilot-scale work with unirradiated fuel.⁴⁰ The lower yields in the alloy preparation runs are attributed to the surface condition of the charge material, which exhibited significant oxide formation.

In the course of carrying out the first thirteen melt refining runs with irradiated fuels, small variations were made in the liquation period (the time during which the fuel is held in a liquid state in a zirconia crucible at 1400°C prior to pouring the ingot) to determine the effect of this variable on pouring yield and on decontamination from fission products and plutonium. The liquation period was shortened from the usual 3 hr to 1½ or 2 hr. No correlation was found between the pouring yield and the liquation time. However, as the average burnup of heavy atoms in the pin charge increased, a definite decrease in gross pouring yield was observed. The slope of the curve corresponded to a decrease of 2.6%⁴¹ in pouring yield

⁴⁰ G. A. Bennett, N. R. Chellew, and D. C. Hampson, The Melt Refining of Irradiated Uranium: Application to EBR-II Fast Reactor Fuel. V. Yields of Fissionable Material Upon Pouring, Nucl. Sci. Eng. 6(6), 511 (1959).

⁴¹ A significant fraction of this decrease represents volatile fission products and fission products removed in the melt re-

for 1 a/o burnup. These data are presented graphically in Figure I-21. The scatter of the data is attributed to two effects:

1. The decanned, chopped fuel was exposed to the Argon Cell atmosphere in some cases for only a few hours, in other cases, for a number of days.

2. The actual pouring is a gross mechanical operation which cannot be exactly duplicated from run to run.

At least part of the decrease in pouring yield at increased burnup is directly attributable to the higher concentration of fission products in the charge which distribute to the slag rather than to the refined ingot. Since about 40% of the fission products do not accompany the alloy, this accounts for about 0.4% loss in yield for 1 a/o burnup.

Fission product decontamination data for a number of the irradiated fuel melt refining runs (MR-1 through -5, and MR-9) are presented in Table I-18. The data show that the removals of those elements which are separated from the melt by selective oxidation are quite adequate for liquation times as short as 2 hr. For a liquation time of 1.5 hr (Run MR-9), both cerium and barium-lanthanum removals decreased. These data indicate that a 2-hr liquation time is the lower limit for effective removal of barium-lanthanum, cerium, and the rare earths for which the behavior of cerium is assumed to be typical.

Cesium is shown to be very effectively (>99.9%) removed within a 1.5-hr liquation period. Iodine removals are quite adequate for liquation times down to 2 hr; no iodine data were obtained for the 1½-hr liquation period (run MR-9).

In general, the removals of iodine, barium-lanthanum, cerium, and cesium obtained in a normal (2 or 3 hr) liquation period are considered quite adequate and compare favorably with results previously obtained in small-scale runs.⁴² Although the data for plutonium were obtained only at very low (<0.1%) concentration levels, it is indicated that the plutonium was effectively retained in the ingot at these concentrations.

Except for zirconium, the noble metals do not show a partitioning from uranium. Yields of molybdenum, ruthenium, rhodium, palladium, and niobium corresponded closely with the yield of alloy. Although the data on zirconium are not precise because of its low

fining operation. This fraction does not represent a decrease in the uranium yield.

⁴² V. G. Trice, Jr., R. K. Steunenberg, Small-Scale Demonstration of the Melt Refining of Highly Irradiated Uranium-Fissium Alloy, ANL-6696.

108-9640

FIG. I-21. Effect of Burnup on Pouring Yield in Melt Refining (The pouring yield represents gross yield, not uranium yield, and has not been corrected for fission product removal.)

initial concentration and its removal tended to vary from batch to batch, they do indicate a fractional partitioning from the uranium. In previous work,⁴³ the depletion of zirconium from the melt has been correlated with the presence of cerium in the melt. In that work, the results of twenty-three runs made with charges not containing cerium showed that $84.5 \pm 10\%$ of the nominal amount of the zirconium originally charged was retained in the ingot. However, the results of six runs made with charges containing cerium showed that $56.5 \pm 8.1\%$ of the nominal amount of the zirconium originally charged was retained in the ingot. A partitioning of zirconium from uranium was also observed in the small-scale runs using irradiated uranium-fission fuel.⁴² It may be concluded that zirconium tends to be separated from uranium in melt refining and therefore should not be considered to behave as a typical noble metal.

Difficulties were previously encountered in charging chopped sodium-coated fuel pins of low burnup (0.1 to 0.5 a/o) to the melt refining crucible; the sodium-coated pins appeared to stick to each other and to the inside of the crucible charging tray (see ANL-7055, p. 74). This sticking problem was not experienced with the higher burnup (0.7 to 0.9 a/o), short-cooled fuel. However, with some of the 0.4 to 0.7

TABLE I-18. REMOVAL OF FISSION PRODUCTS AND PLUTONIUM IN MELT REFINING

	Run No.					
	MR-1	MR-2	MR-3	MR-4	MR-5	MR-9
Average burn-up of fuel charge (a/o)	0.10	0.16	0.12	0.40	0.42	0.71
Liquation time (hr)	3	3	3	2	3	1½
Fission product removals (%) ^a						
Iodine-131	99	—	—	99.8	>99.9	—
Cerium	99	99.2	99.3	99.9	98.0	90.4
Barium-lanthanum	>99.9	—	—	>99.9	>99.9	99.6
Cesium	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
Zirconium	~50	~30	~50	~10	—	~50
Plutonium removal (%) ^b	5.3	3.8	4.5	1.9	9.4	—

^a Percent removal expressed as

$$\left(\frac{\text{Conc. charge} - \text{Conc. ingot}}{\text{Conc. charge}} \right) \times 100.$$

^b All plutonium in the charge is assumed to appear in the ingot or oxide.

⁴³ D. C. Hampson, G. A. Bennett, N. R. Chellew, The Melt Refining of Irradiated Uranium: Application to EBR-II Fast Reactor Fuel. III. Preparation of Experimental Alloys, Nucl. Sci. Eng. 6(6), 501 (1959).

a/o burnup, long-cooled fuel, some minor agglomeration of the chopped pins in the charger was observed; nevertheless all of the fuel was successfully charged without undue difficulty.

Some electrical problems were encountered with the two melt refining furnaces. Failures of the induction coils on both furnaces occurred within a period of about three weeks of each other, after about forty runs on each unit. In each instance, a section (2½ in.) of the top coil which was directly opposite a crack in the furnace insulation melted and arced. The coils failed apparently as a result of the furnace insulation having settled and thus left a crack in the insulation at the top of the furnace assembly. The crack allowed the

susceptor, which operates at 1600 to 1800°C, to radiate heat directly to the coil causing it to melt. (Another possible reason could have been arcing caused by condensation of sodium and cesium in the top layer of the insulation; however, there is no visual evidence of arcing on the outside of the susceptor to substantiate this possibility.) A replacement coil unit has been installed in one of the two furnaces in the Argon Cell and the furnace is operating satisfactorily. Fabrication of the second replacement unit is under way.

The high-frequency feed-throughs for the furnaces were apparently penetrated by moisture with resultant arcing. These feed-throughs were repaired, new sealants applied, and the feed-throughs reinstalled.

2. Disposal of High-Level-Activity Solid Wastes (D. M. PAIGE, W. F. HOLCOMB)³⁹

As described previously (ANL-6925, p. 89), the high-level-activity solid wastes that are generated in the Air Cell and Argon Cell of the Fuel Cycle Facility are remotely packaged in metal containers for final disposal by burial in steel-lined, 12-ft deep pits located in a disposal area adjacent to the EBR-II Reactor area at the National Reactor Testing Station, Idaho. Wastes from the Argon Cell are first placed in a primary container, steel pails 10¾ in. in dia. by 10, 12, or 24 in. high which are sealed with lug clamp-type lids. Several of these pails are then placed in a 12-in. dia. by 6-ft high steel can which is similarly sealed. Bulky wastes from the Air Cell are placed directly in the 6-ft can. The sealed cans are loaded into a shielded cask through the floor shielding plug in the Air Cell. The cans are transported to the burial area using the tractor-trailer unit (Figure I-22) which has positioning devices for locating the cask over a pit. The can is dropped from the bottom of the cask into the pit. Six feet of gravel backfill for shielding is then placed in the pit and a cover is welded to the top of the hole liner. At present, 140 steel-lined pits have been provided in the disposal area, and space is available for several thousand.

Prior to initial pit burial operations with radioactive wastes, the equipment and operating procedures were tested by carrying out a simulated burial operation using a radioactive source (approximately 80 R/hr at 2 in.). Radiation leakage noted during the burial operations was as follows: (1) a 90-mR/hr beam when the source was slowly lowered past the open bottom dumping door of the cask, and (2) 12- to 40-mR/hr beams at points where the bottom of the cask was in contact with a shielding and positioning ring over the pit. These radiation levels indicated that wastes of higher radiation levels could be handled safely with suitable precautions at the areas where these radiation leakages occurred.

Since the test, 6-ft high cans containing radioactive wastes have been placed in 30 of the steel-lined pits. These cans contained an estimated 2100 kg of waste material with an estimated 395,000 curies of activity (at the time of filling the cans). Twelve of the cans were filled with stainless steel scrap and axial and radial blankets from the dismantling of subassemblies in the Air Cell. The weight of these cans varied from 22 kg to 159 kg and their activity contents (estimated) ranged from 2,000 to 50,000 curies. Radiation levels (estimated) varied from 90 to 6000 R/hr at 1 ft. (These radiation levels were based on measurements taken at the top of the cask with the plug open and comparison of these measurements with calibration data obtained from measurements in the subcell of the Fuel Cycle Facility.)

The other eighteen cans were filled with zirconia and graphite crucibles, graphite molds, fume traps, and stainless steel decanning scrap. For a filled can, the average weight was about 60 kg, and the activity level (estimated) ranged from 2000 to 15,000 curies. The radiation level readings (in air) of these cans varied from 1,200 to 45,000 R/hr at 1 ft.

Radiation measurements were taken after the cans were dropped into the pits and the gravel backfill was added. Readings of less than 1 mR/hr at 6 in. from the top of the liner were observed.

Some difficulties have been encountered in remotely capping the 6-ft cans and placing steel pails in the cans in the Air Cell and Argon Cell. Although the capping tool, which places the cover in position and clamps the lugs, is a standard device, its use with a manipulator under conditions of remote operation requires careful placement, leveling, and centering. Lifting and other operations performed on the empty cans may deform them slightly and interfere with

103-G5732

FIG. I-22. Tractor-Trailer Rig for Transporting Waste Cask.

positioning the lid properly on the can. In addition, the tall cans, which are essentially hand-made, have a welded side seam, and are frequently out-of-round in the barrel area. This has required the use of a heavy weight to force the steel pails to the bottom of the 6-ft can.

Lowering the cans from the Air Cell into the cask, and dropping them from the cask into the burial pit causes vigorous air currents which dislodge contaminated particles from the surface of the can and carry them to the outside. This condition has been alleviated in the burial operation by placing a long plastic bag in the pit. The bag is loosely fastened at the top of the pit. As a can is dropped into the pit, it carries the bag with it to prevent air currents from entraining contaminated particles when the gravel is dumped above

Procedures for the disposal of waste carrying fission product iodine have also required attention. A major portion of the iodine-131 released in melt refining is

retained by the fume trap which covers the melt refining crucible (see ANL-6925, pp. 69-72). In one instance, a small amount of iodine was released to the Air Cell atmosphere when a contaminated fume trap, a few weeks after melt refining, was transferred from the Argon Cell in a small can. The iodine is believed to have leaked from the can because of a poor seal. The effect of a small amount of oxygen in argon in augmenting the release of iodine has previously been noted.⁴⁴ Consequently, to avoid a recurrence of such a release, the following procedure has been adopted: (1) Melt refining fume traps (and crucibles) will be stored in the Argon Cell for a period of at least 90 days after discharge of fuel from the reactor in order to provide for iodine decay. (2) Cans will be well capped before transfer as judged by visual in-

⁴⁴ N. R. Chellew, C. C. Honesty, R. K. Steunenber, Laboratory Studies of Iodine Behavior in the EBR-II Melt Refining Process, ANL-6815, January, 1964, p. 34.

spection of the capping lugs. (3) The transfer lock will not be evacuated during transfer of contaminated

fume traps (to avoid loosening the lid, and replacement of argon by air).

3. Surveillance Program (J. P. BACCA, D. E. MAHAGIN, D. L. MITCHELL)³⁹

In continuation of the program (ANL-7055, pp. 77-78) for the examination of fuel from the EBR-II reactor at progressively increasing burnup levels, fifteen additional subassemblies in which the maximum

that no appreciable release of fission gases has occurred. The variation of these parameters with burnup is shown in Figures I-23, I-24, and I-25, respectively.

(3) *Fuel Pin Diameter*. The diameter of the de-

TABLE I-19. EBR-II REACTOR FUEL SURVEILLANCE DATA

Subassembly	Position in EBR-II Reactor	Calculated Max. Burnup (a/o)	Average Sodium Level Above Fuel (cm)	Average Void Volume (cc)	Average Internal Gas Pressure at ~25°C (atm)	Change in Fuel Pin Diameter (in.) ^a	
						Average Increase in Max. Diameter	Average Increase in Min. Diameter
Pre-Irrad. ^b	—	0	1.75	0.487	~1.0	0	0
B314	6E4	0.50	2.60	—	—	—	—
C131	5D2	0.56	2.41	—	—	0.0002	0.0006
L410	5E3	0.69	2.85	—	—	0.0014	0.0009
C148	5C2	0.70	2.72	—	—	—	—
C141	4C1	0.80	2.85	0.352	1.26	0.0018	0.0015
C153	4F3	0.81	2.95	—	—	—	—
C146	3F1	0.88	2.90	—	—	—	—
S601	3D1	0.88	3.30	—	—	0.0045	0.0038
C145	2E1	0.94	3.38	—	—	0.0032	0.0019
C138	1A1	0.95	3.30	0.304	1.48	0.0027	0.0018
S602	3A1	1.01	3.33	0.339	1.11	—	—
C136	3A2	1.06	3.82	0.278	1.31	—	—
C117	3E4	1.07	4.20	0.258	1.60	—	—
C142	3B1	1.16	4.06	0.277	1.56	—	—
L104	3E2	1.20	4.29	0.225	1.85	—	—

^a Measurements made on unclad, sodium-free fuel pin.

^b Based on average of measurements of 1000 EBR-II Mark I production fuel elements.

burnup⁴⁵ levels ranged from 0.56 to 1.20 a/o have been examined in the Fuel Cycle Facility. Pertinent data from the surveillance of these subassemblies are summarized in Table I-19. These data were obtained by making the following measurements:

(1) *Sodium Level*. The level of the sodium within the stainless steel can was measured by means of an eddy current coil. An increase in sodium level within the can results from dimensional changes within the fuel. The increase in sodium level and the decrease in void volume exhibit essentially the same dependence, that is, as the sodium level increases with burnup, the void volume decreases.

(2) *Internal Gas Pressure*. The pressure of the gas in the void above the sodium level was measured at room temperature. An increase in gas pressure indicates a decrease in void volume, thereby indicating

⁴⁵ Burnup calculated as atom percentages of atoms having a mass greater than 225 that underwent fission.

103-G5777

FIG. I-23. Variation of Sodium Level with Burnup.

canned fuel pin was measured after removal of the bonding sodium. The measurements reported here were made on the original fuel not fabricated in the Fuel Cycle Facility, and therefore different equipment is used for post-irradiation measurements than was used for pre-irradiation measurements. Consequently, the change in the fuel pin diameter as a result of irradiation is not as accurately known as it will be in the future when the measurements will be based on pre- and post-irradiation data obtained in the Fuel Cycle Facility. The data to the time of this report, as shown in Table I-19, do indicate a trend toward increase in fuel pin diameter with increase in fuel burnup.

These surveillance data have also been used to estimate the pressures within the fuel element at reactor operating conditions. This is shown in Figure I-26, where the lower curve represents internal pressures measured at room temperature and the upper curve represents calculated internal pressures at maxi-

103-G5706

FIG. I-26. Measured Pressure and Those at Reactor Operating Conditions.

103-G5704

FIG. I-24. Variation of Void Volume with Burnup.

103-G5703

FIG. I-25. Variation of Gas Pressure with Burnup.

103-G5776

FIG. I-27. Fuel Volume Change with Burnup.

imum operating temperatures⁴⁶ in the reactor. It should be noted that although the predicted pressures are well within the mechanical capabilities of the cladding material, the slope of the curve is approaching an infinite value. At that time, minor increments of burnup can be expected to result in extremely high stresses in the cladding.

By assuming that swelling of the fuel pin is manifest as both a linear change in the sodium level of the fuel element and a corresponding decrease in its void volume, the change in fuel volume can be related to burnup. This is shown in Figure I-27. This curve can be expressed mathematically as follows:

⁴⁶ The internal pressures at maximum operating temperatures were calculated from the internal pressure measurements at room temperature.

$$S = AB + CB^k$$

where:

S = fuel pin swelling, volume percent

B = maximum heavy atom burnup, atom percent, in assembly

A = constant based on change in fuel pin volume as a result of solid fission products

C = constant based on change in fuel pin volume as a result of gaseous fission products

k = constant.

In this equation, the burnup term AB accounts for accumulation of solid fission products within the fuel lattice, and the burnup term CB^k describes the contribution of fission gases.

The results shown in Figure I-27 are in reasonable agreement with the results of a theoretical analysis by Greenwood et al,⁴⁷ in which fuel swelling resulting

⁴⁷ G. W. Greenwood, A. J. E. Foreman, and D. E. Rimmer, The Role of Vacancies and Dislocations in the Nucleation and Growth of Gas Bubbles in Irradiated Fissile Material, *J. Nucl. Mater.*, **4**, 305-324 (1959).

from gas accumulation is predicted to be a function of $B^{3/2}$. (The value for the exponential constant k resulting from the ANL data is 1.5 to 2.0.)

As a result of the above information obtained on EBR-II fuel, along with other information developed by the Metallurgy Division, Argonne, Illinois and an assumption that the fuel cladding does not deform under stress, a tentative maximum burnup limit of 1.2 a/o has been imposed for the present fuel composition and configuration. This maximum limit may be increased as additional information on fuel behavior under irradiation is obtained. In addition, a fuel element (designated as Mark 1-A) which contains greater void space and consequently allows for greater fuel pin expansion is being provided for the reactor. This design should permit considerably greater burnup. The changed configuration is produced by shortening (by 0.72 in.) the fuel pin, lengthening the restrainer correspondingly, and utilizing a fuel alloy of slightly greater uranium-235 enrichment to maintain constant reactivity.

II

Fuel Cycle Applications of Volatility and Fluidization Techniques¹

(A. A. Jonke, J. J. Barghusen)

INTRODUCTION

Since nuclear reactor fuels suffer physical damage and lose nuclear reactivity during irradiation, the fuel elements are periodically discharged from the reactor in a partially spent condition. These fuel elements must be processed to separate the valuable fissionable and fertile materials, to re-enrich the recovered material, and to reconstitute the fuel into new fuel elements for return to the reactor. An extensive program is being carried out to develop processing methods for the recovery of uranium and plutonium from spent reactor fuel materials by fluoride volatility techniques. These processes are based on the ability to convert the uranium and plutonium to volatile hexafluorides which can be readily separated from associated fuel materials (cladding, fission products) and purified by established techniques. A significant feature of the fluoride volatility processes is the application of fluidized-bed techniques for conducting the direct chemical conversion of fuel materials into gaseous compounds.

The major objective of the fluoride volatility program is to develop the technical data required for the design of a fluoride volatility commercial reprocessing plant for power reactor fuels. The application of volatility and fluidization techniques to the reprocessing of highly enriched uranium-zirconium and uranium-aluminum alloy fuels has been successfully demonstrated in pilot-scale tests; results of the final tests in the pilot-scale facility were reported in ANL-7055, pp. 148-155. Currently, major attention is being directed toward the demonstration of the fluoride volatility process with low-enrichment $\text{UO}_2\text{-PuO}_2$ fuel clad in Zircaloy. Two alternative process flowsheets for this type of fuel were described in ANL-7055, pp. 99-102. In the first process, the declad oxide fuel is reacted with oxygen and fluorine, using the two-zone oxidation-fluorination technique, to form UF_6 and PuF_6 , which are subsequently separated from each other and

from associated volatile fission product fluorides. In the second process (interhalogen flowsheet), the separation of uranium and plutonium is accomplished in the initial process step by selective fluorination of uranium by bromine pentafluoride. Recovery of plutonium as PuF_6 is accomplished in a subsequent step by fluorination with fluorine gas.

The main steps in the process flowsheet based on the two-zone oxidation-fluorination techniques are being demonstrated with $\text{UO}_2\text{-PuO}_2$ fuel material in an engineering-scale alpha facility. The initial test in the facility with plutonium-containing fuel was completed during the report period. Laboratory-scale studies are being performed in a 2-in. dia. fluid-bed reactor to define optimum conditions for fluorinating $\text{UO}_2\text{-PuO}_2$ pellets containing fission products. Specific emphasis in the laboratory-scale studies is being directed toward the establishment of conditions that would result in a minimum retention of uranium and plutonium on the fluid bed of alumina particles.

Studies of the kinetics of the reactions between BrF_5 and several uranium compounds have been performed to provide data necessary for defining processing conditions for the interhalogen flowsheet. It has been demonstrated in the experiments reported here that none of the plutonium is converted to PuF_6 by reaction between BrF_5 and PuO_2 and that the PuF_4 product can be converted readily to PuF_6 by the high-temperature reaction with fluorine.

Bench-scale tests are under way to demonstrate fluid-bed volatility processes with highly irradiated fuel materials in a 1½-in. dia. fluid-bed reactor. This program involves demonstration tests with highly enriched uranium-zirconium and uranium-aluminum alloy fuels and with Zircaloy-clad $\text{UO}_2\text{-PuO}_2$ fuel material of low enrichment. The primary purpose of these tests is to define clearly the disposition of fission products in the various process steps and the extent of decontamination achieved in the processes.

¹ A summary of this section is given on pages 5 to 10.

A. LABORATORY-SCALE INVESTIGATIONS (M. J. STEINDLER)

1. Fluorination of $\text{UO}_2\text{-PuO}_2$ -Fission Product Pellets in a 2-Inch Diameter Fluidized-Bed Reactor (L. J. ANASTASIA, P. G. ALFREDSON,² J. G. RIHA, G. W. REDDING)

Conditions are being determined for the fluorination of $\text{UO}_2\text{-PuO}_2$ -fission product pellets that will ensure a minimum retention of uranium and plutonium by the alumina in a fluidized bed. Currently, two fluorination agents are being considered: fluorine and bromine pentafluoride (BrF_5). Fluorination with fluorine is carried out by a two-zone oxidation-fluorination process.³ In this process, pulverization of the pellets and fluorination of the resulting fines is carried out simultaneously by reaction of the pellets with oxygen in the lower zone containing the packed bed of pellets and fluorination of the resulting U_3O_8 fines with fluorine in the upper fluid-bed zone of the reactor. In the alternative process, fluorination with bromine pentafluoride is carried out after the pellets are pulverized with oxygen in a separate step.

During the two-zone oxidation-fluorination more than 99% of the uranium and about 75% of the plutonium is removed from the alumina bed as volatile hexafluoride products. Further removal of the plutonium and of the final traces of uranium is accomplished during a recycle-fluorination period with fluorine. During fluorination with bromine pentafluoride, only the uranium volatilizes as hexafluoride product, leaving a residue of plutonium compounds which are subsequently volatilized by recycle-fluorination with elemental fluorine.

This report presents the results of several experiments carried out by the two-zone oxidation-fluorination process and a description of a fluorination experiment using BrF_5 .

a. FLUORINATION OF $\text{UO}_2\text{-PuO}_2\text{-F.P. PELLETS}$ WITH FLUORINE

(1) Equipment and Procedures

The major components in the experimental system are the 2-in. dia. fluidized-bed reactor, hexafluoride collection system, thermal conductivity cell for continuous fluorine analysis, fluorine disposal system, and remote-head diaphragm pump. These components are contained in an alpha glovebox and have been described in detail previously (ANL-6925, pp. 116-118). A detailed description of the experimental procedure has also been reported (ANL-7055, pp. 110-111).

² Guest Scientist from Australian Atomic Energy Commission.

³ L. J. Anastasia and W. J. Mecham, Oxidation-Fluorination of Uranium Dioxide Pellets in a Fluidized Bed, Ind. Eng. Chem. Process Design Develop., 4(3), 338-344 (July 1965).

In a series of runs (Pure-4 through Pure-9), fluorination of $\text{UO}_2\text{-PuO}_2$ pellets containing nonradioactive fission products has been carried out with fluorine in a reaction sequence consisting of two-zone oxidation-fluorination, single-zone fluorination, and recycle-fluorination. In each of these runs, a 2-in. deep fluidized-packed bed of pellets (650 g) was reacted by two-zone oxidation-fluorination for 3 hr. The fluid-bed material consisted of 1100 g of nominal 48 to 100 mesh tabular alumina with the -170 mesh fraction removed. Recycle-fluorination periods from 8.5 to 20 hr were investigated. The single-zone fluorination, which ranged from one to two hour's duration in most runs, was omitted in run Pure-4. The length of each reaction period and the average operating conditions for runs Pure-4 to Pure-9 are listed in Table II-1.

A computer program, based on Pacer-65,⁴ has been written to calculate operating conditions from basic run data for these experiments. The program prepares detailed point-to-point calculations of the operating conditions for the various process steps, and also compiles a summary table of average operating conditions for the overall experiment.

The pellets used in these runs contained, nominally, 0.4 w/o plutonium (as PuO_2), 86 w/o uranium (as UO_2), and 1 w/o fission products (as the oxides). Pellets used in runs Pure-4, -5 and -6 were approximately 94% theoretical density and were made from solid-solution $\text{UO}_2\text{-PuO}_2$ mixed with fission product oxides and sintered in 6 v/o H_2 in N_2 at 1600°C for 2 hr. These pellets will be referred to subsequently as Type I pellets; the composition of these pellets has been reported previously (ANL-7055, p. 111). The supply of Type I pellets was exhausted with the completion of run Pure-6; therefore, in subsequent runs, Pure-7, -8, and -9, pellets (Type II) were obtained from supplies to be used in the Engineering Scale Alpha Facility (see Section II B 1). These pellets were prepared by blending a powdered mixture of UO_2 , PuO_2 , and fission product oxides and sintering the mixture at 1700°C for 6 to 8 hr in an atmosphere of 6 v/o H_2 in nitrogen. The density of the pellets was approximately 88% theoretical density. Detailed composition of the pellets is currently not available, but

⁴ H. A. Mosler, Pacer-65, A Generalized Automatic Computer Flowsheet Calculator, M. S. Thesis Chemical Engineering, Purdue University (1964).

TABLE II-1. AVERAGE OPERATING CONDITIONS FOR RUNS PURE-4 TO -9

*Equipment:**UO₂-PuO₂-F.P. Pellets:*

Size: 0.5-in. dia. by 0.5-in. right cylinders^a
 Weight: 650 g
 Bed Depth: 2 in.
 Bed Support: nickel balls

Alumina Fluid Bed:

Material: Alcoa T-61 alumina
 Size Limits: nominal 48 to 100 mesh (-170 mesh removed)
 Weight: 1100 g
 Static Bed Depth: 12 in.

Diluent Gas: N₂

	Run Pure-					
	4	5	6	7	8	9
<i>Two-Zone Oxidation-Fluorination with O₂-F₂ at 450°C</i>						
Cumulative process time (hr)	0-3	0-3	0-3	0-3	0-3	0-3
Reactor pressure (mm Hg)	1500	1520	1580	1600	1600	1630
Superficial velocity (ft/sec)	0.7	0.7	0.6	0.7	0.6	0.6
Oxygen concentration to pellet bed (v/o)	33	19	20	21	20	18
Fluorine concentration to fluid bed (v/o)	10	9	8	9	8	8
<i>Single-Zone Fluorination with F₂ at 450°C</i>						
Cumulative process time (hr)	— ^b	3-4	3-5	3-4.5	3-5	3-4
Reactor pressure (mm Hg)	—	1080	1530	1400	1520	1490
Superficial velocity (ft/sec)	—	0.8	0.6	0.6	0.7	0.6
Fluorine concentration to fluid bed (v/o)	—	3	6	9	8	8
<i>Recycle-Fluorination with F₂</i>						
Cumulative process time (hr)	3-23	4-17	5-17	4.5-13	5-17	4-24
Reactor pressure (mm Hg)	1450	1400	1350	1400	1390	1400
Superficial velocity (ft/sec)	0.5-0.9	0.7-0.9	0.7-1.1	0.8-1.0	0.8-1.0	0.8-1.0
Fluorine concentration to fluid bed (v/o)	90	90	90	90	90	90
<i>Temperature:</i>						
Cumulative process time at 450°C (hr)	3-8	4-6	5-6	4.5-5.5	5-6	4-9
Cumulative process time at 500°C (hr)	8-13	6-9	6-9	5.5-6 ^c	6-9	9-14
Cumulative process time at 550°C (hr)	13-23	9-17	8-17	6-13	9-17	14-24

^a In runs Pure-7, -8, and -9 pellets used were cylinders 0.5 in. in dia. by 0.4 in. high; CsF was added to the alumina bed.

^b Single zone fluorination was omitted in this run.

^c Temperature was increased from 450 to 550°C during this period.

the concentration of fission products is lower than in the Type I pellets by approximately a factor of 2.

Since cesium is not present in either Type I or Type II pellets, 0.6 g cesium fluoride was added to the alumina beds for runs Pure-7, -8, and -9 to simulate more closely the fission product distribution which might exist in the reprocessing of irradiated fuels. These runs, therefore, differed from previous runs, Pure-1, -2, and -3 (ANL-7055, p. 110) and Pure-4, -5, and -6 (this report), because of the addition of CsF and the use of fuel pellets prepared by a different fabrication method.

(2) Results and Discussion

Agglomeration in the Alumina Beds. In runs Pure-1, -2, and -3, agglomeration of some of the alumina was encountered (ANL-7055, p. 113). A corrosion specimen

holder with six attached coupons may have aggravated the agglomeration; consequently, in subsequent runs the specimen holder was withheld from the reactor. However, in run Pure-4, approximately 45% of the final alumina bed of 903 g was removed as a loosely-bonded agglomerate. The agglomerate contained a total of 25.9 mg plutonium (0.006 w/o) and the free flowing alumina contained 24.8 mg plutonium (0.005 w/o). This result suggests that the agglomerate probably formed during the latter portion of recycle-fluorination at 550°C (see Figure II-4).

Several factors which may contribute to agglomerate formation have been investigated. These factors include: (1) diminution of Alcoa T-61 alumina by attrition and by reaction with fluorine, (2) the behavior of the fluid bed during recycle fluorination, and (3) the possibility of local temperature excursions as a con-

sequence of a rapid reaction of fines with high concentrations of fluorine during the initial stages of the recycle-fluorination period.

To determine the attrition caused by fluidization alone, a bed of Alcoa T-61 alumina with the -170 mesh fraction removed was fluidized for 24 hr in a plastic mock-up of the 2-in. dia. reactor. At the conclusion of this test, 0.4 w/o of the alumina was of a particle size less than 88μ (170 mesh). Diminution of the alumina by combined fluidization and chemical reaction was determined by fluorination of a 2-in. deep bed of UO_2 pellets in a reaction sequence consisting of 3 hr of two-zone oxidation-fluorination and 1 hr of single-zone fluorination at 450°C , followed by recycle-fluorination for 4.5 hr at 450°C , 5 hr at 500°C and 10 hr at 550°C . Prior to this test the -170 mesh fraction in the alumina bed had been removed; after the test, 1.3 w/o of the alumina was less than 170 mesh. This result was comparable with results of experiments made in the high enrichment volatility pilot plant, wherein about 1% of the alumina bed was carried over to the fixed bed filter in each run (ANL-6973, p. 38). The carryover of bed material observed in the pilot plant was attributed to attrition of the alumina fluidized bed. These results indicate that diminution of Alcoa T-61 alumina to this extent is not expected to be a processing problem.

The behavior of the fluidized bed during recycle operation was examined under simulated processing conditions in a plastic mock-up column. In a test using a 1100-g bed of alumina, solids movement in the fluid bed appeared to be good although the remote-head diaphragm pump imposed a pulsation effect on the fluidized bed. Blowback of the column filters had no discernible effect on fluidization in these tests.

Fluid-bed samples taken during runs Pure-1 to -4 indicated that small clusters of 5 to 8 alumina particles began to appear after 1 to 2.5 hr of the initial recycle-fluorination period. In these runs, a fluorine feed of 2 liters/min was used to place the system on recycle

but the reactor was generally not rapped to return elutriated fines to the fluidized bed before the start of recycle-fluorination. Based on measurements taken with the thermal conductivity cell, it is estimated that the fluorine concentration was increased to 90 v/o in 20 min when the system was put on recycle with 2 liters/min fluorine feed. Local temperature excursions may have been caused by accelerated reaction of high concentrations of fluorine with reactive fines which were returned to the bed by rapping the disengaging and filter sections of the reactor in the early stages of recycle-fluorination. These temperature excursions probably caused agglomeration of some of the alumina bed material.

To avoid the formation of agglomerates, operational procedures for increasing the fluorine concentration at the beginning of recycle-fluorination and for controlling the return of fines to the bed were modified. Beginning with run Pure-6, a lower fluorine flow rate of 0.5 liter/min was employed and the reactor was rapped at frequent, regular intervals. With 0.5 liter/min fluorine feed, 70 v/o F_2 was reached in 45 min; the fluorine feed was then increased to 2 liters/min to raise the fluorine concentration to 90 v/o. The modified procedure has been effective; no agglomeration of the alumina was encountered in run Pure-6 or in subsequent runs.

Variation of Uranium and Plutonium Concentration with Alumina Particle Size. The uranium and plutonium concentrations as a function of alumina particle size have been obtained from samples of the alumina bed after recycle-fluorination from run Pure-2. The results are shown in Table II-2. Both the uranium and plutonium concentrations increased significantly in particles less than 170 mesh (88 microns). Although the concentrations of both uranium and plutonium in -170 mesh alumina were approximately 6 times the concentrations in larger particles, the bulk of uranium and plutonium was associated with the larger sized alumina particles. Similar results have been reported for uranium on an alumina bed used to process UO_2 pellets (i.e., run Sure-8, ANL-7055, p. 110).

Uranium and Plutonium Removal from Alumina Bed. The uranium and plutonium concentrations in the alumina fluidized bed for runs Pure-5 and -7 are shown in Figures II-1 and II-2, respectively. Plutonium concentrations as a function of recycle-fluorination time are shown in Figure II-3 for runs Pure-6 and -8 (total recycle-fluorination time 12 hr) and in Figure II-4 for runs Pure-4 and -9 (total recycle-fluorination time 20 hr).

Changes of plutonium concentration in the fluidized alumina bed during recycle-fluorination in runs Pure-1, -2, -3, (ANL-7055, Figures II-5, -6, and -7) and

TABLE II-2. URANIUM AND PLUTONIUM CONCENTRATIONS IN FINAL ALUMINA BED AS A FUNCTION OF ALUMINA PARTICLE SIZE, RUN PURE-2^a

U.S. Mesh Size	Average Particle Size (microns)	U (w/o)	Pu (w/o)
-40+60	335	0.0024	0.009
-60+80	214	0.0024	0.006
-80+120	151	0.0025	0.006
-120+170	107	0.0031	0.009
-170+325	66	0.011	0.054
-325	—	0.018	0.049

^a Operating conditions reported in ANL-7055, p. 112.

Pure-4 (Figure II-4, this report) indicated that the highest rates of removal occurred during the first few hours of recycle-fluorination at a given temperature and that the overall recycle-fluorination time could be reduced without adversely affecting the final plutonium retention on the alumina. In runs Pure-5 and -6 (Figures II-1 and II-3), total recycle-fluorination time was reduced from 20 hr to 13 and 12 hr, respectively. The removal of uranium and plutonium in these runs was similar to that obtained with the longer recycle-fluorination periods; the final uranium and plutonium concentrations in the alumina bed were 0.004 and 0.007 w/o, respectively. The recycle-fluorination sequence in run Pure-6 consisted of 1 hr at 450°C, 3 hr at 500°C, and 8 hr at 550°C. In all the runs that used Type I fuel pellets, uranium removal from the alumina was greater than 99.99% and plutonium removal was 97%, for a single use of the alumina bed.

In runs Pure-7, -8, and -9, wherein Type II pellets and cesium fluoride were added to the alumina bed, significantly higher retention of uranium and plutonium on the alumina was observed after recycle-fluorination times of 8.5, 12, and 20 hr. The final uranium and plutonium concentrations in the alumina bed were:

108-9286

FIG. II-1. Uranium and Plutonium Concentrations in Alumina Fluidized Bed, Run Pure-5. (Type I pellets.)

108-9291

FIG. II-2. Uranium and Plutonium Concentrations in Alumina Fluidized Bed, Run Pure-7. (Type II pellets, CsF added.)

Run Pure-	Total Recycle-Fluorination Time (hr)	Final Concentration	
		U (w/o)	Pu (w/o)
7	8.5	0.018	0.018
8	12	0.022	0.014
9	20	0.021	0.021

These concentrations correspond to 93, 94, and 91% removal of the plutonium charge from the alumina bed in runs Pure-7, -8, and -9, respectively. Uranium removal in these runs averaged 99.96%. It may be noted that the final plutonium concentration in run Pure-9 which used a 20-hr recycle-fluorination sequence is greater than that obtained in runs Pure-7 and -8 which used shorter sequences. This result is contrary to past experience and will be further investigated.

The courses of plutonium removal from the alumina beds during 12 hr of recycle-fluorination in runs Pure-6 and -8 are compared in Figure II-3. The removal of plutonium during recycle-fluorination at 550°C appears to be much less effective in reducing the final plutonium concentration to a low value in run Pure-8 wherein Type II pellets and cesium fluoride were added

108-9284

FIG. II-3. Plutonium Concentration in Alumina Fluidized Bed, Runs Pure-6 and Pure-8.

Pure-6: Type I pellets

Pure-8: Type II pellets, CsF added

to the alumina bed. Comparison of the corresponding data for runs Pure-1, -2, and -3, (ANL-7055), and -4 with -9 (Figure II-4) indicates a similar effect. At present it is not possible to separate the effects of the added cesium fluoride and the use of pellets with different characteristics; runs are in progress to evaluate these effects. However, incomplete results from recent work indicate that higher plutonium removals are

108-9293

FIG. II-4. Plutonium Concentration in Alumina Fluidized Bed, Runs Pure-4 and Pure-9.

Pure-4: Type I pellets

Pure-9: Type II pellets, CsF added

achieved by different fluorination procedures which use lower initial fluorination temperatures.

b. FLUORINATION OF $\text{UO}_2\text{-PuO}_2\text{-F.P. PELLETS}$ WITH BrF_5

The first run, Purse-1, in which uranium (as U_3O_8) was selectively fluorinated with BrF_5 has been completed. In this run, a 1-in. deep fluidized-packed bed of $\text{UO}_2\text{-PuO}_2\text{-F.P. pellets}$ (330 g, Type II) was oxidized with 20 v/o O_2 in nitrogen at 450°C for 2 hr. The uranium was then fluorinated with about 10 v/o BrF_5 in nitrogen at 400°C for 3 hr. Fluorination of the plutonium was carried out by recycle-fluorination at 450, 500, and 550°C with fluorine. Complete analytical results for this run are pending.

2. Reactions of Bromine Pentafluoride (R. JARRY, J. STOCKBAR)

An investigation is being made of the feasibility of using BrF_5 as a selective fluorinating agent in the separation of uranium and plutonium. If, as expected, BrF_5 converts plutonium compounds only to non-volatile PuF_4 while converting uranium compounds to volatile UF_6 , then a separation between the volatile UF_6 and the nonvolatile PuF_4 can be achieved in a single fluorinating step. This fluorination scheme is being considered for the fluid-bed volatility process flowsheet being developed for reprocessing low-enrichment nuclear power reactor fuels.

In a previous report on this study (ANL-7055, p. 114), results were given for the following: (1) determination of the temperature dependence of the rates of reaction of UO_2F_2 with BrF_5 and UF_4 with BrF_5 over the temperature range 175 to 300°C ; (2) determination of the temperature dependence of the reaction rate of BrF_5 with mixtures containing UO_2F_2 , UF_4 , alumina, and fission products over the temperature range 175 to 250°C ; (3) determination of the reaction conditions necessary to remove greater than 99% of the uranium from mixtures of UO_2F_2 , UF_4 ,

alumina, and fission products, and (4) the effect of the addition of stainless steel or Zircaloy decladding products on the conversion of uranium oxides to UF_6 .

This report presents results of experiments to determine: (1) the BrF_5 fluorination conditions required for the volatilization of 99% of the uranium from mixtures containing U_3O_8 , alumina, fission product oxides with and without decladding products present; (2) the extent of plutonium volatilization during reaction with BrF_5 and the subsequent reactivity of the PuF_4 product towards fluorine; (3) the rates of reaction of U_3O_8 with BrF_5 over the temperature range 250 to 400°C; and (4) the dependence of the rate of the U_3O_8 - BrF_5 reaction at 250°C on the BrF_5 partial pressure.

a. EXPERIMENTAL

The specifications for the BrF_5 , diluent nitrogen, alumina, fission product mixture, and stainless steel and Zircaloy decladding products used in these experiments and a description of the experimental apparatus and procedure were given in a previous report (ANL-7055, p. 114). Other materials used in these experiments were: U_3O_8 , containing 84.47% uranium (theoretical, 84.80%) and having an average particle diameter of 10 microns (-325 mesh), and finely divided PuO_2 powder containing 89.68% plutonium (theoretical, 88.19%).

b. RESULTS AND DISCUSSION

(1) Fluorination of U_3O_8 -Alumina-Fission Product Mixture

Experiments were performed to determine the extent of uranium conversion to UF_6 by the reaction of BrF_5 with mixtures containing U_3O_8 , alumina, and fission products and with such mixtures to which was added either stainless steel or Zircaloy decladding product prepared by the HF-promoted oxidation reaction. Preliminary fluorinations, using only U_3O_8 , had indicated that a temperature of 350°C or greater and a reaction time of about 60 min would be needed to convert 99% or greater of the uranium to UF_6 . The solid reaction mixtures contained 5.9 g U_3O_8 , 10 g alumina, 0.07 g fission product mixture, and in some experiments either 0.89 g of stainless steel decladding product or 2.6 g of Zircaloy decladding product. The experiments were performed at reaction temperatures of 350 or 400°C; the reaction time was 60 min. The BrF_5 flow rate was about 0.5 g/min in a gas phase containing 26 v/o BrF_5 and 74 v/o nitrogen at a total flow rate (at 25°C) of 250 ml/min.

The results obtained for these experiments are listed in Table II-3. Also listed in Table II-3 for comparison

TABLE II-3. EFFECT OF TEMPERATURE AND THE PRESENCE OF STAINLESS STEEL OR ZIRCALOY DECLADDING PRODUCT ON THE REACTION BETWEEN BrF_5 AND URANIUM, ALUMINA, AND FISSION PRODUCT MIXTURES

Reaction time: 60 min
 BrF_5 flow rate: 0.5 g/min
 Total gas flow rate: 250 ml/min at 25°C (74 v/o N_2 , 26 v/o BrF_5)
 Linear velocity of gas at 300°C: 0.04 ft/sec

Temp. (°C)	Additive	% Uranium Volatilized ^a
A. U_3O_8 -Alumina-F.P. Mixtures ^b		
350	none	97.6
400	none	99.8
400	S.S. ^d	99.8
400	Zirc. ^e	99.6
B. UO_2F_2 - UF_4 -Alumina-F.P. Mixtures ^c		
250	none	98.2
300	none	99.8
300	S.S. ^d	99.6
300	Zirc. ^e	99.2

^a Based on uranium analysis of residue and uranium content of original uranium compounds.

^b Mixtures contained 5.9 g U_3O_8 , 10 g alumina, 0.07 g F.P. (see ANL-7055, Table II-10 for composition of F.P. mixture).

^c Mixtures contained 4.2 g UO_2F_2 , 2.2 g UF_4 , 10 g alumina, and 0.07 F.P. (see note (b) above). Results for these experiments were previously reported in ANL-7055, p. 120.

^d The stainless steel decladding product was prepared by the HF-promoted oxidation of type 304 SS, and contained 47.6% Fe, and 12.8% Cr; 0.89 g of the decladding product was added to the solid mixtures described in (b) and (c).

^e The Zircaloy decladding product was prepared by the HF-promoted oxidation reaction and was primarily ZrF_4 ; 2.6 g of the decladding product was added to the solid mixtures described in (b) and (c).

are results previously reported (ANL-7055, p. 120) for similar experiments in which the solid reaction mixture contained UO_2F_2 , UF_4 , fission products, and, in some experiments, decladding products. The results for mixtures containing U_3O_8 show that a temperature of 400°C is necessary for conversion of 99% or more of the uranium to UF_6 . The data also show that the presence of stainless steel or Zircaloy decladding product in the solid reaction mixture did not affect the conversion of uranium to UF_6 . The principal difference between the mixtures containing U_3O_8 and those containing UO_2F_2 and UF_4 was that a higher temperature was required for high conversion to UF_6 for the mixtures containing U_3O_8 . The concentrations of the principal elemental constituents of the decladding products (Sn and Zr for Zircaloy, and Fe and Cr for stainless steel) were monitored by X-ray fluorescence

analysis of the reaction residues to determine whether any of these elements was volatilized during the BrF_5 fluorination. The analyses indicated that no volatilization of the component elements occurred during the BrF_5 fluorination.

(2) Fluorination of U_3O_8 - PuO_2 -Alumina-Fission Product Mixtures

In a series of experiments, solid reaction mixtures containing U_3O_8 , PuO_2 , alumina, and fission products or mixtures containing only PuO_2 and alumina were reacted with BrF_5 to determine if any of the plutonium would be converted to PuF_6 . The reaction conditions chosen (400°C , 60 min reaction time, gas phase containing 26 v/o BrF_5 and 74 v/o nitrogen at a total flow rate of 250 ml/min) were those which resulted in the conversion of more than 99% of the uranium to UF_6 (see subsection (1) above). In two experiments in which the solid reactant contained U_3O_8 (5.8 g), PuO_2 (0.2 g),⁵ fission products (0.07 g), and alumina (10 g), the reaction residue remaining after the BrF_5 reaction was fluorinated with elemental fluorine at 550°C using gas phase recycle conditions.

To determine if plutonium was volatilized during the BrF_5 step, all of the gaseous reaction products (UF_6 , excess BrF_5 , BrF_3 , and PuF_6 if any was produced) leaving the reactor were passed through a trap, containing soda lime at 100°C , to convert the reaction products to nonvolatile material. After the termination of the BrF_5 step, the contents of the trap were removed, ground to a fine powder, homogenized, and samples were taken and analyzed for uranium and plutonium content. Portions of unreacted, plutonium-free soda lime were also ground and sampled to determine the background concentration of plutonium in the sample preparation equipment.

For the two experiments in which the starting material contained both uranium and plutonium, the plutonium concentrations on the soda lime after the BrF_5 step were 0.94 and 0.44×10^{-3} mg/g of solid. These concentrations represent 0.24 and 0.11 mg of plutonium on the soda lime, corresponding to 0.13 and 0.06% of the original plutonium in the starting material, respectively. However, blanks of soda lime ground just prior to grinding of the experimental samples, showed plutonium contents of 2.8 and 0.56×10^{-3} mg/g of solid for the first and second experiments, respectively. The apparatus used to grind the soda lime samples had been previously used to grind solid samples from a fluid-bed reactor using plutonium. The level of plutonium found in the blank samples strongly suggests

that the plutonium contents of the experimental samples were the result of cross-contamination during the grinding operation. In an experiment in which the solid reaction mixture contained only PuO_2 and alumina, the quantity of PuO_2 was greater by a factor of ten than in the other two experiments. After the BrF_5 step the soda lime contained 0.33×10^{-3} mg of plutonium per gram of solid, which was attributed to cross-contamination during the grinding operation. In this experiment the weight gain of the solid reaction mixture indicated that 88% of the PuO_2 had been converted to PuF_6 . The uranium content of the solid reaction mixture after the BrF_5 fluorination period was determined in two separate experiments which were terminated after the BrF_5 step. These solid residues showed an average concentration of 0.067 w/o uranium, equivalent to >99.9% removal of uranium.

The solid reaction residues remaining after the BrF_5 step for the first two experiments were fluorinated using 100% fluorine at 550°C for 5 or 8 hr under recycle conditions. The alumina residues, after reaction with fluorine, contained 0.011 and 0.038 w/o plutonium and 0.010 and 0.018 w/o uranium for the 8 and 5 hr fluorinations, respectively. The plutonium concentrations on the alumina correspond to removal of 99.5 and 97.7% of the plutonium originally contained in the solid mixtures for the eight and five hour tests, respectively. The uranium concentrations on the alumina correspond to removal of more than 99% of the original uranium present.

These results indicate that essentially none of the plutonium is converted to volatile PuF_6 by reaction with BrF_5 at 400°C for 1 hr, and that 99% or more of the plutonium remaining in the solid mixture can be converted to PuF_6 by a subsequent fluorination using fluorine at a temperature of 550°C and a reaction period of less than 10 hr.

(3) Kinetics of the U_3O_8 - BrF_5 Reaction

A preliminary study was made of the kinetics of the U_3O_8 - BrF_5 reaction over the temperature range 250 to 400°C . About five grams of U_3O_8 were used in each experiment. The gas phase contained 26 v/o BrF_5 and 74 v/o nitrogen at a total flow rate of 250 ml/min, corresponding to a linear gas velocity in the reactor of 0.04 ft/sec. The extent of reaction, i.e., conversion of U_3O_8 to UF_6 , in an experiment was calculated from the weight change of the solid. In some cases, this method for calculating the fraction reacted was checked by uranium analyses of the residues; agreement in all cases was excellent.

The data were treated using a diminishing-sphere model in which F , the fraction reacted, is related to a rate constant k' , min^{-1} , and a reaction time t by the

⁵ The ratio of plutonium to uranium (1:25) in these mixtures was greater by a factor of 10 than the 1:250 ratio in the nominal fuel (0.4 w/o plutonium in uranium).

108-9295

FIG. II-5. The $\text{U}_3\text{O}_8 + \text{BrF}_5$ Reaction: Plots of $(1 - F)^{1/3}$ versus Reaction Time, t . Temperature Range, 250 to 400°C.

expression $(1 - F)^{1/3} = 1 - k' t$. The relationship between $(1 - F)^{1/3}$ and the reaction time at several reaction temperatures is shown in Figure II-5. At reaction temperatures of 300°C or greater, the plots show a change in slope, indicating an increase in the rate of uranium conversion to UF_6 with increasing reaction time. Rate constants, k' (min^{-1}), calculated for the data represented in Figure II-5 are plotted in Figure II-6 against $1/T$. Also presented in Figure II-6 are lines representing the temperature dependence of the rate constants for the $\text{UO}_2\text{F}_2\text{-BrF}_5$ and the $\text{UF}_4\text{-BrF}_5$ reaction. Chemical analyses of the reaction residues for total uranium and water-soluble uranium suggested that the residues were composed of U_3O_8 and UO_2F_2 . However, X-ray diffraction analyses of the residues indicated the presence of U_3O_8 , and an unidentified phase which was not UO_2F_2 , UF_4 , a uranium oxide, or a uranium bromide. (Chemical analyses showed no indication of the presence of bromine in the reaction residues.) The fraction of the reaction residue that was water soluble increased both with reaction time at a given temperature (see Figure II-7) and with temperature at a given reaction time (see Figure II-8). However, even after conversion of 97% of the uranium to UF_6 the major part of the residue was still U_3O_8 , the water soluble fraction of the residue constituting only about 20%. Since the unidentified phase could not be characterized, subsequent discussion of the mechanism assumes that all of the water-soluble uranium is UO_2F_2 . Rampy⁶ indicated that the reaction of U_3O_8 and UF_6 is not simple but may involve undefined intermediates.

⁶ G. A. Rampy, GAT-L-366, (June 5, 1957).

The rate behavior observed for the $\text{U}_3\text{O}_8\text{-BrF}_5$ reaction suggests the occurrence of a concomitant reaction which initially hinders the production or volatilization of UF_6 , but whose effect is diminished after a period

108-9279

FIG. II-6. Temperature Dependence of Rate Constants for $\text{U}_3\text{O}_8\text{-BrF}_5$ Reaction over the Temperature Range 250 to 400°C. (Gas phase: 26 v/o BrF_5 in nitrogen.)

108-9288

FIG. II-7. Distribution of Original Uranium as UO_2F_2 and U_3O_8 in the Reaction Residues and as Volatilized UF_6 for the $\text{U}_3\text{O}_8\text{-BrF}_5$ Reaction at 400°C.

108-9285

FIG. II-8. Fractions of the Solid Residues Present as U_3O_8 and UO_2F_2 during Reaction of U_3O_8 with BrF_5 .

of time, which then leads to higher rates of production or volatilization of UF_6 . A clue to a probable process was found in the work on the U_3O_8 -fluorine reaction reported by G. A. Rampy.⁶ This work concerned the fluorination at $530^\circ C$ of U_3O_8 . Rampy found that UO_2F_2 and UF_4 were formed as intermediate products in the fluorination of U_3O_8 and that the UF_6 formed as the final product reacted with U_3O_8 to form UO_2F_2 and UF_4 . The reaction between U_3O_8 and UF_6 was found to be rapid relative to the U_3O_8 -fluorine reaction. Rampy concluded from the experimental results that during the first half of the reaction period the UF_6 volatilization was due almost entirely to the reaction between UF_4 and fluorine, and that the remaining U_3O_8 was converted to UO_2F_2 . During the second portion of the reaction the UF_6 volatilization rate regularly increased owing to the fluorination of the accumulated UO_2F_2 . This reaction sequence suggests the following behavior: an initial weight gain, followed by a slow rate of UF_6 volatilization, and finally by a rapid increase in UF_6 production and volatilization rate.

The reactions involved in the fluorination of U_3O_8 with BrF_5 can be expressed as:

1. $U_3O_8 + 4BrF_5 \rightarrow 2UO_2F_2 + UF_4 + 4BrF_3 + 2O_2$
2. $UO_2F_2 + 2BrF_5 \rightarrow UF_6 + 2BrF_3 + O_2$
3. $UF_4 + BrF_5 \rightarrow UF_6 + BrF_3$
4. $U_3O_8 + 2UF_6 \rightarrow 4UO_2F_2 + UF_4$

Reactions 2, 3, and 4 are considered to be faster than reaction 1. Application of the approach derived for the U_3O_8 -fluorine reaction by Rampy⁶ to the U_3O_8 - BrF_5 reaction becomes difficult on two counts; firstly, the

residues did not contain any UF_4 , and secondly, the residues always contained U_3O_8 as well as UO_2F_2 . The results for the analyses of residues for total uranium and water soluble uranium were used to calculate the fraction of the original uranium present as U_3O_8 , UO_2F_2 or volatilized UF_6 . The results of these calculations are shown in Figure II-7. These results show no peak in the UO_2F_2 concentration in the residues but rather that the UO_2F_2 concentration is a small fraction of the original uranium at the start of the reaction and diminishes regularly with increasing reaction time. It is not surprising to find no UF_4 in the residues considering the high reaction rate that could be expected for the UF_4 - BrF_5 reaction at these temperatures (see plot of temperature dependence of rate for UF_4 - BrF_5 reaction in Figure II-6).

A reaction sequence has been proposed which appears to explain the change in reaction rate observed for the U_3O_8 - BrF_5 reaction. During the initial, lower rate portion of the reaction, which was observed at 300 to $400^\circ C$ and which constituted the entire observed reaction period at $250^\circ C$, the interaction of UF_6 with U_3O_8 reduces the extent of volatilization of UF_6 through the formation of a layer of UO_2F_2 on the U_3O_8 particles. This process continues until the thickness of the UO_2F_2 layer begins to act as an effective diffusion barrier to the reaction between UF_6 and U_3O_8 . At this time, indicated by the breaks in the plots of Figure II-5 at 300 to $400^\circ C$, further production of UF_6 results in greater volatilization of UF_6 and in a marked increase in the rate of the reaction. The shorter times required for the change in rate to occur at increased temperatures (see Figure II-5) appear to support this proposed reaction mechanism. At higher temperatures and, hence, increased reaction rates, the buildup of UO_2F_2 on the solid reactant should occur sooner, thereby resulting in a reduction in the back reaction. While the fraction of the original uranium present as UO_2F_2 in the solid residues decreases with reaction time, the fraction of UO_2F_2 in the residue increases with both reaction time and temperature (see Figure II-8).

The absence of a break in the reaction rate at $250^\circ C$ can be explained on the basis of generally lower reaction rates. The fractions of the original uranium present in the solid residue as U_3O_8 and UO_2F_2 and as volatilized UF_6 are shown in Figure II-9. These plots show a greatly reduced rate of production of UF_6 and a steady buildup of UO_2F_2 in the residues, when compared with similar plots (Figure II-7) for the reaction at $400^\circ C$. These results lead to the conclusion that the reaction time (30 min) at $250^\circ C$ was not sufficient to allow the change in rate to be realized. The similar behavior in the accumulation of UO_2F_2 in the reaction

residues (Figure II-8) suggests that there is no change in the reaction mechanism with changing temperature.

(4) Comparison of the Reactions of U_3O_8 , UO_2 , and UO_3 with BrF_5

Rate data were obtained for the reactions between UO_3 or UO_2 and BrF_5 at 300°C and compared with data obtained at 300°C for the U_3O_8 - BrF_5 reaction. Rampy⁷ has shown that interactions between UF_6 and both UO_3 and UO_2 occur. It was therefore reasonable to assume that the fluorination of these oxides using BrF_5 would result in the same type of rate behavior as was obtained for the U_3O_8 - BrF_5 reaction. For the UO_3 - BrF_5 reaction the following reactions could be expected to occur:

1. $\text{UO}_3 + \text{BrF}_5 \rightarrow \text{UO}_2\text{F}_2 + \text{BrF}_3 + \frac{1}{2}\text{O}_2$
2. $\text{UO}_2\text{F}_2 + 2\text{BrF}_5 \rightarrow \text{UF}_6 + 2\text{BrF}_3 + \text{O}_2$
3. $2\text{UO}_3 + \text{UF}_6 \rightarrow 3\text{UO}_2\text{F}_2$

For the UO_2 - BrF_5 reaction the following equations should apply:

1. $\text{UO}_2 + 2\text{BrF}_5 \rightarrow \text{UF}_4 + 2\text{BrF}_3 + \text{O}_2$
2. $\text{UF}_4 + \text{BrF}_5 \rightarrow \text{UF}_6 + \text{BrF}_3$
3. $\text{UF}_4 + \text{UF}_6 \rightarrow 2\text{UF}_5$
4. $2\text{UF}_5 + \text{BrF}_5 \rightarrow 2\text{UF}_6 + \text{BrF}_3$
5. $\text{UO}_2 + \text{UF}_6 \rightarrow \text{UO}_2\text{F}_2 + \text{UF}_4$

In both of these cases, the reaction between UF_6 and the uranium oxide would result in a lower initial rate of reaction if the same mechanism as postulated for the U_3O_8 - BrF_5 reaction is applied. The low initial rate of volatilization of UF_6 would then be followed by a higher rate after further interaction was hindered by the accumulation of a layer of UO_2F_2 on the surface of the oxide particles.

The data for the reactions of BrF_5 with UO_3 , UO_2 and U_3O_8 are compared in Figure II-10. Also shown in this figure are data previously reported (ANL-7055, pp. 118-119) for the reaction of BrF_5 with UO_2F_2 at 300°C , and for the reaction of BrF_5 with UF_4 at 275°C . These data show that both the UO_3 - BrF_5 and UO_2 - BrF_5 reactions undergo a change in reaction rate similar to that observed for the U_3O_8 - BrF_5 reaction. The data also indicate that the rate of reaction of BrF_5 with these uranium compounds decreases in the order UF_4 , UO_2F_2 , UO_2 , UO_3 , U_3O_8 .

X-ray diffraction analyses of the residue for the UO_3 - BrF_5 reaction showed only the presence of UO_3

108-9287

FIG. II-9. Distribution of Original Uranium as UO_2F_2 and U_3O_8 in the Reaction Residues and as Volatilized UF_6 for the U_3O_8 - BrF_5 Reaction at 250°C .

108-9274

FIG. II-10. Comparison of Reactions of U_3O_8 , UO_3 and UO_2 with BrF_5 at 300°C .

and UO_2F_2 . For the UO_2 - BrF_5 reaction, X-ray diffraction analysis showed the presence of UO_2 , UO_2F_2 , UF_4 , and U_3O_8 in the residues. The U_3O_8 could be present as the result of the oxidation of the UO_2 by elemental oxygen.

⁷ G. A. Rampy, GAT-265 (1959).

108-9294

FIG. II-11. $\text{U}_3\text{O}_8\text{-BrF}_5$ Reaction at 250°C : Effect of BrF_5 Partial Pressure on the Conversion of Uranium to UF_6 .

108-9289

FIG. II-12. Variation of Rate Constant, k' , with Partial Pressure of BrF_5 for $\text{U}_3\text{O}_8\text{-BrF}_5$ Reaction at 250°C .

(5) Effect of Partial Pressure of BrF_5 on Rate Constants for the $\text{U}_3\text{O}_8\text{-BrF}_5$ Reaction at 250°C

The use of a lower temperature for the BrF_5 fluorination step, during which the uranium is removed from the fluid bed, might result in more efficient removal of the plutonium in the subsequent fluorination with fluorine. In earlier work performed in a $1\frac{1}{2}$ -in. fluid-

bed reactor, it was shown⁸ that the use of low temperatures (450°C rather than 500 or 550°C) for the initial fluorination with fluorine, during which the greater part of the uranium was removed, resulted in more efficient removal of plutonium in succeeding fluorination steps at 500°C and 550°C . A series of experiments was performed to determine the effect of BrF_5 partial pressure on the rate of conversion of U_3O_8 to UF_6 at 250°C . A substantial increase in the reaction rate with an increase in BrF_5 pressure would be required in order to employ a temperature of 250°C in the processing of U_3O_8 . For example, the rate constant at 250°C would have to increase to about 0.0396 min^{-1} , the value obtained for the reaction at 400°C using 26 v/o BrF_5 (Figure II-6). Under the latter conditions, more than 99% of the uranium was converted to UF_6 in a 1-hr reaction period (Table II-3).

Experiments were performed at 250°C using 26, 46, and 66 v/o BrF_5 in nitrogen as the gas phase, corresponding to BrF_5 partial pressures of 198, 250, and 502 mm of Hg, respectively. The total gas flow rate (calculated at 250°C) was $490 \pm 20 \text{ ml/min}$, resulting in a linear velocity in the reactor of $0.038 \pm 0.002 \text{ ft/sec}$.

These experiments resulted in reaction rates of

⁸ R. L. Jarry et al, Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part IX. The Fluid-Bed Fluorination of Simulated Nuclear Fuel Containing Plutonium in a $1\frac{1}{2}$ -Inch Diameter Reactor, ANL-7077 (1965) (in press).

0.0051, 0.0131, and 0.0235 min^{-1} at 26, 46, and 66 v/o BrF_5 , respectively. These data are shown in Figure II-11 as plots of the function $(1 - F)^{1/3}$ versus the reaction time in minutes, and in the log-log plot of Figure II-12 showing the dependence of the rate constant on the partial pressure of BrF_5 . Examination of the data shows that the rate constants obtained at 46 and 66 v/o BrF_5 approached the values of the rate constant obtained using 36 v/o BrF_5 at 300°C and 350°C, respectively (Figure II-6). To obtain a value of the rate constant at 250°C equal to that obtained

at 400°C and 26 v/o BrF_5 would require, as indicated by extrapolation of the plot of Figure II-12 a gas phase containing greater than 86 v/o BrF_5 . The use of a high concentration of BrF_5 may be practical for processing U_3O_8 in fluid-bed equipment if the utilization efficiency of the BrF_5 is sufficiently high.

Experiments are planned to obtain data on the pressure dependence of the BrF_5 - U_3O_8 reaction. Concurrently, data on the dependence of the rate constants on the partial pressure of BrF_5 will be obtained for the UO_2F_2 - BrF_5 and UF_4 - BrF_5 reactions.

3. Chemistry of Neptunium Hexafluoride (T. GERDING)

Neptunium-237 can be expected to be a significant contaminant in highly irradiated, low-enrichment fuels.⁹ A knowledge of the pertinent physical and chemical properties of neptunium hexafluoride is necessary in order to establish processing conditions for achieving a complete separation of uranium and plutonium from neptunium by the fluoride volatility process. Little information on the chemistry of neptunium hexafluoride is available and hence, a study of the properties of neptunium hexafluoride has been initiated. The absorption spectrum of NpF_6 has been previously reported (ANL-7055, p. 124). The work reported here concerns determining the rate of fluorination of neptunium tetrafluoride (NpF_4) by elemental fluorine in the temperature range 250 to 400°C.

a. EXPERIMENTAL

The equipment for the fluorination of NpF_4 was constructed from nickel and Monel; Teflon gaskets were used throughout the system. The reaction vessel, a 1-in. OD nickel tube with a flange at each end, was heated in a horizontal clam-shell furnace. The exit line leading from the tube to standard $\frac{3}{4}$ -in. flare traps and all other connecting lines were made from $\frac{3}{8}$ -in. OD nickel tubing.

The sample of NpF_4 was contained in a nickel boat ($3\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{1}{4}$ in.) which was placed within the furnace on a hemicylindrical holder shaped to provide thermal contact between the boat and the furnace tube. Reaction temperature was measured by an Inconel-clad, chromel-alumel thermocouple located in a well within the hemicylindrical holder.

Auxiliary equipment consisted of a vacuum manifold, storage vessels, and traps, all constructed of nickel. Gas flow through the system was measured by a thermal flow meter. Fluorine was disposed of in a trap filled with activated alumina. The reaction tube,

furnace, and auxiliary equipment were housed in a CENHAM glovebox.

Neptunium-237 in the form of the dioxide (NpO_2) was obtained from Oak Ridge National Laboratory. Analysis of the dioxide indicated the presence of 0.13%

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FIG. II-13. Variation of Rate Constant for the NpF_4 - F_2 Reaction over the Temperature Range 250 to 400°C.

⁹ D. R. Bondy, J. A. Lane, and A. T. Gresky, Ind. Eng. Chem. Process Design Develop., **30**, 293 (1964).

plutonium and 0.04% uranium in the sample. Spectrographic analysis showed only minor metallic impurities.

Neptunium tetrafluoride was prepared by the reaction of NpO_2 with hydrogen fluoride-oxygen gas mixture at 500°C . X-ray analysis of the material produced by this reaction indicated the product to be NpF_4 , and weight gain data showed a conversion to NpF_4 of greater than 99%.

The following experimental procedure was employed in this study: a weighed sample of neptunium tetrafluoride was placed in the boat. The boat was positioned in the furnace tube and the system was heated to the reaction temperature in an atmosphere of flowing nitrogen. When thermal equilibrium was reached, fluorine was substituted for nitrogen. At the conclusion of the experiment, nitrogen was substituted for fluorine and the furnace was allowed to cool before the boat was removed. The boat and contents were weighed and, on the basis of the change in weight of the sample, reaction rate data were obtained.

b. RESULTS

Reaction rates were measured for the $\text{NpF}_4\text{-F}_2$ reaction over the temperature range 250 to 400°C . The data were treated using the "diminishing sphere model". In this kinetic model, which was developed by Anderson,¹⁰ the reaction between a gas and a solid is related to the solid presenting a spherical interface

continuously diminishing with reaction time. The final equation developed is:

$$(1 - F)^{1/3} = 1 - k't$$

in which F is the fraction of the solid reacted, and k' is a reaction constant, related to the true reaction constant by the expression $k' = k/r_o\rho_o$ (r_o = initial radius, ρ_o = bulk density) and t is the reaction time.

The values of the reaction rate constant, k' , for the $\text{NpF}_4\text{-F}_2$ reaction varied from 0.0007 min^{-1} at 250°C to 0.0547 min^{-1} at 400°C . These values of k' were used in the integrated form of the Arrhenius equation:

$$\log k' = C - \left(\frac{E}{2.303 R} \right) \frac{1}{T},$$

where C is a constant and E is an activation energy. From this equation an apparent activation energy of 20 kcal/mole was calculated. Figure II-13 is a graphic representation of $\log k'$ versus $1/T$. Two batches of NpF_4 were used to obtain the data presented. Although the rate constants at constant temperature were slightly different for each batch of NpF_4 , the apparent activation energies of both batches were identical.

The activation energy for the reaction of $\text{UF}_4 + \text{F}_2$ is reported¹¹ as $15\text{--}20 \text{ kcal/mole}$ in the temperature range $265\text{--}348^\circ\text{C}$, and a value of $10\text{--}13 \text{ kcal/mole}$ is reported¹² for the reaction of $\text{PuF}_4 + \text{F}_2$ over the temperature range $100\text{--}600^\circ\text{C}$.

4. Vapor-Liquid Equilibria in the System $\text{PuF}_6\text{-UF}_6$ (D. STEIDL, L. TREVORROW)

Vapor-liquid equilibrium data for the system $\text{PuF}_6\text{-UF}_6$ are necessary for the design of a fractional distillation column intended to separate mixtures of PuF_6 and UF_6 produced in the fluid-bed fluoride volatility process. The purpose and a general outline of the investigation of vapor-liquid equilibria in this system have been published (ANL-6875, p. 114, ANL-6925, pp. 120-122). It would also be of fundamental interest if two such similar molecules as PuF_6 and UF_6 differed significantly from ideality in their vapor-liquid equilibrium behavior. The PuF_6 and UF_6 molecules are regular octahedra with very similar cell dimensions.¹³

a. APPARATUS

After consideration of the several methods commonly used for obtaining vapor-liquid equilibrium

data, the isothermal, mechanical recirculation method was chosen for this work. A diagram of the apparatus used for the vapor-liquid equilibrium determinations appeared in ANL-6875, p. 115. In addition to the apparatus directly concerned with the study of vapor-liquid equilibria, auxiliary equipment for the preparation, purification, and containment of PuF_6 was also constructed (ANL-6925, p. 120).

The loop containing the circulating $\text{PuF}_6\text{-UF}_6$ vapor was enclosed in an insulated, isothermal box. Temperature regulation of the box was accomplished by use of six electrical finstrip heaters controlled by Variacs. Temperature during an individual experiment was maintained within $\pm 0.2^\circ\text{C}$.

The vapor-liquid loop and auxiliary vacuum manifold were constructed from nickel and Monel components, joined by welding or silver-soldering. Several brass-bodied, 1-in. ID Vactronic bellows valves were used in the sample treatment portion of the equipment. Teflon gaskets were used in flare or flanged connections.

Pressure measurements were made through use of

¹⁰ J. S. Anderson, Bull. Soc. Chim. **20**, 781 (1953).

¹¹ V. Labaton and J. Johnson, J. Inorg. Nucl. Chem. **10**, 74 (1959).

¹² M. J. Steindler et al, Nucl. Sci. Eng. **6**, 333 (1959).

¹³ M. J. Steindler, ANL-6753, pp. 23-24 (1963).

Booth-Cromer, null point pressure transmitter¹⁴ connected to an absolute, well-type mercury manometer. Calibration of the pressure-measuring system was accomplished by introducing an appropriate quantity of nitrogen into the vapor-liquid loop and comparing pressure measurements made directly with the mercury manometer with subsequent measurements made through the use of a pressure transmitter. Results of these measurements agreed within ± 3 torr over the required pressure range from 0–2400 torr.

Temperature measurements were made with chromel-alumel thermocouples. One thermocouple was introduced into a well which extended into the liquid contents of the equilibrium cell. Another thermocouple was inserted into a well ending in the vapor space in the cell. A third thermocouple was attached to the surface of the vapor sample bulb. Readings obtained from the thermocouples by use of a K-3 potentiometer during an equilibrium determination agreed with each other within ± 0.01 mv or approximately $\pm 0.2^\circ\text{C}$. (The thermocouple indicating the temperature of the liquid phase in the equilibrium cell usually indicated the lowest temperature.)

The PuF_6 - UF_6 vapor was circulated through the loop by a remote head of a Lapp diaphragm pump fitted with a nickel diaphragm. The measured flow of vapor delivered by the pump was 380 ml/min. Performance of the pump was monitored by a thermal flowmeter which indicated flow as the variable output of a thermopile across the legs of an inverted, U-shaped section of the vapor loop which had a small resistance heater at the apex of the U.¹⁵

Samples of the liquid phase were withdrawn through a Hoke diaphragm valve. The sample treatment section of the apparatus included another Booth-Cromer pressure transmitter for pressure measurements in the sample manifold; a flanged vessel for reacting PuF_6 - UF_6 samples with SF_4 to separate the constituents for subsequent analysis; and an auxiliary manifold for measurement, addition, and disposal of SF_4 .

Initial tests on the experimental apparatus involved the determination of the vapor-liquid equilibria for the ethanol-water system to establish if any significant deficiencies existed in the apparatus. The liquid and vapor phase compositions and pressures obtained on the ethanol-water mixtures were in reasonable agreement with published values for this system.

Some preliminary experiments were made with UF_6 alone. Vapor pressures obtained for UF_6 at several temperatures were within 1% of published values.¹⁶ Vapor density determinations of UF_6 gave an average

molar compressibility factor, Z , ($Z = PV/RT$) of 0.935 at 85°C which compares favorably with factors calculated from the data of Weinstock¹⁶ (0.924) and Magnuson¹⁶ (0.929). It was recognized that alpha radiation from plutonium would produce both PuF_4 and UF_4 in the system by decomposition of the respective hexafluorides. In order to determine if the presence of solid fluoride in the system would produce errors in vapor pressure measurements or cause difficulties in sampling, 170 grams of UF_6 were added to 10 grams of UF_4 in the cell. No effect on the vapor pressure of UF_6 or difficulty in the sampling procedures was observed.

b. EXPERIMENTAL PROCEDURE

The equilibrium cell was charged by vacuum distillation of the PuF_6 and UF_6 from supply vessels attached to the auxiliary vacuum manifold. Plutonium hexafluoride was prepared by reaction of PuF_4 and fluorine in a tube furnace at 550°C . The total quantity of material charged to the equilibrium cell was usually 200–220 g.

At the beginning of each equilibrium determination, the equilibrium cell was cooled to -78°C with a trichloroethylene-dry ice bath to condense the PuF_6 and UF_6 in the system. Fluorine, produced by the alpha decomposition of PuF_6 , was then removed from the system by vacuum pumping. The isothermal box was then heated to the desired temperature and, when the system reached the selected temperature, the Lapp pump was started to recirculate the PuF_6 - UF_6 vapor through the loop. Temperature and pressure of the system were observed throughout the equilibration, usually at 1-hr intervals. The temperature and pressure were quite steady throughout a determination after an initial circulation period of about 1 hr. In the initial equilibrium determination, successive samples of the liquid phase were taken at $4\frac{1}{2}$ and $6\frac{3}{4}$ hr to determine if sufficient time was being allowed for equilibration of the system. On the basis of analyses of these samples, an equilibration time of $6\frac{1}{2}$ hr was chosen.

At the end of an equilibration, the Lapp pump was stopped and samples of the liquid phase and vapor phase were obtained. The liquid sample was collected in a 2.3-ml volume isolated by two valves. The PuF_6 - UF_6 liquid sample was transferred to the PuF_6 - SF_4 reaction vessel by vacuum distillation and treated with SF_4 for 17 hr at 80°C to reduce the PuF_6 to PuF_4 . (Uranium hexafluoride is not reduced by SF_4 .) After the excess SF_4 and the SF_6 formed during the reduction had been removed, the UF_6 was distilled from the reaction vessel into a weighing vessel and the UF_6 content of the sample determined by weighing. The

¹⁴ S. Cromer, MDDC-803 (1947).

¹⁵ R. W. Kessie, ANL-6531 (1962).

¹⁶ R. DeWit, GAT-280, p. 98 (August, 1960).

PuF_4 remaining in the reaction vessel was dissolved in 4M HNO_3 -0.1M $\text{Al}(\text{NO}_3)_3$ solution and the plutonium content determined by radiochemical methods. This technique for analyzing PuF_6 - UF_6 mixtures is discussed in greater detail by Wagner (ANL-6800, pp. 208-210).

The equilibrium cell was then cooled to -78°C to condense the PuF_6 - UF_6 remaining in the loop. The material in the loop which did not condense at -78°C was assumed to be fluorine formed by the alpha decomposition of PuF_6 . The fluorine pressure in the loop was measured. The vapor sample bulb was removed from the vapor loop, weighed, and attached to the sample manifold. The contents of the bulb were then vacuum-distilled into another SF_4 - PuF_6 reaction vessel and treated in the same manner as the liquid sample.

The technique for analysis of PuF_6 - UF_6 mixtures was evaluated by comparing the amount of PuF_6 - UF_6 in the vapor sample bulb, as determined by weighing, with the amount indicated by the analytical procedure. At the completion of each experiment, the vapor sample was removed from the line and weighed. Comparison of this weight with a tare weight gave the total weight of the UF_6 - PuF_6 sample. The contents of the bulb were then vacuum distilled into the larger SF_4 reaction vessel. An appropriate amount of SF_4 was then condensed into the reaction vessel at -196°C , the vessel was removed from the vacuum manifold, heated to 80°C , and maintained at this temperature for four hours or longer. The reaction vessel was then returned to the vacuum manifold, cooled to -78°C , and the residual SF_4 and the SF_6 produced by the reaction of SF_4 with PuF_6 were pumped off. The reaction vessel was then warmed and the UF_6 from the original mixture was condensed into another vessel and weighed. The PuF_4 remaining in the reaction vessel was dissolved with 4M HNO_3 -0.1M $\text{Al}(\text{NO}_3)_3$ solution and the resulting solution submitted for chemical analysis. In fourteen determinations the average material balance was 96.3%.

While the UF_6 - PuF_6 mixture is held in the equilibrium cell, PuF_6 decomposes to PuF_4 and fluorine owing to alpha radiation from the plutonium. A portion of the UF_6 is also reduced. The volatile UF_6 and PuF_6 were periodically distilled from the equilibrium cell and the solid material remaining in the cell was removed. This material was pink to buff in color, suggestive of PuF_4 . A total of 17.40 g of the material was collected over the course of the determinations. X-ray diffraction analysis of the material indicated PuF_4 as the major phase. The uranium concentration in the solid material was approximately 0.5%. If the uranium is assumed to be present as UF_4 , the pluto-

nium and remaining fluoride were present in the proportion indicative of PuF_4 .

c. RESULTS AND DISCUSSION

The experimental results obtained in the equilibrium determinations are given in Table II-4. The compositions of the liquid and vapor phases were calculated from the results of radiochemical analyses for plutonium and from direct weighing of UF_6 . Three different methods were used to correct the gross pressure measurement for the fluorine pressure in the system. The total pressure value reported in Table II-4 as "measured" was obtained by correcting the gross pressure measurement for the noncondensable gas in the system when the equilibrium cell was cooled to -78°C . The total pressure value reported as " MF_6 " was calculated from the expression:

$$P_{\text{MF}_6} = \frac{gRT - 38 PV}{315 V}$$

where

$$\begin{aligned} P_{\text{MF}_6} &= \text{total pressure of } \text{PuF}_6 \text{ and } \text{UF}_6 \\ g &= \text{weight of vapor sample} \\ P &= \text{gross pressure} \end{aligned}$$

This expression was derived by assuming that the molecular weights of PuF_6 and UF_6 are the same, an assumption that introduces an error of 1 part in 353 into the calculations. The total pressure value given under "analytical" was obtained by calculating pressures for PuF_6 and UF_6 from analytical results on the vapor sample using the equation of state:

$$P = \frac{ZgRT}{MV}$$

The compressibility factor (Z) for UF_6 was obtained from the vapor density determinations made in checking out the equipment. Z was assumed to be 1.0 for PuF_6 . The activity coefficients were calculated from the following equation:

$$\gamma = \frac{PY}{P^0X},$$

where

$$\begin{aligned} \gamma &= \text{activity coefficient} \\ X &= \text{mole fraction of component in the liquid phase} \\ Y &= \text{mole fraction of component in the vapor phase} \\ P &= \text{total pressure} \\ P^0 &= \text{vapor pressure of pure component} \end{aligned}$$

It is assumed in the use of this equation that any deviation from ideality occurs in the liquid phase only.

TABLE II-4. VAPOR-LIQUID EQUILIBRIUM DATA IN THE SYSTEM UF₆-PuF₆

Temp (°C)	X_{UF}	Y_{UF_6}	Pressure (torr)			Activity Coefficient, γ Calculated from Pressures ^a						Average Pressure (torr) Corrected to 73, 81, or 89°C
						Measured ^b		MF ₆		Analytical		
			Mea- sured ^b	MF ₆ ^c	Analyti- cal ^d	UF ₆	PuF ₆	UF ₆	PuF ₆	UF ₆	PuF ₆	
73.6	0.989	0.992	1525	1551	1504	1.00	0.97	1.02	0.99	0.99	0.96	1499
76.7	0.976	0.982	1709	1756	1731	1.03	1.08	1.06	1.10	1.04	1.09	1546
73.3	0.959	0.969	1516	1549	1521	1.01	1.09	1.03	1.12	1.01	1.09	1515
72.4 ^e	0.939	0.956	1507	1568	f	1.04	1.05	1.08	1.09	f		1565
72.9 ^e	0.922	0.879	1536	1599	1533	0.98	2.23	1.02	2.32	0.98	2.22	1561
80.8 ^e	0.999	0.999	1864	1893	1791	0.99	1.39	1.01	1.41	0.95	1.33	1859
79.9	0.893	0.918	g	1895	1815	g		1.06	1.11	1.02	1.06	1913
79.8 ^e	0.822	0.749	1743	1985	1565	0.87	1.88	0.99	2.14	0.78	1.69	1822
80.8 ^e	0.780	0.688	1789	1744	1674	0.84	1.89	0.82	1.84	0.78	1.77	1745
89.2	0.987	0.991	2362	2427	2405	0.99	0.99	1.03	1.01	1.02	1.01	2385
88.4 ^e	0.989	0.942	2392	2355	2250	0.98	7.37	0.97	7.26	0.92	6.94	2370
89.8	0.888	0.907	g	2038	2319	g		0.99	1.14	0.94	1.12	2289
89.0 ^e	0.675	0.631	2159	2195	2062	0.86	1.45	0.87	1.48	0.82	1.38	2139
89.6 ^e	0.524	0.388	2101	2038	2036	0.66	1.57	0.61	1.47	0.64	1.52	2006

^a γ = activity coefficient = PY/P^0X X = mole fraction in the liquid phase Y = mole fraction in the vapor phase P = total pressure P^0 = vapor pressure of pure component^b Corrected for noncondensable gas in the system when cell is cooled to -78°C .^c Calculated from vapor density data (see text).^d Calculated from plutonium and uranium analysis of vapor sample.^e Uncertainty in results resulting from small liquid sample (see text).^f Weight of vapor sample in doubt.^g Fluorine correction not obtained owing to leak in equilibrium cell when cooled to -78°C .

A diagram of total pressure as a function of composition was prepared for temperatures of 73, 81, and 89°C (Figure II-14). Since the three methods of calculating the total pressure appear to be equally valid, the average of the three values was used. Pressures were adjusted to exactly 73, 81, and 89°C by applying the following correction to the average pressure for an individual determination:

$$\Delta P = (X_{UF_6})(\gamma_{UF_6}) \left(\frac{dP^0}{dT} \right)_{UF_6} \Delta T \\ + (1 - X_{UF_6})(\gamma_{PuF_6}) \left(\frac{dP^0}{dT} \right)_{PuF_6} \Delta T$$

where dP^0/dT was calculated for the temperature interval of interest from the published^{16, 17} vapor pressure equations for PuF₆ and UF₆. For purposes of these calculations it was necessary to assume that the activity coefficient did not change substantially over the temperature interval of the correction. The cor-

rected values appear in Table II-4 as "Average Pressure Corrected to 73, 81, or 89°C ".

The lines in Figure II-14 described as "Ideal Liquid Composition" for 73, 81, and 89°C , respectively, were obtained from a Raoult's Law calculation for an ideal solution of UF₆ and PuF₆ and are included for reference. All the data obtained are included on the graph even though the difficulties experienced in several experiments in the liquid sampling procedure may have affected the accuracy of some of the results. The difficulty in the liquid sampling procedure was presumably the result of plugging of the liquid sample valve orifice by solid PuF₄ present in the equilibrium cell. Complete filling of the liquid sample space resulted in a liquid sample of several grams. However, in several cases, liquid samples varying from 0.03 to 0.4 g were obtained. Nevertheless, all the values obtained are in reasonable agreement with values calculated on the basis of ideal behavior.

In Figure II-15 the mole fraction of PuF₆ in the liquid phase is plotted against the mole fraction of PuF₆ in the vapor phase. The ideal case of equal mole

¹⁷ B. Weinstock, E. E. Weaver, and J. Malm, J. Inorg. Nucl. Chem., **11**, 104-114 (1959).

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FIG. II-14. Pressure-Composition Diagram: Plutonium Hexafluoride-Uranium Hexafluoride.

108-9301

FIG. II-15. Vapor-Liquid Equilibrium for the System Plutonium Hexafluoride-Uranium Hexafluoride.

fractions of PuF_6 in the liquid and vapor phases is designated by the line labeled as "Ideal". The values obtained closely follow the ideal case.

d. CONCLUSIONS

In the region of low PuF_6 concentration studied, the system $\text{PuF}_6\text{-UF}_6$ differs, within the limits of experimental uncertainty, only slightly from ideal be-

havior. Activity coefficients calculated for UF_6 in these mixtures are very close to 1.0. This is to be expected since the activity coefficient of a pure component is considered to be 1.0 for calculations of this type. The activity coefficients for PuF_6 are generally greater than 1.0, indicating a possible slight positive deviation from ideality. Any wide deviation from ideality would be surprising in two substances as similar as UF_6 and PuF_6 . Inspection of the system according to methods of Hildebrand's regular solution theory¹⁸ predicts only very small deviations from ideality. The molar volumes of UF_6 and PuF_6 are assumed to be equal for this calculation.

The plot of mole fraction PuF_6 in the liquid phase against mole fraction PuF_6 in the vapor phase (Figure II-15) indicates that there is no azeotrope in the range of concentrations over which reliable data are available. If an azeotrope were present, the experimental points would cross the line of equal compositions in the liquid and vapor phase at the composition of the azeotrope.

Since the results indicate that the $\text{PuF}_6\text{-UF}_6$ vapor-liquid system is close to ideal in the UF_6 -rich mixtures studied, the purposes of the investigation have been substantially realized. A continuous fractional distillation of $\text{PuF}_6\text{-UF}_6$ mixtures would generally deal with UF_6 -rich mixtures, and a distillation column could be designed on the basis of ideal behavior of the system.

¹⁸ J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, 3rd Ed., Reinhold Publishing Co., New York, 1950, p. 210.

In addition, there is little fundamental interest in a system that exhibits ideal behavior. Extension of the determination of the vapor-liquid equilibrium into the region of PuF_6 -rich mixtures would result in an increase in the magnitude of problems already en-

countered as a result of PuF_4 deposition in the system and would eventually result in a significant radiation problem from the (α, n) reaction. Consideration of these factors resulted in a decision to discontinue the determinations.

5. Corrosion of Materials (W. H. GUNTHER)

a. INTRODUCTION

The fluid-bed fluoride volatility program is designed to develop processes for the recovery of uranium and plutonium from partially spent nuclear reactor fuels by the formation of the volatile hexafluorides of uranium and plutonium, which are subsequently separated from the volatile fission product fluorides. Nickel or nickel alloys such as Monel are commonly used as the material of construction for process equipment that is to be exposed to fluorine and to corrosive fluorides at elevated temperatures, since extensive attack on these materials is generally prevented by the formation of a protective nickel fluoride scale which limits further reaction. In order to make estimates of the expected useful lifetimes of equipment exposed to UF_6 , PuF_6 , fluorine, and the volatile fission product fluorides at temperatures up to 550°C , a knowledge of corrosion rates by these fluorides is required.

A series of static corrosion experiments have been performed at 500°C in which nickel-200, Monel, and Inconel coupons were exposed to GeF_4 , AsF_5 , SeF_6 , MoF_6 , and TeF_6 individually and in the presence of fluorine for periods up to 29.5 hr. Nickel-200, nickel-201 (low carbon), Monel, and Inconel coupons were exposed to UF_6 gas at 500°C for 8.0 and 28.8 hr. Corrosion rates were calculated from the weight change of the coupons after reaction. Intergranular penetration of the base metal was observed in many of the coupons.

Two experiments investigating the corrosion of nickel-200 coupons suspended in a 2-in. dia. fluid-bed reactor during fluorination of UO_2 and UO_2 - PuO_2 -fission product mixtures have been carried out.

Two 1½-in. dia. fluid-bed reactors, which had been exposed to UF_6 , PuF_6 , and fluorine for periods of 442 hr and 658 hr at temperatures up to 550°C , have been sectioned at various locations and the total amount of intergranular penetration measured.

b. CORROSION BY FLUORINE, UF_6 , AND FISSION PRODUCT FLUORIDES

(1) Experimental

The reactions were carried out in a ¾-in. OD 12 in. long nickel test tube. The temperature was maintained at $500 \pm 10^\circ\text{C}$ by control of a vertical, 1¼-in. dia.

resistance tube furnace through a proportionally circuited Variac connected to a pyrometer controller. The pyrometer was activated by a chromel-alumel thermocouple attached to the reaction vessel wall. The reaction vessel was always prefluorinated with fluorine at 550°C overnight prior to use.

The nickel, Monel, and Inconel coupons were used as received after an initial degreasing step. The fission product fluorides and UF_6 were purified by vacuum distillation, and their purities were ascertained by vapor density, vapor pressure, and infrared spectral measurements. The fluorine was passed through a NaF trap heated to 100°C to remove trace quantities of HF prior to use.

The specimen coupons were approximately 1 by 1.5 cm and ranged in thickness from 0.15 to 0.34 cm. The coupons, which had small holes drilled in each end, were weighed and connected together by nickel wire. After ten coupons were connected the top coupon was then fastened to a hook welded onto a ¾-in. male flare fitting and the reaction vessel was sealed to the flare fitting with a copper gasket. The reactant gas or gases were added to the reactor while the reactor was at room temperature. The pressure (measured at operating temperatures) of fluorine was maintained at 575 ± 100 and the pressure of fission product fluorides or UF_6 was maintained at 100 ± 20 mm. When fluorine was not present, fission product fluorides or UF_6 were periodically added to the reaction vessel when the pressure dropped to 80 mm as a result of consumption of reagents. However, when fluorine was present with a fission product fluoride, the reactor was evacuated and a fresh mixture was added when required. When the reaction temperature of 500°C was reached, the pressure was recorded and the experiment was started. At the conclusion of an experiment, the reactor was evacuated and allowed to cool slowly to room temperature. The coupons which did not show appreciable spalling of the fluoride scale were reweighed and corrosion rates were calculated from the weight gain of the coupon, assuming that only NiF_2 formed on the surface of the coupon.

In the systems under consideration, it is recognized that calculated corrosion rates based on specimen weight gain may be inaccurate for a variety of reasons: (1) the fission product fluorides may thermally

decompose, resulting in deposition of a lower fission product fluoride on the surface of the coupon; (2) compounds other than NiF_2 may be formed on the coupons during the reaction; and (3) spalling of the fluoride scale may occur during the reaction. Thermal decomposition of the fission product fluoride on the corrosion coupon would result in rates of corrosion seemingly greater than those actually occurring. Formation of compounds other than NiF_2 in the corrosion scale would result in similar errors. Spalling of the scale at any time during the exposure would result in apparent rates of corrosion less than those actually occurring. A procedure which allowed corrosion rates to be calculated from weight loss involved a method based on descaling of coupons. This method was successfully demonstrated by Chilenskas and Gundersen¹⁹ in similar corrosion studies. The method consisted of immersion of the specimens in an equimolar salt bath of potassium nitrate-sodium nitrate at 500°C for 1/2 hr. To determine the effect of this salt bath on the metals, fresh coupons of nickel-200, Monel, and Inconel were placed in the bath at 500°C for 1 1/2 hr, i.e., three times longer than the exposure of the test coupons. The longer descaling period for the new coupons resulted in apparent corrosion rates of less than 0.0005 mil/hr for all of the metals tested.

Intergranular penetration was determined by microscopic examination of exposed coupons which had been polished and etched. The following etchants were used:

Nickel-200 and nickel-201. A 1:1 mixture of concentrated nitric acid and glacial acetic acid for 10 to 30 sec.

Monel. Electrolytic etch in a 5% sulfuric acid solution for 10 to 30 sec at current densities of 0.5 to 2 amps/cm².

Inconel. A CuCl_2 -saturated aqua regia solution for 10 to 30 sec.

(2) Results

The results of the corrosion of nickel-200, Monel, and Inconel by some of the volatile fission product fluorides, UF_6 , and fluorine are tabulated in Table II-5, as mils of nickel reacted per hour of exposure. All of the rates obtained are averages of results for two to five coupons. The results of the microscopic examination are listed in Table II-6 as total penetration in mils.

Germanium Tetrafluoride. Nickel-200, Monel, and Inconel coupons were exposed to GeF_4 alone, and in the presence of fluorine at 500°C for 8.0 and 8.4 hr,

respectively. When the coupons were exposed to GeF_4 alone, a dark, uniform, adherent scale was formed. X-ray diffraction analysis of this scale showed the presence of NiF_2 and possibly GeO_2 . When GeF_4 and fluorine were the reactant gases, the nickel-200 and Monel coupons showed little visual evidence of attack. However, the Inconel coupons were severely corroded and were covered with a yellow-green scale.

Arsenic Pentafluoride. Nickel-200, Monel, and Inconel coupons were exposed to AsF_5 alone, and in the presence of fluorine, at 500°C for 7.0 and 7.2 hr, respectively. The exposure to AsF_5 resulted in the formation of a uniform scale on the coupon surface which varied in color from light green to black. When AsF_5 and fluorine were reacted with the coupons, a slight weight loss of all of the coupons was observed. The nickel-200 and Monel coupons showed no visual evidence of spalling. The Inconel coupons, however, were badly corroded and covered with a yellow-green scale.

Selenium Hexafluoride. Nickel-200, Monel, and Inconel coupons were exposed at 500°C to SeF_6 for 7.0 and 29.5 hr and to SeF_6 plus fluorine for 6.6 hr. When only SeF_6 was the reactant gas, very slight discoloring of all of the coupons occurred. When SeF_6 and fluorine were the reactant gases, the nickel-200 and Monel coupons showed very little reaction, but the Inconel coupons were badly corroded and covered with a yellow-green scale.

Molybdenum Hexafluoride. Nickel-200, Monel, and Inconel coupons were exposed at 500°C to MoF_6 for 7.0 and 9.2 hr and to MoF_6 plus fluorine for 6.0 and 7.0 hr. A darkening of all coupons was observed when exposed to MoF_6 alone. Representative coupons of all three metals after exposure for 9.2 hr were submitted for X-ray spectrochemical analysis for molybdenum before and after descaling. In all cases the amount of molybdenum found on the coupons before descaling was considerably greater than that found after descaling. A quantitative statement as to the amount of molybdenum removed by descaling cannot be made. When the coupons were exposed to a mixture of MoF_6 and fluorine, the nickel-200 and Monel coupons showed very little reaction, but the Inconel coupons were severely corroded and were covered with a yellow-green scale.

Tellurium Hexafluoride. Nickel-200, Monel, and Inconel coupons were exposed at 500°C to TeF_6 for 5.7, 7.6, and 18.9 hr and to a mixture of TeF_6 and fluorine for 7.8 hr. When the coupons were exposed to TeF_6 alone, corrosion rates for nickel-200, Monel, and Inconel ranged from 0.004 to 0.608, 0.007 to 0.250, and 0.006 to 0.025 mil/hr, respectively. The reason for the wide discrepancy in rates is not known. The coupons showing the highest corrosion rates were those located

¹⁹ A. A. Chilenskas and G. E. Gundersen, Engineering Development of Fluid-Bed Fluoride Volatility Processes, Part 7, The Corrosion of Nickel in Process Environments, ANL-6979 (March 1965).

TABLE II-5. CORROSION OF NICKEL AND NICKEL-CONTAINING ALLOYS BY SELECTED VOLATILE FLUORIDES

Temperature: 500 $\pm$ 10°C
 UF₆ or F.P. fluoride pressure: 100 $\pm$ 20 mm
 Fluorine pressure: 575 $\pm$ 100 mm

Run Number	Corrosive Environment	Time (hr)	Corrosion Rate ^a (mils/hr)			
			Nickel-200	Monel	Inconel	Nickel-201
12	GeF ₄	8.0	0.002 —	0.004 —	0.002 —	— —
18	GeF ₄ + F ₂	8.4	0.002 (nil)	0.002 (0.001)	^b (0.130)	— —
14	AsF ₅	7.0	0.006 (0.001)	0.004 (nil)	0.002 (nil)	— —
19	AsF ₅ + F ₂	7.2	^c (0.002)	^c (0.003)	^b (0.202)	— —
15	SeF ₆	7.0	nil (0.001)	0.001 (0.001)	0.002 (0.002)	— —
26	SeF ₆	29.5	nil ^d	nil ^d	0.001 ^d	— —
20	SeF ₆ + F ₂	6.6	0.003 (0.001)	0.005 (0.001)	^b (0.097)	— —
9	MoF ₆	7.0	0.002 —	0.008 —	0.005 —	— —
24	MoF ₆	9.2	0.003 (0.001)	0.003 (nil)	0.002 (0.001)	— —
16	MoF ₆ + F ₂	6.0	0.001 (0.001)	0.002 (nil)	0.063 (0.197)	— —
29	MoF ₆ + F ₂	7.0	0.001 ^d	0.002 ^d	^b (0.284)	— —
10	TeF ₆	7.6	0.004 —	0.007 —	0.006 —	— —
25	TeF ₆	18.9	^b (0.040)	^b (0.008)	^b (0.011)	— —
30	TeF ₆	5.7	^b (0.608)	^b (0.250)	^b (0.025)	— —
17	TeF ₆ + F ₂	7.8	0.001 (0.001)	nil (0.001)	0.095 (0.179)	— —
27	SF ₆	28.7	nil (nil)	nil (nil)	nil (nil)	— —
8	UF ₆	8.0	^b —	0.008 —	0.010 —	— —
28	UF ₆	28.8	0.004 (0.001)	— —	— —	0.004 (nil)
13	F ₂	7.0	0.002 (0.003)	nil (0.001)	^b (0.044)	— —
23	F ₂	8.6	0.003 —	0.004 —	^b (0.138)	— —

^a Corrosion rates were calculated from weight gain of coupons assuming that only NiF₂ was formed on the surface of the coupon. The numbers in parentheses are calculated from weight loss data following immersion of the coupons in an equimolar KNO₃-NaNO₃ salt bath at 500°C for ½ hr, assuming complete removal of all scale. Corrosion rates are expressed in mils of metal reacted per hour of exposure. Rates reported as nil are less than 0.001 mil/hr.

^b Excessive spalling of corrosion scale; weight gain data unreliable.

^c Weight gain data not obtained since a weight loss of all coupons was observed prior to descaling.

^d Scale was not completely removed by exposure of the coupons to a KNO₃-NaNO₃ bath at 500°C for ½ hr.

near the top of the vertical reactor, but there is no evidence that a significant temperature gradient existed along the length of the reactor. At the conclusion of the 18.9-hr experiment, it was observed that the nickel reaction vessel was completely filled with a light gray solid. The nickel wire supporting the coupons had separated. The uppermost coupon (nickel) was free from any scale but had lost nearly half its weight. The next lower coupon (Monel) showed extreme lateral outgrowth of a black scale from all six surfaces. Small, shiny, metallic-appearing crystals were interspersed within the scale on all surfaces. Close inspection of the coupon showed the scale to be composed of layers. The remaining eight coupons showed lesser degrees of corrosion and exhibited many areas where spalling of the scale had occurred. The corrosion rates for all coupons except the top two are listed in Table II-5. X-ray diffraction analyses of the solid reaction products are listed in Table II-7.

The buildup of solid reaction products in the vessel to such an extent that the products eventually engulfed the coupons may have contributed to the apparent de-

crease in corrosion rates from the top to the bottom of the reactor; therefore, the design of the nickel reactor was modified. The modified nickel reactor was constructed with a large reservoir at the bottom and located outside of the heated zone. During the reaction, the spalled reaction products collected in this reservoir, thus allowing the reactant gas free access to the coupons. Nickel-200, Monel, and Inconel coupons were exposed to TeF₆ for 5.7 hr at 500°C in this reactor. Again, as in the 18.9-hr experiment, the coupons closest to the top of the reactor showed the greatest amount of corrosion. However, the difference in corrosion rates from top to bottom of the reactor was not as marked as previously observed. A metallic-appearing substance had condensed onto the nickel support wire immediately above the hot zone. X-ray diffraction analysis showed this substance to be metallic tellurium. The vapor pressure of tellurium at 500°C is 0.9 mm.²⁰ The nickel coupons were the most severely corroded and were coated with a gray scale. Both the Monel and

²⁰ G. Gattow and A. Schneider, *Angew. Chem.* **71**, 189 (1959).

TABLE II-6. RESULTS OF MICROSCOPIC EXAMINATION OF CORROSION SPECIMENS EXPOSED TO FISSION PRODUCT FLUORIDES AT 500°C
For composition of etching solutions, see text

Corrosion Environment	Reaction Time (hr)	Microscopic Examination			
		Nickel-200	Monel	Inconel	Nickel-201
GeF ₄	8.0	No I.G. ^a attack	No I.G. ^a attack	No I.G. ^a attack	—
GeF ₄ + F ₂	8.4	Uniform I.G. attack to 0.4 mil, isolated areas to 0.8 mil	Isolated areas of I.G. attack to 0.4 mil	No I.G. attack	—
AsF ₅	7.0	I.G. attack on about 60% of surface to about 0.4 mil	Very slight attack, isolated areas to 0.3 mil	No I.G. attack	—
AsF ₅ + F ₂	7.2	Uniform I.G. attack to 0.4 mil, isolated areas to 0.8 mil	Isolated areas of I.G. attack to 0.4 mil	No I.G. attack	—
SeF ₆	7.0	Uniform I.G. attack to 1.0 mil, isolated areas to 1.5 mils	No I.G. attack	No I.G. attack	—
SeF ₆	29.5	Uniform I.G. attack 0.5 to 2.0 mils, isolated areas to 2.5 mils	About 25% of surface area shows I.G. attack to 0.2 mil	No I.G. attack	—
SeF ₆ + F ₂	6.6	Uniform I.G. attack to 0.4 mil, isolated areas to 0.8 mil	No I.G. attack	No I.G. attack	—
MoF ₆	7.0	No I.G. attack	Isolated areas of I.G. attack to 0.3 mil	No I.G. attack	—
MoF ₆	9.2	Isolated areas of I.G. attack to 0.4 mil	Isolated areas of I.G. attack to 0.4 mil	No I.G. attack	—
MoF ₆ + F ₂	6.0	Uniform I.G. attack to 0.4 mil, isolated areas to 0.8 mil	Isolated areas of I.G. attack to 0.5 mil	No I.G. attack	—
TeF ₆	7.6	No I.G. attack	No I.G. attack	No I.G. attack	—
TeF ₆	18.9	About 50% of the surface area has I.G. attack to 0.2 mil, remaining areas show no I.G. attack. Coupons having the higher corrosion rates show very little I.G. attack	No I.G. attack	No I.G. attack	—
TeF ₆ + F ₂	7.8	Uniform I.G. attack to 0.4 mil, isolated areas to 0.8 mil	No I.G. attack	No I.G. attack	—
SF ₆	28.7	Extreme I.G. attack at all grain boundaries from 2.0 to 4.0 mils, isolated areas to 8.0 mils	About 50% of surface area shows I.G. attack to 0.3 mil, isolated areas to 0.7 mil	About 10% of the surface has I.G. attack to 0.2 mil	—
UF ₆	8.0	Isolated areas of I.G. attack to 0.2 mil	Isolated areas of I.G. attack to 0.5 mil	No I.G. attack	—
UF ₆	28.8	Uniform I.G. attack to 0.4 mil	—	—	Uniform I.G. attack to 0.8 mil, isolated areas to 1.5 mils
F ₂	7.0	Uniform I.G. attack to 1.0 mil	No I.G. attack	No I.G. attack	—
F ₂	8.6	Uniform I.G. attack to 0.4 mil, isolated areas to 1.0 mil	Isolated areas of I.G. attack to 0.4 mil	No I.G. attack	—

^a I.G. = Intergranular.

Inconel coupons were coated with a black scale, the Inconel coupons showing the least corrosion.

The Monel coupon from the 18.9-hr experiment, which showed the greatest amount of corrosion, was submitted for electron probe analysis.²¹ Two different types of analyses were performed. In the first, continuous transverse traces were made from the Monel matrix across the corrosion layers, and the relative concentra-

²¹ The assistance of Dr. N. R. Stalica is gratefully acknowledged.

tions of nickel, copper, and tellurium were recorded as a function of distance. The second type of analysis consisted of fixed point measurements at various points along the first trace. In this type of analysis, the number of X-ray quanta emanating from a given point in the sample were recorded as a function of time. This type of analysis yields more accurate results while the first type gives a more graphic representation of the concentration variation in the sample. Both types of analyses were combined to identify the various layers.

TABLE II-7. X-RAY DIFFRACTION ANALYSES OF SOLIDS FROM THE REACTION OF TeF_6
WITH NICKEL-200, MONEL, AND INCONEL
Temperature: $500 \pm 10^\circ\text{C}$
 TeF_6 pressure: 100 ± 20 mm

Sample Identification	Analyses of Solids	
	18.9-hr Experiment	5.7-hr Experiment
Gray scale from surface of nickel coupon Black scale from surface of Monel coupon	NiF_2 , NiTe_2 and NiTe Major: Cu_{2-x}Te Minor: Possibly NiTe_2 Cu-Te (36.1-36.4% Te) NiF_2	NiF_2 and NiTe_2 Major: NiTe_2 Cu _{2-x} Te Minor: Probably NiF_2 CuTe
Black scale from surface of Inconel coupon	Major: NiF_2 Minor: NiTe_2 , Possibly CrF_3^a CuTe, Te, Possibly NiF_2	Major: NiF_2 , NiTe_2 Minor: Possibly CrF_3 —
Metallic-appearing solid found on surface of Monel coupon	—	—
Metallic-appearing solid found on nickel support wire	—	Tellurium metal only

^a Inconel contains about 15% chromium.

108-9271

FIG. II-16. Photomicrograph of Monel Coupon after Exposure to TeF_6 for 18.9 hr at 500°C .

The extensive black scale, approximately 800μ thick, was, for the most part, identified as NiF_2 .²² Interspersed in this scale were numerous violet layers tentatively identified as Cu_4Te_3 with a 0.95 w/o nickel impurity (see Figure II-16). A white band located about 100μ from the coupon surface was identified as a mixture of copper and nickel tellurides. A 50μ wide

metallic-lustered band adjacent to the Monel coupon was identified as NiTe_2 with traces of copper and iron impurities. No tellurium metal was determined to have diffused into the Monel coupon. The metallic-appearing crystals imbedded in the black scale were colored rose and blue-gray and were identified as CuTe. The copper and tellurium concentrations varied by less than 0.5 w/o from one color region to another. The colors may have been due to trace impurities of manganese, iron, or nickel which were not readily detected. A gray

²² The material was probably hydrated NiF_2 ; water was used to polish and prepare the sample.

108-9399

FIG. II-17. Comparison of Intergranular Penetration of Nickel-200, Monel, and Inconel at 500°C by SF₆, SeF₆, and TeF₆.

coating surrounding the CuTe crystals was shown to be metallic tellurium.

When nickel-200, Monel, and Inconel coupons were exposed to a mixture of TeF₆ and fluorine for 7.8 hr at 500°C, the nickel and Monel coupons showed very little evidence of reaction. However, the Inconel coupons were severely corroded and were covered with a yellow-green scale. The corrosion experiments involving TeF₆ will be repeated in order to resolve the ambiguous results obtained to date.

Sulfur Hexafluoride. Nickel-200, Monel, and Inconel coupons were exposed to SF₆ at 500°C for 28.7 hr. Although sulfur is not a fission product, the study of the corrosiveness of SF₆ permits an intercomparison to be made of the corrosive effects of Group VI (S, Se, Te) hexafluorides. The surfaces of all of the coupons were only slightly dulled as a result of the exposure to SF₆. Negligible corrosion rates were obtained.

Uranium Hexafluoride. Nickel-200, Monel, and Inconel coupons were exposed to UF₆ for 8.0 hr at 500°C. The nickel coupons showed the most corrosion and were coated with a green and black scale and much spalling of the scale was evident. The scale was shown by X-ray diffraction analysis to be: major, UF₄; very minor, possibly NiF₂. Nickel-200 and nickel-201 (low carbon) coupons were exposed to UF₆ for 28.8 hr at 500°C; localized corrosion of the metal resulted. Some of the

areas of the coupons remained relatively bright and shiny, whereas other areas were coated with a bright green deposit identified as UF₄ by X-ray diffraction analysis. The corrosion of nickel metal by UF₆ has been previously studied by Langlois.²³ He found that at UF₆ pressures of 220 to 240 mm, corrosion rates of 0.0008 and 0.002 mil/hr were obtained at 455 and 535°C, respectively. Langlois' results compare favorably with the results obtained in our study in which a corrosion rate of 0.001 mil/hr (based on data of weight loss of coupon after descaling) was obtained at 500°C and a UF₆ pressure of 100 ± 20 mm.

Fluorine. Nickel-200, Monel, and Inconel coupons were exposed to fluorine for 7.0 and 8.6 hr at 500°C. Corrosion rates of the metals by fluorine alone must be known in order to evaluate the effect of the presence of both fluorine and fission product fluorides on the corrosion rates of these metals. Corrosion rates for nickel-200 of 0.002 and 0.003 mil/hr were obtained for exposure times of 7.0 and 8.6 hr, respectively. These data compare very favorably with those of Jarry et al²⁴ who obtained a rate of 0.002 mil/hr after an 8-hr exposure at 500°C.

(3) Discussion

If the behavior of nickel^{19, 24} is also considered typical of Monel, then it can be anticipated that rates of corrosion derived from short-term experiments such as these should be considerably greater than rates derived from long-term experiments. For this reason, data such as those listed in Table II-5 should represent maximum corrosion rates for the indicated metals. Since a rate of 0.001 mil/hr is equivalent to about 8.8 mils/yr, the rates for nickel-200 and Monel given in Table II-5 indicate that these alloys are promising materials of construction for equipment for fluoride volatility processes. Because of the high rate of corrosion of Inconel by fluorine and by fluorine together with a fission product fluoride at 500°C, this alloy is presently considered to be unacceptable for process use.

A comparison of the intergranular penetration caused by SF₆, SeF₆, and TeF₆ on nickel-200, Monel, and Inconel is shown in Figure II-17. The effect of sulfur on nickel has long been recognized to be severe although the chemistry of the intergranular attack is undefined. The data illustrated in Figure II-17 suggest that, although the intergranular attack of nickel and nickel alloys by SF₆ is significant, TeF₆ attacks nickel-200, Monel, and Inconel to a lesser degree (based on rates of penetration) than does either SeF₆ (a fission product of low yield) or SF₆. Hence, excessive concern regarding the intergranular corrosion by TeF₆ seems unwarranted. It should be noted, however, that TeF₆, unlike

²³ G. Langlois, French Report CEA-2385 (1963).

²⁴ R. Jarry, W. Gunther, and J. Fischer, ANL-6684.

SF_6 and SeF_6 , does cause corrosion of nickel-200, Monel, and Inconel by surface reaction to form tellurides of nickel and copper and, to a lesser extent, to form NiF_2 . Although the rates of corrosion of nickel-200 and Monel by TeF_6 at 500°C are not clearly defined at the present time, it appears that at relatively high TeF_6 pressures severe corrosion of the metals will result. It should be noted that the pressure of TeF_6 gas in the fluid-bed reactor under process conditions should be considerably less than 1 mm Hg.

No increase in the corrosion rates of nickel-200, Monel, and Inconel by fluorine at 500°C was observed when GeF_4 , AsF_5 , SeF_6 , MoF_6 , or TeF_6 were present with the fluorine during exposure to the metals.

c. CORROSION OF COUPONS AND LABORATORY-SCALE FLUID-BED REACTORS BY PuF_6 , UF_6 , AND FLUORINE

(1) Corrosion of Coupons in a Two-inch Fluid-Bed Reactor

Two experiments have been completed to determine and evaluate the corrosion of nickel-200 in the 2-in. dia. fluid-bed reactor during fluorination of UO_2 or UO_2 - PuO_2 -fission product mixtures at temperatures up to 550°C . In each experiment a total of six coupons were suspended in the reactor, three located a few inches above the bed during fluidization, and three located directly in the bed. The temperatures of both sets of coupons were approximately equal at all times. In each set of three coupons, one coupon contained an area of nickel-200 weld (about 5–10% of the total surface area). The corrosion rates were calculated from the weight loss of the coupons after descaling in a fused salt bath. The coupons were subsequently mounted in plastic, polished, etched, and microscopically examined for intergranular attack.

The experimental conditions and the results obtained from corrosion rate and intergranular penetration measurements are presented in Table II-8. These results indicate that, for both experiments, the rates of corrosion of the coupons in the bed are about two to three times the rates of the coupons suspended above the bed. This can be attributed to erosion of the protective NiF_2 scale by the alumina fluidized bed. In addition, the coupons which contained an area of nickel-200 weld and which were exposed for 40 hr showed a greater corrosion rate than the other coupons. Comparison of the corrosion rates between experiments should not be made because of differences in the environmental conditions, namely, longer exposure times and the presence of plutonium. In both experiments all of the coupons showed a uniform intergranular attack of the nickel at nearly all of the grain boundaries on the metal surface. The depth of intergranular penetra-

TABLE II-8. THE CORROSION OF NICKEL-200 COUPONS IN A TWO-INCH DIAMETER FLUID-BED REACTOR

A. Six coupons were exposed to the environment of a 2-in. dia. fluid-bed reactor for a total of 40 hr under the following conditions: 3 hr oxidation-fluorination (O_2 - F_2) at 450°C , 28 hr fluorination (F_2) at 450 – 550°C , and 9 hr HF-O_2 at 400 – 450°C . A total of 2627 g of UO_2 pellets were fluorinated.

Corrosion Rate ^a (mils/year)		Microscopic Examination
In Reactor Directly Above Bed	In Fluid Bed	
1	6	Uniform intergranular attack of all coupons and the welded area of 0.4 to 0.8 mil, isolated areas to 1.2 mils.
3 ^b	10 ^b	
1	16	

B. Six coupons were exposed to the environment of a 2-in. dia. fluid-bed reactor for a total of 68 hr under the following conditions: 10 hr oxidation-fluorination (O_2 - F_2) at 450 – 500°C , 3 hr of single zone fluorination (F_2) at 450 – 550°C , and 55 hr of recycle fluorination (F_2) at 450 – 550°C . A total of 1961 g of UO_2 - PuO_2 pellets containing nominally 86 w/o uranium, 0.4 w/o plutonium, and 1 w/o non-radioactive fission products (as the oxides) were fluorinated.

Corrosion Rate ^a (mils/year)		Microscopic Examination
In Reactor Directly Above Bed	In Fluid Bed	
12	36	Uniform intergranular attack of all coupons and the welded area of 1.0 to 2.0 mils, isolated areas to 3.5 mils.
24 ^b	33 ^b	
57	32	

^a Rates calculated from weight loss of the coupons after descaling in an equimolar KNO_3 - NaNO_3 salt bath at 500°C for $\frac{1}{2}$ hr.

^b Coupon contains an area of nickel-200 weld.

tion of the welded areas of the coupons was similar to that of unwelded coupons. It should be noted, however, that the total intergranular penetration for a given area of the welded sections of coupons from both experiments was considerably less than that of the remaining metal because of the much larger grain size of the weld as compared to the base metal. In neither experiment was appreciable grain growth of the metal, including the welded areas, observed after exposure in the fluid bed. No increase in intergranular penetration was seen at the junction of the base metal and the areas containing the nickel-200 welds.

(2) 1½-Inch Fluid-Bed Reactor

Two 1½-in. dia. nickel fluid-bed reactors which had been exposed to UF_6 , PuF_6 , and fluorine for periods of 442 hr and 658 hr and at temperatures up to 550°C were sectioned at the following locations in preparation for microscopic examination: (1) the reactor wall at an

TABLE II-9. MICROSCOPIC EXAMINATION OF SECTIONED 1½-INCH DIAMETER FLUID-BED REACTORS AFTER EXPOSURE TO UF₆, PuF₆ AND FLUORINE

Areas of Examination	442-hr Exposure ^a	658-hr Exposure ^b
Reactor wall above fluidized bed in heated zone	Internal ^c —uniform penetration 1.5 to 2.0 mils, isolated areas to 2.5 mils External ^d —uniform penetration 2.0 to 2.5 mils, isolated areas to 3.5 mils	Internal ^c —fairly uniform penetration 0.6 to 1.2 mils, isolated areas to 2.5 mils External ^d —uniform penetration 0.4 to 0.8 mil, isolated areas to 2.0 mils
Reactor wall 1-in. above conical section	Internal ^c —uniform penetration 1.0 to 1.5 mils, isolated areas to 2.0 mils External ^d —uniform penetration 0.6 to 1.0 mils, isolated areas 1.5 mils	Internal ^c —uneven penetration from zero to 2.0 mils External ^d —uniform penetration 0.8 to 2.0 mils, isolated areas to 2.5 mils
Welded tip of thermocouple well	Internal ^c —uniform penetration 1.2 to 1.8 mils, isolated areas to 2.5 mils	Internal ^c —very uneven penetration up to 9 mils
Cross section of thermocouple well immediately below tip	Internal ^c —uniform penetration 0.8 to 1.2 mils, isolated areas to 1.5 mils External ^d —uniform penetration 2.0 to 3.0 mils, isolated areas to 3.5 mils	Internal ^c —uniform penetration 4.0 to 6.0 mils, isolated areas to 9 mils External ^d —uniform penetration 2.0 to 3.0 mils, isolated areas to 4.0 mils

^a This reactor had been exposed to process gases for 220 hr at 550°C, 110 hr at 500°C, 97 hr at 450°C, and 15 hr at 300°C.

^b The exposure period for this reactor had been 374 hr at 550°C, 111 hr at 500°C, and 173 hr at 450°C.

^c Internal: surface of the reactor that had been exposed to UF₆, PuF₆, and fluorine.

^d External: surface of the reactor that had been exposed to the atmosphere.

elevation above the bed during fluidization but in the heated zone, (2) the reactor wall which was exposed to the fluid bed at a location one inch above the conical gas distributor, and (3) a thermocouple well located within the fluid bed near the conical gas distributor. Two sections of the well were made: one at the welded tip and one immediately adjacent to the tip. The thermocouple well was a ¼-in. dia. nickel tube entering the reactor from the bottom through the conical section and extending about 3 in. into the reactor. Samples taken from the reactor wall were obtained from opposite sides of the reactor. The samples were mounted in plastic, etched and examined for intergranular attack. The results are shown in Table II-9.

Both the internal (exposed to the reactor environment) and external (exposed to the atmosphere) surfaces of the reactors were examined. In the case of the reactor that had been exposed to the corrosive fluorides

for a total of 442 hr, the intergranular attack was quite uniform at all locations examined and averaged 1 to 2 mils in depth. In the case of the reactor that had been exposed for 658 hr, a wide variation was observed in the depth of intergranular penetration, which ranged from zero to 9 mils. The surface of the internal wall of the reactor was very uneven, thereby indicating extensive reaction of the metal followed by spalling of the NiF₂ scale. Erosion of the NiF₂ scale by the fluidizing bed may have also been a factor. Corrosion observed on the external surfaces of the reactors has been attributed to the oxidation of nickel by air.

d. FUTURE WORK

Additional experiments designed to define the effect of PuF₆ on the corrosion rates are planned. In addition, other alloys which may be applicable to the fluid-bed fluoride volatility process are to be examined.

B. ENGINEERING-SCALE INVESTIGATIONS OF FLUID-BED FLUORIDE VOLATILITY PROCESSES (A. A. JONKE)

1. Recovery of Uranium and Plutonium from Uranium Dioxide Fuels in the Engineering-Scale Alpha Facility (N. LEVITZ, G. J. VOGEL, I. KNUDSEN, E. L. CARLS, J. V. NATALE, L. YOUNGBLOOD,²⁵ R. LAMBERT,²⁶ W. A. MURPHY, R. KINZLER, B. KULLEN, J. HEPPERLY, M. DEERWESTER, C. SCHOFFSTOLL, J. GERARD²⁷)

A process scheme having three alternative routes is currently being evaluated for the recovery of uranium

²⁵ Temporary staff appointee from ORNL.

²⁶ Industrial trainee from the General Electric Co.

²⁷ Co-op student from Purdue University.

and plutonium from oxide fuels. This scheme is shown in Figure II-1, ANL-6925, p. 108 and consists of the following major steps: decladding, fluorination, distillation, thermal decomposition, and conversion to final products. These steps may be combined in three

different series depending on the desired form of the products.

An engineering-scale alpha facility has been constructed to permit demonstration of the main steps of fluid-bed fluoride volatility reprocessing schemes for $\text{UO}_2\text{-PuO}_2$ fuels. Process equipment is housed in the larger of two alpha boxes comprising the facility. The smaller box contains off-gas scrubbers and other auxiliary equipment.

Three pilot systems are to be operated in this facility: a fluorinator for processing batches of oxide pellets to hexafluorides; a second fluid-bed unit (referred to as a converter) for studies of the conversion of $\text{UF}_6\text{-PuF}_6$ mixtures to dense, mixed $\text{UO}_2\text{-PuO}_2$ particles and for studies of thermal decomposition²⁸ as a means of separating plutonium as PuF_4 from $\text{UF}_6\text{-PuF}_6$ mixtures; and a distillation column for studies of $\text{UF}_6\text{-PuF}_6$ mixtures. The first two units are now operational with plutonium-bearing materials. A complete description of the alpha facility and these two processing systems is given in a topical report.²⁹ The distillation column (described in ANL-7055, pp. 138-141) has been fabricated and is now installed in a mock-up area. Upon completion of performance tests, the unit will be installed in the alpha facility for work on process mixtures.

Process steps of the ANL Reference Flowsheet of January 1, 1965 (Figure II-1, ANL-7055, pp. 99-100) are under current investigation. In this scheme the fluorinator and thermal decomposer (or converter) are operated in tandem. Initial plans are for three fluorination-thermal decomposition experiments to be made with $\text{UO}_2\text{-PuO}_2$ pellets under near-identical conditions to obtain information on plutonium behavior (extent of recovery, disposition, material balances). Partial results from the first of these runs with $\text{UO}_2\text{-PuO}_2$ are reported here. Data that will assist in the establishment of accountability procedures are to be obtained. The sequence of operations involves the processing of a batch of fuel pellets in the fluorinator system to a $\text{UF}_6\text{-PuF}_6$ mixture by the two-zone oxidation-fluorination method (see ANL-7055, p. 99). The reactions are conducted in a bed of inert solids (high-fired alumina) which serves as a heat transfer medium. The hexafluoride product is collected in cold traps, vapor-transferred to a product receiver, and then fed as vapor

through the fluid-bed thermal decomposer. The non-decomposed fraction (mainly UF_6) is re-collected in the fluorinator cold traps. A final vapor transfer of the hexafluoride from the cold traps to a product receiver after the thermal decomposition step completes the sequence of operations.

Final shakedown experiments using uranium feed materials and the initial experiment with uranium-plutonium feed material were performed in the fluorinator and in the converter. The converter tests included both the conversion of UF_6 to UO_2 and thermal decomposition using a feed containing UF_6 only. Overall facility systems (ventilation, alarm circuits) and written operating procedures were given final checks in the shakedown period. The initial experiment with uranium-plutonium feed material involved fluorination of the feed material and thermal decomposition of the $\text{UF}_6\text{-PuF}_6$ product. Fairly complete operational data but only preliminary analytical data are presented on this experiment.

Overall Facility Work. Final facility checks included leak-testing of both alpha boxes. Pressure testing was carried out after the windows were sealed in place; a room-temperature-curing silicone rubber was used as sealant. Tests were made with the alpha boxes under a positive pressure of 2.5 in. H_2O even though the boxes are normally operated at 0.5-in. negative water pressure with normal single-pass air flow through the large and small boxes at rates of 600 and 150 cfm, respectively. The tests were made to insure that no major leaks remained. At 2.5 in. of water pressure, leakage rates were 0.11 and 0.06 cfm (0.42% and 0.07% of box volume per hour) for the large and small box, respectively. (For purposes of making comparisons, it might be noted that the leakage through a 0.25-in. dia. opening is 1 cfm at 2-in. H_2O pressure.) Both measured values of the leakage rate were about an order of magnitude smaller than that for the reference leak. A helium mass spectrometer leak detector was used extensively in this work.

a. FLUORINATION EXPERIMENTS

A simplified equipment flowsheet of the fluorination pilot plant is shown in Figure II-18. The pilot plant includes a fluorination fluid-bed reactor (3-in. dia. nickel pipe) with disengaging and filter sections, two cold traps (each mounted on a continuous-readout scale) for desublimating the hexafluorides, a backup NaF -filled trap, a gas recycle pump, and a thermal conductivity cell (TCC) for continuous in-line fluorine analysis. Auxiliary equipment includes activated alumina traps for fluorine disposal and a scrubber system.

Pellet fuel is processed in the fluorinator using the two-zone oxidation-fluorination scheme. In this scheme, the pellets are loaded into the fluorinator to form a

²⁸ L. E. Trevorrow, J. Fischer, and J. G. Riha, Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part III. Separation of Gaseous Mixtures of Uranium Hexafluoride and Plutonium Hexafluoride by Thermal Decomposition, ANL-6762, August 1963.

²⁹ G. J. Vogel, E. L. Carls, and W. J. Mechem, Engineering Development of Fluid-Bed Fluoride Volatility Processes, Part 5. Description of a Pilot-Scale Facility for Uranium Dioxide-Plutonium Dioxide Processing Studies, ANL-6901, December 1964.

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FIG. II-18. Fluorination Process Equipment.

packed bed, and sufficient alumina is added to the reactor to fill the voids within the packed bed and to provide a fluid bed 2 ft deep above the pellets. A mixture of oxygen and nitrogen is introduced into the pellet zone, causing pulverization of the pellets and the formation of U_3O_8 and PuO_2 fines. These fines are transported in the gas stream to the upper fluidization zone where they are fluorinated to UF_6 and PuF_6 by reaction with a separate fluorine stream. As shown in Figure II-18, four fluorine inlets at different elevations are provided on the fluorinator. As the pellet bed is consumed by reaction with oxygen, fluorine is introduced at successively lower ports. The hexafluoride recovery step is completed by a one-zone fluorination period followed by a cleanup period with 90 v/o fluorine to remove the last traces of uranium and plutonium from the alumina bed material.

The fuel material for the fluorination experiments was $\frac{1}{2}$ -in. dia. UO_2 or UO_2 - PuO_2 right cylinders of 90% theoretical density. Fission product oxides were added to the UO_2 - PuO_2 pellets to simulate more closely the processing of irradiated fuel.

Procedure and Conditions. Processing conditions employed for the current series of experiments are described below.

Fuel charge:	8.8 kg of pellets (~12 to 14-in. deep fluidized-packed bed depending on pellet density)
Alumina charge:	Sufficient to give about a 2-ft depth above the pellets (~6-7 kg of Alcoa Tabular T-61, nominal 48-100 mesh alumina)

Fuel support:	3-in. deep bed of nickel balls ($\sim \frac{1}{8}$ - to $\frac{1}{4}$ -in. dia.)
Vertical temperature gradient in the pellet bed:	50 to 100°C
Superficial fluidizing gas velocity	
Lower zone:	~ 1.0 ft/sec
Upper zone:	~ 1.5 ft/sec

For the period of two-zone operation, the maximum bed temperature was 450°C; maximum reactant concentrations for oxygen and fluorine in the reactor were 25 and 15 v/o, respectively. A fluorination period at 450°C using up to 15 v/o fluorine with the gas being admitted at the bottom of the reactor followed the two-zone operation. Recycle was employed in this period for fluorine economy. When the rate of hexafluoride production during this fluorination period appeared to have ceased, as indicated by absence of changes in weight of the cold trap (scale sensitivity, about 20 g), final cleanup of the residual uranium and plutonium from the alumina bed was accomplished by recycle-fluorination with 90 v/o fluorine. Generally, bed temperatures were increased gradually from 450 to 500°C and finally to 550°C and were maintained at each level for about 3 to 4 hr. Table II-10 summarizes some of the conditions and results of the three recent runs.

Discussion of Runs 3, 4, and Pu-1. The experiment with plutonium-containing materials, run Pu-1 was the shortest in overall duration, and was, perhaps, the most satisfactory in terms of overall hexafluoride pro-

TABLE II-10. SUMMARY OF RECENT FLUORINATION RUNS
 Fuel charge: 8.8 kg of UO_2 pellets in shakedown runs 3 and 4
 2.3 kg UO_2 + 6.5 kg of 0.5 w/o PuO_2 - UO_2 pellets in run Pu-1

	Total Duration (hr)	Two-Zone Reaction Period			Duration of Single-Zone Fluorination Period ^b (hr)	Cleanup Period (Total Recycle)		Final Bed Analysis (w/o)	
		Duration (hr)	Average Hexafluoride Production Rate to 95% Collection Point ^a (kg/hr)	Average Fluorine Utilization (%)		Duration (hr)	Maximum Temperature (°C)	U	Pu
Shakedown Run 3	27.0	15.0	0.5	~50	8.0	4.0	500	0.046	—
Shakedown Run 4	35.8	20.5	0.4	~50	5.3	10.0	500	0.025	—
Run Pu-1	20.5	8.0	1.0	~50	4.2	8.3	550	0.018 ^c	0.025 ^c

^a This point coincides approximately with the end of the two-zone reaction period.

^b Gas was fed either once-through or recycled during this period, depending on fluorine utilization.

^c Analyses of sample of fluid bed taken at end of run. Values do not represent the uranium and plutonium in the held-up fines.

duction and general operability. Hexafluoride rates twice the average (i.e., at ~2 kg/hr) were sustained for 30- and 60-min periods, thereby giving the best overall average UF_6 production rate, 1.0 kg/hr, in the two-zone reaction period.

For shakedown run 4, the two-zone reaction period was considerably longer than those of the other experiments because of a test of an automatic fluorine control system. Input fluorine was controlled by the fluorine exit concentration which was continuously measured by an in-line thermal conductivity cell. Control was successful, but the system requires more on-stream time to be considered fully operational. In general, fluorine utilization was good, near 50%, in the two-zone reaction periods of the three runs.

The higher uranium removals in run 4 and run Pu-1 are a result of longer cleanup times (10 hr in run 4 vs 4 hr in run 3) and higher final temperatures during the recycle-fluorination period (550°C for run Pu-1). For run Pu-1, the final values of 0.018 and 0.025 w/o for uranium and plutonium concentrations in the alumina bed represent >99.9 and 95% removals, respectively, for this single use of the bed. These values do not take into consideration the uranium and plutonium which was present as fines in the dumped bed.

The data in Figure II-19, which pertain to run Pu-1, show the change in concentration of uranium and plutonium in the fluorinator alumina bed as the cleanup fluorination period progressed. The data were obtained from grab samples taken at approximately hourly intervals. It is apparent from the figure that an increase in temperature improves both plutonium and uranium removal. Each temperature period is generally characterized by a period of high removal rate followed by a period in which the removal rate for all practical purposes diminishes to zero. The plutonium data show

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FIG. II-19. Uranium and Plutonium Removal from Fluorinator Alumina in Run Pu-1.

this trend rather well; the uranium data showed considerable scatter, but the overall decrease in concentration is apparent.

The high uranium and plutonium concentrations in the final dumped bed (Fig. II-19) may be explained as follows: quantities of fines (-200 mesh) were elutriated from the bed by the fluidizing gas and held up in the reactor above the main reaction zone on horizontal surfaces, e.g., flanges, tops of filters, thermo-

couple wells. These fines which contained uranium and plutonium were returned to the bed after the run in the process of dumping the bed, when the column was rapped and vibrated, and contaminated the bed. In subsequent experiments the column will be rapped at regular intervals throughout the run in an effort to return the fine uranium and plutonium particles to the bed. Also, alumina containing up to 5 w/o minus 170 mesh particles will be provided in the starting bed material. Future reactor design should aim at providing minimal surface for holdup of solids.

Excellent uranium material balances, >99%, were realized in the shakedown runs. Collection of the hexafluoride product in the shakedown runs was highly efficient. The two cold traps (operated at -60°C) and the sodium fluoride backup trap, respectively, collected 97%, 2% and 1% of the hexafluoride product. Data on the plutonium experiment await analysis of numerous solid, liquid, and vapor samples.

b. THERMAL DECOMPOSITION AND CONVERSION

Shakedown tests with UF_6 only were made on both the conversion process (run CU-2) and the thermal decomposition process (run UD-3) to evaluate equipment performance. The initial operation with UF_6 - PuF_6 mixed feed (run DUP-4) was made as a feasibility study of the fluid-bed thermal decomposition process.

The converter and its auxiliaries, described in a previous report (ANL-6925, pp. 136-139) include gas supply and metering systems, a gas preheater, a 2-in. dia. reactor with a 4-in. dia. integral filter section, a backup filter in a separate 4-in. dia. section, an off-gas analysis system, an exit gas scrubber, and dry chemical traps. The reactor is fabricated of Inconel; other equipment and lines are of nickel and Monel. For the thermal decomposition step, the converter hexafluoride feed system, the reactor, and the backup filter are used in conjunction with the fluorinator cold traps, NaF trap, and activated alumina towers.

Thermal Decomposition. A test of the thermal decomposition process with UF_6 - PuF_6 feed, run DUP-4, was carried out under the following nominal conditions:

Bed temperature:	350°C
Bed material:	18-in. static depth (2.4 kg) of Alcoa-100 mesh T-61 alumina
Superficial fluidizing gas velocity:	0.15 ft/sec
Hexafluoride feed rate:	22 g/min
Inlet gas composition:	40% hexafluoride in nitrogen

The relatively low gas velocity and relatively deep bed gave average gas residence times on the order of

5 to 10 sec. For full process application, the bed would be PuF_4 . Process regions other than the bed are maintained near 80°C . Operation of all equipment components was entirely satisfactory during the 9.6-hr run in which a total of 10.6 kg of mixed hexafluorides were processed. Analyses of the process streams are not yet available.

The thermal decomposition shakedown test with UF_6 feed alone, run UD-3, made prior to the plutonium experiment, employed similar conditions. Included in this experiment was a prefluorination period. Experience in gas sampling (sampling of the UF_6 off-gas stream) was obtained. At the end of run UD-3, about 0.1 w/o of the feed was retained in the alumina bed, as determined from fluoride and uranium analysis. During the 9.6-hr run, 10.6 kg of hexafluoride was processed.

Conversion to Oxide. Operation of the converter for the direct production of oxide from hexafluoride is based on results of previous studies with UF_6 in a 3-in. dia. unit.³⁰ The hexafluoride is reacted with steam and hydrogen in a fluidized bed of uranium oxide particles at 650°C to produce solid UO_2 which deposits on the UO_2 bed particles with consequent particle growth. Conversion of the UF_6 to solids is virtually complete. The converter is designed to operate at a hexafluoride feed rate of 22 g/min [84 lb U/(hr) (sq ft reactor cross section)].

The conversion procedure utilizes alternate periods of hexafluoride feed and product cleanup (to remove fluoride), each period being of 30-min duration. During the hexafluoride feed period, a low steam rate (steam/ UF_6 mole ratio of 2), which favors the production of dense oxide, is used; the hydrogen rate is maintained at a high value (hydrogen/steam mole ratio near 3) to give the desired superficial fluidizing gas velocity (~ 1 ft/sec) in the fluid bed. During the fluoride cleanup period, the steam rate is increased, giving a hydrogen/steam ratio of one; the higher steam rate enhances fluoride removal. Part of the product is withdrawn at the end of each cleanup period through an electrically operated plug valve near the bottom of the reactor.

An auxiliary step that has been developed is an oxidation-reduction treatment for in-place size reduction of the bed particles. This step is performed after a fluoride cleanup period. Oxidation is conducted at 400°C with 20% air diluted with nitrogen. Quantities of air equivalent to about 0.25 times the stoichiometric amount required for conversion of the UO_2 bed to U_3O_8

³⁰ I. E. Knudsen, N. M. Levitz, and A. A. Jonke, Engineering Development of Fluid-bed Fluoride Volatility Processes. Part 6: The Fluid-bed Conversion of Uranium Hexafluoride to High-Density Uranium Dioxide, ANL-6902, December 1964.

are used. The oxidized bed is then reduced using conditions identical to those used in the cleanup step of the conversion cycle.

The initial test of the conversion equipment and procedure with UF_6 was described in the previous report (ANL-7055, p. 137). A second shakedown test, run CU-2, with UF_6 feed was made recently; two cycles, each consisting of a hexafluoride feed period (particle growth), a fluoride cleanup period, and an oxidation-reduction (size reduction) period, were completed. A total of 5.47 kg of UF_6 was processed during the 15 hr of converter operation. Hexafluoride feed rates were as high as 18 g/min. The final bed of the previous run, run CU-1, was used as the starting bed; the initial bed weight was 3.3 kg, and its temperature was maintained at 650°C.

Chemical analyses of the oxide product showed about 0.03 w/o fluoride, 1 w/o hexavalent uranium, and an oxygen-to-uranium ratio of 2.03. These values are similar to those obtained in previous work. Particle size behavior during the run was as follows:

	Initial and Final Mean Particle Sizes
a) Hexafluoride feed period (3.10 kg UF_6 fed during ten 0.5-hr feeding periods)	280 μ to 366 μ
b) Oxidation-reduction period (0.13 equivalent of oxygen fed)	366 μ to 344 μ
c) Hexafluoride feed period (2.38 kg UF_6 fed during five 0.5-hr feeding periods)	344 μ to 392 μ

2. Process Development Studies for Uranium Dioxide Fuels (D. RAMASWAMI, J. GABOR, D. RAUE, J. STRAND, W. KREMSNER)

Uranium dioxide fuels of low enrichment are commonly clad with either Zircaloy-2 or stainless steel. These fuels, either in the spent form discharged from nuclear reactors or in the scrap form rejected in the fuel fabrication facilities, require reprocessing to recover the valuable uranium and plutonium constituents. The initial steps in the fluid-bed fluoride volatility processes for recovery of uranium and plutonium from low-enriched fuels consist of (1) separation of the cladding from the fuel material, and (2) conversion of the uranium and plutonium compounds to hexafluorides by reaction with fluorine. A development program is underway to investigate (1) decladding of fuel bundles in a 6-in. dia. pilot-scale reactor, (2) alternative processing schemes in a 3-in. dia. pilot-scale reactor, and (3) exploratory studies in a 1.5-in. dia. bench-scale reactor. Current work in these three programs is being conducted with uranium-bearing fuels in the absence of plutonium because operations are thereby simplified.

Initial and
Final Mean
Particle Sizes

d) Oxidation-reduction period (0.27 equivalent of oxygen fed)

392 μ to 140 μ

Differences in the particle growth rates can be attributed to variations in bed weight and feed rates for the successive feed periods. The results of the particle breakup treatments indicate the effectiveness of the procedure and possible limits for future operation. The average bulk density of the oxide product remained at a uniform value of 8.4 g/cc throughout the run.

Preliminary results of the off-gas monitoring system, a thermal conductivity cell designed to measure the HF content of the off-gas, were good in that reproducible traces were obtained over the feed and cleanup periods. This system has not been calibrated as yet.

Future Work in the Engineering-scale Alpha Facility. Two additional fluorination-thermal decomposition experiments with $\text{UO}_2\text{-PuO}_2$ feed are scheduled. Upon completion of these experiments all equipment will be fluorinated to recover any plutonium deposited in the lines and equipment as the tetrafluoride as a result of thermal and radiation (alpha) decomposition of PuF_6 .³¹ It is planned that the converter will be used in studies on the preparation of stable mixed-oxide materials, at the same time serving to reclaim material for possible re-use as feed for the fluorinator. Emphasis of the work may then shift to studies with hexafluoride mixtures in the distillation column.

a. DECLADDING OF ZIRCALOY-2-CLAD URANIUM DIOXIDE FUELS IN A PILOT-SCALE REACTOR

Studies were performed in the pilot-scale facility on the decladding of Zircaloy-2-clad UO_2 fuel bundles by reaction with HCl using procedures developed previously for processing uranium alloy fuels.³² The Zircaloy cladding is removed by reaction with HCl gas at a temperature above the sublimation point of ZrCl_4 (331°C), and the ZrCl_4 gas is pyrohydrolyzed to a solid oxide waste by reaction with steam in a second fluid-bed reactor (or pyrohydrolyzer).

The principal objectives of these studies are:

³¹ R. P. Wagner, W. A. Shinn, J. Fischer, and M. J. Steindler, Laboratory Investigations in Support of Fluid-bed Fluoride Volatility Processes. Part VII. The Decomposition of Gaseous Plutonium Hexafluoride by Alpha Radiation, ANL-7013, May 1965.

³² J. T. Holmes, Howard Stethers, and John J. Barghusen, Nucl. Appl. 1(4), 301-309 (August 1965).

(1) to observe the progress of decladding of simulated fuel bundles by periodic gamma-ray photographs of the fuel bundle and by continuous analysis of the off-gas stream;

(2) to determine the effect of oxygen impurity in the feed gases on the generation of U_3O_8 fines by reaction with the UO_2 ;

(3) to evaluate the use of packed beds of alumina as a means of retaining the U_3O_8 fines within the system;

(4) to investigate the performance of the halogenation reactor, the packed-bed filter, and the fluid-bed pyrohydrolyzer during the decladding operation; and

(5) to determine the chloride contents of the bed materials at the end of the decladding step.

Equipment and Operating Procedure. The main components of the equipment are a 6-in. dia. halogenation reactor, a 9-in. dia. down-flow packed-bed filter, and a 6-in. dia. pyrohydrolysis reactor. The operating procedure includes charging of alumina beds, prefluorinating of the beds, charging of the fuel bundle, bringing the temperatures of the various components of the system to the specified values, maintaining the various beds under fluid or static conditions as specified, and feeding of the reagents at the specified gas velocities.

The process equipment and operating conditions in the seven decladding runs were similar to those used for the hydrochlorination of uranium-Zircaloy-2 alloy fuels.³² The alumina³³ charges were: 8.0 kg ($1\frac{1}{2}$ - to $\frac{1}{4}$ -in. size) to the halogenation reactor as the static bed support for the fuel, 19.8 kg (48 to 100 mesh) to the halogenation reactor as the fluid-bed material, 15.0 kg (14 to 48 mesh) to the packed-bed filter as the filter media, and 10.0 kg (48 to 100 mesh) to the pyrohydrolysis reactor as the fluid-bed material. In one run, the fuel charge was a fuel bundle which simulated a segment of the form used for "Type I" fuel bundles in the Dresden nuclear reactor.³⁴ This fuel bundle consisted of 25 rods (28-in. long Zircaloy-2 tubes loaded with UO_2 pellets) and held in a square array with a 0.14-in. spacing between them. The inside diameter of the tubes was ~ 0.435 in., the wall thickness of the tubes was ~ 0.030 in., and the total weight of Zircaloy-2 in the fuel bundle (including the end plugs) was 3.8 kg. The UO_2 pellets were cylindrical, 0.43 by 0.43 in., and the total weight of UO_2 in the fuel bundle was 15.8 kg. In a separate run, a fuel bundle containing only 6 rods was used. In five other runs, 3.8 to 13.9 kg of unclad UO_2 pellets was used.

During decladding, the fluid bed in the halogenation reactor was maintained at 395°C , the static bed in the packed-bed filter was maintained at 340°C , and the fluid bed in the pyrohydrolysis reactor was maintained at 346°C . The feed gas to the halogenation reactor consisted of 40 to 85 v/o HCl in nitrogen, and the gas velocity was ~ 0.5 ft/sec at the reactor temperature and pressure. Progress of the decladding was monitored by gamma-ray photography and by continuous analysis of the off-gas stream.

Results and Discussion. The halogenation reactor, the packed-bed filter, and the pyrohydrolysis reactor operated smoothly during the entire period of hydrochlorination.

A scrutiny of the entire sequence of gamma-ray pictures revealed that the fuel bundle was gradually reacted from the bottom of the bundle to the top, and the fuel bundle gradually settled into the bed as the lower portion was hydrochlorinated. A sequence of pictures illustrating the settling is shown in Figure II-20.

Both the gamma-ray pictures and the off-gas analysis indicated that decladding of the 25-rod fuel bundle was completed in 4.4 hr. Both the hydrochlorination rate (0.9 kg/hr) and the average HCl efficiency (17%) during the decladding of the 25-rod fuel bundle were similar to values obtained in processing uranium-Zircaloy-2 fuels (1.0 kg/hr and 25%, respectively). The temperatures of the fuel rods during hydrochlorination, as measured by skin thermocouples mechanically attached to the outside walls of the cladding at various heights, were similar to those of the fluidized bed.

The uranium loss by transport through the packed-bed filter was less than 0.04% of the uranium charged to the halogenation reactor. In the runs made without the Zircaloy cladding and with oxygen in concentrations up to 2.5 v/o in the feed gas, $<5.6\%$ of the UO_2 charge was converted to U_3O_8 fines and the uranium losses in the gas stream leaving the filter were $<0.002\%$. The packed-bed filter did not cake or agglomerate, but remained free-flowing, and the pressure drop across the filter remained relatively constant throughout each run. These results suggest that static beds of alumina are effective in retaining the uranium particulate generated during the decladding step.

At the end of the decladding step, the chloride concentrations in the alumina were ~ 0.097 w/o for the fluid bed in the halogenation reactor and averaged 0.078 w/o for the static bed in the packed-bed filter. The total chloride content of the two beds was <29.8 g. In the packed-bed filter itself, the concentration of chloride was localized and ranged from 6.14 w/o in the top layer to 0.02 w/o in the bottom layer. This

³³ Sintered alumina, Type T-61, manufactured by Aluminum Company of America.

³⁴ Directory of Nuclear Reactors, Vol. IV, Power Reactors (Revised and Supplemented Edition of Vol. 1), International Atomic Energy Agency, Vienna, 1962, pp. 91-96.

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FIG. II-20. Decladding of Zircaloy-2-Clad UO_2 Fuel Bundle in a Fluid-bed Reactor.

magnitude of the chloride content indicates that the chloride in the two beds may not need to be displaced before exposing the beds to elemental fluorine.

Future Work. The effect of extent of immersion of a fuel bundle in the fluid bed on the progress of hydrochlorination will be determined in the future work.

b. PROCESSING OF DECLAD URANIUM DIOXIDE

In the fluoride volatility process, declad UO_2 containing PuO_2 is converted to volatile UF_6 and PuF_6 in a two-zone oxidation-fluorination³⁵ step. In this step, the UO_2 pellets are oxidized in the fluidized-packed bed to form $\text{U}_3\text{O}_8\text{-PuO}_2$ fines; these are transported to the superincumbent fluidized bed where they are fluorinated to the hexafluorides. Development studies on this step in a 3-in. dia. reactor were conducted by Anastasia and Mecham,³⁵ who reported that the rates of elutriation to the upper zone limit the rates of fluorination. The oxidation conditions, such as gas velocity, gas composition, and temperature, affect the re-

sults of fluorination since the oxidation and fluorination are conducted simultaneously. In this two-zone oxidation-fluorination method, plutonium-uranium compounds cannot be readily sampled for plutonium accountability purposes. A method which overcomes this difficulty comprises two steps: the oxidation of the pellets to $\text{U}_3\text{O}_8\text{-PuO}_2$ fines, followed by the fluorination of these fines to the hexafluorides with fluorine. Since oxidation produces a mixture of uranium oxide and plutonium oxide fines in alumina which is more homogeneous with respect to U/Pu ratio than is the fuel charge, the beds may be sampled after the oxidation step. Studies were therefore initiated on two alternative methods for processing UO_2 pellets (a two-step oxidation-fluorination procedure and a three-step oxidation - hydrofluorination - fluorination procedure) that result in batches of fines. The objectives of these studies are to determine the feasibility of sampling the fluid beds for accountability purposes after the pellets have been oxidized to fines and to improve the overall flexibility in the processing conditions.

Equipment and Operating Procedure. The equipment, a 3-in. dia. nickel fluid-bed reactor used in the previous studies³⁵ of the two-zone oxidation-fluorina-

³⁵ L. J. Anastasia and W. J. Mecham, Oxidation-Fluorination of Uranium Dioxide Pellets in a Fluidized Bed, *Ind. Eng. Chem. Process Design Develop.* 4(3), 338-344 (July 1965).

tion method, was modified to accommodate the two- or three-step procedure. The modifications included installation of (1) four sintered nickel filters instead of one in the disengaging chamber and a blowback system for returning the elutriated fines, (2) fluid-bed sampling equipment for sampling the bed at four elevations, (3) off-gas analysis apparatus for determining oxygen and moisture, and (4) temperature-actuated control valve for fluorine feed with an option of selecting any of the six thermocouples in the fluid bed. The alumina bed material was prefluorinated prior to each run.

Three runs were performed to evaluate the oxidation-fluorination scheme, and one run was made using

the oxidation-hydrofluorination-fluorination sequence. The weight of UO_2 pellets (0.43 by 0.43 in. cylinders) charged ranged from 2.2 to 4.4 kg (6-in. deep bed). In two of the runs, alternate 1-in. layers of depleted (0.2198% ^{235}U) and normal (0.7218% ^{235}U) UO_2 pellets were charged to the reactor. The ^{235}U fraction served as a stand-in for the plutonium fraction. Equal quantities of the two enrichment types were used. The alumina charge was from 3.4 to 6.8 kg (an amount that would result in 40 w/o uranium oxide fines in the fluid bed). The average diameter of the alumina particles was about 68 to 84 μ .

Oxidation was conducted for 4 to 6 hr at 450°C, using oxygen concentrations of 5 to 25 v/o in the feed

FIG. II-21. Gamma Ray Pictures of Uranium Dioxide Pellets at Several Stages of Oxidation.

Temperature: 450°C

Initial Charge: 4.4 kg of UO_2 ; 6-in. deep bed

Oxygen in Feed: 13 v/o

gas. Gas velocities in the column ranged from 1.5 to 1.8 ft/sec. The hydrofluorination step, used only for one run, involved passing 5 to 44 v/o HF in nitrogen at 450°C through the reactor at 0.95 ft/sec for 3.5 hr. The fluorination step was conducted in two periods. During the initial fluorination period, 5 v/o fluorine in nitrogen was fed to the reactor at 400°C. Operating conditions in the final period were 90 v/o fluorine at a bed temperature of 550°C. Total fluorination time ranged from 6 to 10 hr. During all of the process steps, radiographs of the fluid-bed section were taken periodically.

Results and Discussion. Oxidation proceeded smoothly in all four runs. A series of radiographs taken during oxidation of a 6-in. deep bed of pellets are shown in Figure II-21. The overall white appearance of the bed after 5.5 hr shows that oxidation was essentially complete.

In a run with UO₂ pellets of two enrichments, bed samples taken at the end of the oxidation step from sampling points 8, 28, and 38 in. above the bottom of the fluid bed contained 0.4645, 0.4650, and 0.4714% ²³⁵U, respectively, thus indicating bed homogeneity with respect to ²³⁵U. These values differ by only about 1% from the average input ²³⁵U concentration of 0.4708%. Total uranium contents of samples taken at these three levels were 28.3, 31.5, and 32.3 w/o, as compared with 32.2 w/o (based on the uranium recovered from all process streams) and with 33.6 w/o (based on uranium estimated to be in the charge). These results suggest that a fluid bed of alumina containing large quantities of fines can be sampled representatively for accountability purposes.

In the three-step run, hydrofluorination was controlled easily, and the operation was satisfactory. A good indication of the reaction end point was obtained from the analysis of moisture in the off-gases.

In the two-step runs, fluorination rates of 65 to 80 lb UF₆/(hr) (sq ft of reactor cross section) were achieved for periods of 1 to 2 hr when large quantities of uranium fines were present in the fluid bed.

Future Work. In future runs, the effect of oxidation time on the uranium concentration in fluid-bed samples taken during the oxidation step and the effect of cracked UO₂ pellets (simulating irradiated pellets) on

the progress of the oxidation reaction will be determined. Also, the effects of lower temperature and of excess fluorine on the progress of fluorination of U₃O₈ fines will be determined. Optimization of reactant concentrations, temperatures, and gas velocities will be attempted.

c. EXPLORATORY STUDIES IN A BENCH-SCALE UNIT

The use of BrF₅ as a fluorinating agent is presently being considered for selectively fluorinating uranium from UO₂ fuels as volatile UF₆ while converting plutonium oxide to nonvolatile PuF₄. Through the use of BrF₅, a separation of uranium and plutonium can be achieved. Plutonium is recovered as PuF₆ in a subsequent step by fluorination of PuF₄ with fluorine. Bench-scale tests for development of the BrF₅ process have been initiated.

The objectives of the bench-scale tests are:

- (1) to establish the optimum temperature, BrF₅ concentration in the feed gas, and fluidization velocity;
- (2) to determine the operability of a fluidized-bed reactor for this process (bed caking is the prime concern); and
- (3) to develop means of monitoring both the compositions and the flows of gas streams continuously and conveniently.

A 1½-in. dia. reactor has been modified for feeding of BrF₅ and collecting and disposing of off-gas products. Methods for off-gas analysis and UF₆ collection are currently under consideration. The off-gas would consist of UF₆, BrF₅, bromine, oxygen, and nitrogen. Because of the complexity of the off-gas stream, direct analysis is not presently possible. It is currently planned to determine the bromine content of the gas stream by converting the bromine to BrF₅ by reaction with fluorine.

Initial tests will be made to determine operability of the fluidized-bed reactor using BrF₅ as a fluorinating agent and to determine the lowest temperature for satisfactory fluorination of U₃O₈ produced by oxidative pulverization of the UO₂ fuel. Development of the off-gas analysis and collection system will proceed simultaneously with the experimentation.

3. Cleanup of Cell Exhaust Air Contaminated with Plutonium Hexafluoride

(R. KESSIE, D. RAMASWAMI, L. MAREK)

The high toxicity of plutonium requires that the quantity released to the environment be strictly limited during fluoride volatility processing. The volatility of PuF₆ requires special techniques to assure its removal from the air used to ventilate the equipment enclosures

for this process. The gas cleanup systems now used for cleansing exhaust air from alpha facilities utilize the reaction of PuF₆ with moist air in the glovebox to produce the solid reaction product PuO₂F₂ which, depending on the concentration of the reactants, may deposit

on a solid surface or appear as a fume. Airborne plutonium compounds are effectively removed from the exhaust air by high-efficiency (AEC) filters.

Previous work has shown that when moisture concentrations are limited to those normally present in the atmosphere the hydrolysis of PuF_6 with moist air produces solid PuO_2F_2 (ANL-6800, p. 245). Higher concentrations of moisture can produce PuO_2 and PuF_4 . For limited moisture, the overall reaction is

At low reactant concentrations, the reaction occurs principally on any solid surface available to the reactants. The reaction rate is now believed to be first order with respect to both PuF_6 and H_2O , and second order over-all. An analysis of the experimental results indicates that the adsorption of HF may be the rate-controlling step, although the evidence is not strong enough to rule out the surface reaction as the rate-controlling step. The rate is probably independent of the surface composition because the surface is rapidly covered with the solid product PuO_2F_2 . At high reactant concentrations, most of the PuO_2F_2 is produced in the gas phase as particles of less than 0.1μ diameter (ANL-6725, p. 157). The loading of the filters and the effects of agglomeration of this size of particles in the gas phase are significant in filtration.

The use of AEC type filters appears to be the best method for promoting the surface reaction and for collecting the fine particulate material. The previously reported results on particulate penetration of AEC type filters (ANL-6596, p. 123) had a large variation that made separation of the effects of variables difficult or impossible. The fraction of released plutonium passing through two filters in series was the most reproducible expression of penetration and ranged between 10^{-9} and 10^{-6} at a filter flow rate of 40% of the rated flow (the rated flow is 2.5 cm/sec). Theoretically derived effects of agglomeration and loading accounted for about one order of magnitude in this variation but these effects could not be unambiguously confirmed because of the large residual variation (ANL-6725, pp. 157-166). All of this previous work is covered in detail in a recently issued topical report.³⁶

An aspect of the reproducibility of the results from past and future experiments involves any variation in the performance of small sections of filter media used in these experiments. The amount of the variation due to the filters was unknown. Small sections of the filter

media would be expected to have greater variations in performance than large sections because of averaging effects in the large sections. Equipment was, therefore, constructed to test the ability of samples of AEC filter material (10-cm dia. disks mounted in a holder) to remove aerosol particles from gas flowing through the filter at various flow rates and also to determine the effect of a small hole on filter behavior. The principal components of this equipment are an aerosol generator and a light-scattering photometer to measure the aerosol concentration.

Experimental Equipment and Procedure. The aerosol generator used in these tests was based on a design (Model III) described by Echols and Young.³⁷ In this generator, DOP [di(2-ethylhexyl)-phthalate] is dispersed by a jet of air submerged in the liquid DOP, and the coarser particles are removed by a jet impactor stage. With a 25 psig supply of air pressure, this generator produces aerosol with a flow rate of 86 liters/min, a mass concentration of 1.64 mg/liter, a geometric mean particle diameter of 0.69μ , and a geometric standard deviation of 1.26. This generator is much easier to construct and operate than the condensation-type aerosol generators commonly used for producing homogeneous aerosols.

The aerosol concentration is measured with a light-scattering device. A 90° average scattering angle is used in this device instead of the more conventional forward scatter of less than 15° . Although this 90° instrument probably has a higher background reading,³⁸ it should have a higher relative sensitivity to smaller particles.³⁹ The light source is an American Optical Company Illuminator Model 653. The detector is a Photovolt Multiplier Photometer Model 520-M. Dual series sinusoidal constant-voltage transformers are used for both the light source and photometer to achieve drift-free readings.

The filter penetration at any one flow rate is determined from four readings on the photometer: (1) a reading of the raw smoke, (2) a background reading of clean filtered air, (3) a reading of filtered smoke, and (4) a second reading of raw smoke. Depending on the flow rate, each reading requires between $\frac{1}{2}$ and 5

³⁷ W. H. Echols and J. A. Young, Studies of Portable Air-Operated Aerosol Generators, U.S. Naval Research Laboratory, Washington, D. C., NRL Report 5929, July 1963.

³⁸ H. W. Knudsen and Locke White, Development of Smoke Penetration Meters, U.S. Naval Research Laboratory, Washington, D. C., NRL-P-2642, September 1945, p. 19.

³⁹ R. B. Penndorf, Approximation Methods to the Mie Scattering Theory of Colloidal Spheres, Analytical Chemistry in Nuclear Technology, Particle-Size Analysis, Second Conference, Gatlinburg, Tennessee, September 29-October 1, 1958, TID-7568 (Pt 3), April 1959, p. 30.

³⁶ R. Kessie and D. Ramaswami, Removal of Plutonium Hexafluoride from Cell Exhaust Air by Hydrolysis and Filtration, ANL-7066, 1965.

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FIG. II-22. DOP Testing of AEC Filter Media.

min to stabilize to a constant value; the longer times are required at the lower flow rates. The penetration is computed by first subtracting the background reading from the other three readings and then dividing the filtered smoke reading by the average of the two raw smoke readings. The two raw smoke readings never differed by more than 10% and in most of the tests differed by ~3%.

Results and Discussion. Typical results on the effect of flow rate on filter penetration are shown in Figure II-22. As the flow rate was reduced from 115 to 30% of rated flow, the penetration of a filter media disk by aerosol particles rapidly decreased from 0.03 to 0.002%. However, for the same disk with a pinhole in it, the penetrations were an order of magnitude higher and increased with decrease in the flow rate. The area of the pinhole is only $6 \times 10^{-4}\%$ of the entire filter area (10-cm dia.). The large effect of the small hole is

due to the high flow rate of air through the hole. These results are similar to those reported by Adley⁴⁰ who used a homogeneous 0.3- μ dia. DOP aerosol and full-size AEC type filters.

Loading effects are significant during DOP testing of the filters. After filtration has continued for one hour at the rated flow, penetration of aerosol will be greater by about a factor of two. This increase in penetration is expected for the collection of a liquid, as opposed to the expected decrease in penetration with loading of the filter with solid material. In order to minimize this loading effect on experimental results, the exposure time employed in the DOP testing of the filters used in experiments with PuF_6 will be limited to less than 10 min.

Samples of filter media taken from the supply used for 30 months prior to the experiment were tested for any variation in the rate of penetration of DOP aerosol. The supply consisted of a 2 ft by 100 ft sheet of media obtained by disassembly of a large AEC filter. The filter disks used to date are from a 20-ft section of one end of this sheet. In the current work, four samples (10-cm OD) from the same region near this end of the sheet, and three samples from positions spaced throughout the remaining length of the sheet were tested at 30 and 100% of rated flow.

The penetration at 30% of rated flow averaged 0.0012% and had a standard deviation of 19% for the separate values. At 100% of rated flow, the average penetration was 0.023% and the standard deviation was 8%. There was a continuous change in penetration for the samples taken along the length of the media sheet; the change amounted to 45% at the lower flow rate and 20% at the higher flow rate. These local variations in penetration would be significant in a refined experimental program, but are not a significant part of the variations experienced in some of the past experimental results on filter penetrations of PuF_6 hydrolysis product.

Future Work. Experiments to resolve the surface reaction and particulate penetration in AEC type filter media will be continued. A major attempt at reducing the scatter of data on particulate penetration encountered in the previous tests is planned. These experiments will be made with the same equipment used in the previous packed-bed studies (ANL-6925, p. 146) but a series of four separately packaged AEC filters (10-cm dia. media disks) will be substituted in place of the packed-bed section.

⁴⁰ F. E. Adley, The Effect of Holes on the Performance Characteristics of High-Efficiency Filters, HW-77912 (Rev.), Hanford Atomic Products Operation, September 1963.

4. Bench-Scale Studies with Irradiated Fuel (A. CHILENSKAS, J. T. HOLMES, J. KINCINAS, G. POTTS)

A program demonstrating the fluid-bed fluoride volatility process with irradiated feed materials is in progress. Experiments are being conducted in a 1½-in. dia. reactor installed in the senior cave facility of the Chemical Engineering Division. Irradiated feed materials of various types including high-enrichment uranium-Zircaloy, uranium-aluminum, and low-enrichment uranium dioxide have been processed to date. The aims of the program are to obtain information regarding (1) the distribution of fission products during the various process steps, (2) decontamination factors that may be realized, and (3) the effects, if any, of irradiation and the presence of fission products on uranium and plutonium recovery. The results of four experiments with irradiated uranium-aluminum and a summary of the work with irradiated high-enriched uranium alloy fuel materials are presented.

The facility consists of a 1½-in. dia. fluid-bed reactor and a packed-bed filter with associated equipment for the containment of volatile chlorides and uranium hexafluoride produced in the process. Volatile zirconium tetrachloride or aluminum trichloride produced by reaction (at 220 to 250°C) of the fuel alloy with hydrogen chloride is condensed to a solid chloride which is readily disposed by dissolution in dilute hydrochloric acid and subsequent solidification in cement. The uranium hexafluoride produced by reaction of uranium trichloride with fluorine at 260 to 520°C is decontaminated by a sorption-desorption operation in a series of four sodium fluoride traps maintained at temperatures between 20 and 400°C. The hexafluoride product is subsequently collected in a series of refrigerated traps.

The feed material used for the four uranium-aluminum runs was cut from highly enriched uranium-aluminum alloy fuel tubes used in the CP-5 reactor. These tubes had been irradiated in a thermalized flux of about 5×10^{13} n/(cm²) (sec) to produce a uranium burnup of about 50%.

The feed material for the first two runs (runs 1 and 2) consisted of alloy pieces that had a total weight of about 107 g and contained 4.3 g of uranium. The fuel tubes were cooled about 7 months.

The feed material for the two later runs (runs 3 and 4) consisted of a mixture of irradiated and non-irradiated uranium-aluminum alloy. The irradiated portion weighed about 40 g, contained 1.7 g of uranium, and had been cooled about 3 months prior to processing. The nonirradiated alloy weighed 60 g and contained 2.3 g uranium.

The equipment and procedures used for these experiments are described in previous semiannual progress reports (ANL-6925, p. 147, and ANL-7055, pp. 147-148, 155-156). A diagram of the bench-scale unit originally published in ANL-7055 is presented here as Figure II-23.

Analyses for uranium, gross gamma, gross beta, Ce, Sr, Cs, Ru, Sb, Zr, Nb, Tc, Mo, and Te were performed for runs 1 and 2. The average analyses for the two runs are shown in Table II-11. Runs 3 and 4 were performed to determine the fate of radioactive iodine and to obtain additional information on uranium decontamination. The decontamination factors obtained in all four runs are shown in Table II-12.

a. RUNS WITH 7-MONTH COOLED URANIUM-ALUMINUM ALLOY FUEL

(1) Movement of Activities During Hydrochlorination

As is shown in Table II-11, about 30% of the total gamma activity was volatilized from the reactor during the hydrochlorination step. The activities which are apparently nonvolatile under these conditions are cerium, cesium, and ruthenium. The earlier work with irradiated uranium-Zircaloy (ANL-7055) showed that strontium is also nonvolatile under these process conditions. The activities which were found to be only slightly volatile were antimony (7.5%) and tellurium (0.6%). The earlier work also showed that antimony is partially volatilized and indicated that technetium (1.95%) and uranium (0.4%) are also only slightly volatile. The principle volatile activities are zirconium, niobium, and krypton. As is shown, over 50% of the amounts of zirconium and niobium in the fuel were volatilized from the reactor. The values found for zirconium and niobium are believed low since the glass wool filter located immediately downstream of the condenser was not sampled and its activity content was not included in the calculations. Krypton was monitored in the cave stack with a beta counter calibrated for ⁸⁵Kr. The observed release of krypton agreed fairly closely with the calculated krypton input to the reactor, indicating that the bulk of the krypton was released to the stack during hydrochlorination. Analyses for molybdenum were not performed since molybdenum is expected to be nonvolatile under these conditions. Further, volatilization of molybdenum during hydrochlorination would not constitute a processing problem since the isotopes of molybdenum are

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FIG. II-23. Bench-Scale Fluid-bed Fluoride Volatility Unit Installed in the Senior Cave.

TABLE II-11. DISTRIBUTION OF URANIUM AND FISSION PRODUCTS FOLLOWING FLUID-BED FLUORIDE VOLATILITY PROCESSING—AVERAGE VALUES FOR RUNS 1 AND 2 WITH IRRADIATED URANIUM-ALUMINUM ALLOY

Isotope or Activity	Percent of Charge ^a				
	Volatilized During HCl Step	Remained with Reactor Bed and Filter Bed After Fluorination	Found in Fission Product Traps After Fluorination	Found in Uranium Product Traps	Total Found ^b
Uranium	N.A.	0.4	0.5	96.0	102.8
Gross γ	29.9	11.9	2.2	0.0006 ^c	44.4
Gross β	0.5	53.6	0.1	0.0005 ^c	54.3
Ce	nil ^d	68.2	e	0.00004 ^c	68.2
Sr	N.A.	70.5	N.A.	0.00002 ^c	70.5
Cs	nil ^d	26.0	0.007	0.00003 ^c	26.0
Ru	nil ^d	58.3	0.4	0.02 ^c	58.7
Sb	7.5	3.6 ^c	93.0 ^c	0.0003 ^c	106.3 ^c
Zr	51.3	1.8	3.3	0.00003 ^c	61.4
Nb	52.7	2.2	17.5	0.00007 ^c	72.5
Tc	N.A.	N.A.	N.A.	34.8 ^c	51.2
Mo	N.A.	11.8 ^c	N.A.	2.2 ^c	21.4
Te	0.6	N.A.	N.A.	0.002 ^c	54.3

^a Each value represents the average of two experiments except where noted otherwise.

^b Includes activity found in the NaF backup trap and the fluorine disposal trap.

^c One experiment only. Product desorption step employed in that experiment.

^d Not detected by gamma ray spectrometric analyses.

^e Trace detected by gamma-ray spectrometric analyses.

N.A.—Not Analyzed.

stable (except the molybdenum isotopes found in very short-cooled fuels) and would be easily handled.

(2) Movement of Activities During Fluorination

The movement of fission product and uranium fluorides for runs 1 and 2 is shown in Table II-11. Except where noted otherwise, the values shown are each the average of the two runs.

(a) *The Recovery of Uranium.* The average removal of uranium from the beds of the reactor and packed-bed filter was 99.6%. The uranium concentration in the reactor bed was 0.001 w/o, which compares closely with the values obtained for the runs with non-irradiated uranium-aluminum alloys. This result leads to the conclusion that fission products and the presence of a radiation field do not adversely affect the removal of uranium from the reactor. The average uranium collection in the product traps was 96.0%, with an overall material balance of 102.8%. These values are con-

sidered satisfactory in view of the small uranium input of about 4.3 g.

(b) *The Nonvolatile Fission Products, Cerium, Cesium, and Strontium.* Earlier work with irradiated uranium-Zircaloy feed materials (ANL-7055) showed that only trace quantities of cerium and cesium are volatilized (or entrained) and found downstream of the packed-bed filter. The uranium-aluminum runs confirmed the trace movement of cesium and cerium. Analysis for strontium in the fission product trap was not performed; hence, its nonvolatile character can only be inferred from its high retention in the reactor and filter beds (70.5%).

(c) *Volatile Fission Products.* The fission products which are partially or completely volatilized during the fluorination step are listed in Table II-11 and are discussed below.

Ruthenium. Ruthenium appears to be only slightly volatile under these fluorination conditions. About 0.4% was found in the fission product trap for the uranium-aluminum runs. This value compares closely to the 0.45% found volatilized in the earlier work with irradiated uranium-Zircaloy fuel.

Antimony. The antimony which remains in the re-

TABLE II-12. URANIUM DECONTAMINATION FACTORS OBTAINED BY FLUID-BED FLUORIDE VOLATILITY PROCESSING OF IRRADIATED ALUMINUM-URANIUM ALLOY

Element or Activity	Decontamination Factor ^a			
	Run 1 ^b	Run 2 ^c	Run 3 ^c	Run 4 ^c
Gross γ	5×10^3	1.6×10^5	2.0×10^7	2.8×10^7
Gross β	3×10^4	2.1×10^5	1.6×10^6	1.3×10^6
Ce	7.2×10^4	2.6×10^6	3.5×10^7	6.7×10^6
Sr	9.5×10^3	4.6×10^6	1.3×10^7	1.4×10^7
Cs	2.7×10^4	2.7×10^6	3.9×10^6	4.4×10^6
Ru	1.7×10^4	5.4×10^3	7.0×10^5	5.4×10^5
Sb	1.2×10^3	3.6×10^5	3.5×10^5	7.5×10^5
Zr	4.7×10^3	3.7×10^6	1.0×10^8	3.5×10^7
Nb	3.2×10^3	1.4×10^6	7×10^7	1.0×10^7
Tc	1.5	2.9	1.9	0.52
Mo	5.0	44.6	N.A.	N.A.
Te	6.8×10^2	5.9×10^4	N.A.	N.A.
Np	N.A.	N.A.	3.5	1.3
Pu	N.A.	N.A.	5.7×10^4	3.0×10^4

activity per gram U in
fuel charge

^a Decontamination factor = $\frac{\text{activity per gram U in fuel charge}}{\text{activity per gram U in trap}}$

^b Uranium product collected on NaF. No desorption step performed.

^c Uranium desorbed from NaF and collected in cold traps.
N.A.—Not Analyzed.

actor after the hydrochlorination step is almost completely volatilized and collected in the fission product traps during fluorination. That antimony is not completely fluorinated to a volatile species is indicated since 3.6% remains in the reactor and filter beds. The behavior of antimony was found to be similar to that observed in earlier work with irradiated uranium-Zircaloy, wherein 15.4% of the antimony remained in the reactor and filter beds after fluorination.

Zirconium and Niobium. As already noted, the bulk of the zirconium and niobium is removed prior to fluorination by hydrochlorination. It appears likely that some fractionation between zirconium and niobium occurs during the hydrochlorination step since the amounts of these activities collected on the fission product traps during fluorination indicate that considerably more niobium than zirconium was present at the start of fluorination. From these results, it appears that zirconium as well as niobium forms volatile fluoride compounds and that both are largely removed from the reactor and filter beds.

Technetium. Technetium closely follows uranium in the processing steps. Only a small amount (1.95%) is volatilized during the hydrochlorination step while the remainder volatilizes during the fluorination step and collects with the uranium in the product traps. As shown in Table II-11, about 34.8% of the technetium was found with the uranium in the cold traps following a desorption step from the sodium fluoride product trap. In run 1 (in which no desorption step was employed), 64.5% of the technetium was found with the uranium in the sodium fluoride product trap. This result confirms the earlier work with uranium-Zircaloy fuel in which 77.2% of the technetium was found with the uranium in the sodium fluoride product trap.

Molybdenum. The earlier work with uranium-Zircaloy showed that the bulk of the molybdenum volatilizes during fluorination and is distributed largely between the product sodium fluoride trap at 100°C and a backup sodium fluoride trap at 25°C. Some molybdenum may pass through the backup trap and be picked up by the downstream activated alumina trap. Sufficient data to confirm this supposition have not been obtained. The uranium-aluminum runs showed that about 19.8% of the molybdenum was trapped with the uranium when sodium fluoride was used at 100°C. As shown in Table II-11, about 2.2% was collected with uranium when an additional desorption step was employed following collection on NaF at 150°C. A residue, containing 11.8% of the molybdenum in the fuel, was found in the reactor and filter beds, indicating that the removal of molybdenum during fluorination is not complete under these process conditions.

Tellurium. The bulk of the tellurium volatilized dur-

ing the fluorination step and collected with the fluorine on the activated alumina traps. This trap operates with internal temperatures up to 550°C owing to the heat of reaction between fluorine and alumina. Only trace amounts of tellurium were found in a charcoal trap operated at 200°C, in a caustic scrubber in series downstream of the alumina trap, and in the cell exhaust system; this indicates that the alumina trap was highly efficient for tellurium removal. In run 1, about 0.14% of the tellurium was collected with the uranium on the product sodium fluoride trap held at 100°C, while in run 2, in which a desorption step was employed, 0.0017% was collected with the uranium in the cold traps.

b. RUNS WITH 3-MONTH COOLED URANIUM-ALUMINUM ALLOY FUEL

Runs 3 and 4 were performed with uranium-aluminum fuel irradiated in the CP-5 reactor and cooled three months prior to processing. The objectives of these experiments were to determine the fate of radioactive iodine, to evaluate the performance of a MgF_2 trap for the removal of technetium and neptunium activities, and to obtain additional uranium decontamination data.

(1) Movement of Iodine during Hydrochlorination and Fluorination

The bulk of the iodine was found to have volatilized during the hydrochlorination step in runs 3 and 4. In run 3, 61.5% of the iodine was collected in the caustic scrubber while 87.0% was collected in run 4. A trace amount of iodine was detected on the activated alumina bed in the fluorine absorption trap. This indicates that a small amount of iodine may remain in the reactor-filter system at the end of the HCl step and volatilize during the fluorination step. Monitoring of exhaust gas passing through the stack during both steps indicated that only trace amounts of iodine, well below the maximum permissible amounts,⁴¹ were released to the atmosphere.

(2) Removal of Technetium and Neptunium Fluorides in a MgF_2 Trap

Traps containing MgF_2 have been successfully employed to separate the volatile fluorides of technetium and neptunium from UF_6 .⁴² Accordingly, a small (100-g) MgF_2 trap was installed between the sodium fluo-

⁴¹ Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and Water for Occupational Exposure, U.S. Dept. of Commerce National Bureau of Standards Handbook 69.

⁴² Chemical Technology Division Annual Progress Report for Period Ending May 31, 1964, ORNL-3627, p. 32.

ride product trap and the cold traps. The MgF_2 trap was held at 125°C during runs 3 and 4. Analyses of the MgF_2 at the end of each run indicated that 3.1% of the technetium and 4.5% of the neptunium in the fuel was removed from the gas stream (average for two runs). The uranium product contained 43.3% of the charged technetium and 21.0% of the neptunium. Since the conditions employed in these tests were significantly different from those used at Oak Ridge National Laboratory,⁴² it is not possible to infer from these data that MgF_2 is not an ineffective agent for removing these species from the UF_6 stream. It is expected that additional studies with MgF_2 traps will be made to determine their potential use in uranium decontamination from technetium and neptunium.

c. URANIUM DECONTAMINATION FACTORS FOR FOUR RUNS WITH IRRADIATED URANIUM-ALUMINUM ALLOY FUEL

The decontamination factors obtained for the series of four runs with irradiated-aluminum fuel materials are shown in Table II-12. Runs 1 and 2 were made with 7-month cooled material, while runs 3 and 4 were made using 3-month cooled fuel material. The general operating procedure for all of the runs was the same except in the methods employed to purify and decontaminate the UF_6 product. For the first run, the UF_6 product was collected on a sodium fluoride trap at 100°C . The decontamination factors for this run are based upon the analyses of the NaF bed. In the second run, the UF_6 product was sorbed on a sodium fluoride bed at 150°C and subsequently was desorbed, passed through a sintered-metal filter, and collected in a cold trap. The decontamination factors obtained in this run are based upon the analyses of the product removed from the cold traps. The third and fourth runs employed a procedure similar to that used in the second run except that a MgF_2 trap at 125°C was interposed between the sodium fluoride product trap and the cold traps.

It can be seen that, by desorbing the UF_6 product from the NaF trap and collecting the product in refrigerated traps, the uranium decontamination factors are increased by one or more orders of magnitude. However, decontamination from technetium is not improved by desorption of UF_6 from sodium fluoride, and in the final run an apparent enrichment of technetium in the UF_6 product was observed.

The increase in decontamination factor for molybdenum from 5.0 in the first run to 44.6 in the second run is ascribed to an increase in the operating temperature of the sodium fluoride product trap from 100°C to 150°C . By increasing the sodium fluoride temperature, most of the molybdenum hexafluoride passed unaf-

fected through the trap while the UF_6 was sorbed on sodium fluoride. This technique for purifying UF_6 streams has been employed at ORNL.⁴²

Gamma spectrometric analyses of the uranium product obtained in runs 3 and 4 showed that the principal gamma-emitting substances were ^{237}U , ^{103}Ru and ^{106}Ru , and ^{95}Zr - ^{95}Nb with the preponderant activity due to ^{237}U . This result suggests that further improvements in decontamination techniques will not be of value in processing high-burnup short-cooled fuels (~ 3 months) since the gamma-activity level will be determined by ^{237}U . Improvements in the fission product traps and filtration technique will be of value in processing longer-cooled fuels since the ^{237}U activity decays fairly rapidly ($T_{1/2} = 6.7$ days). For example, an additional $1\frac{1}{2}$ months cooling would decrease the ^{237}U contribution by several orders of magnitude, and, therefore, the ruthenium and Zr-Nb gamma contribution would become predominant. Techniques to increase the uranium decontamination factor from the volatile fission products ruthenium and Zr-Nb are available.

d. SUMMARY AND CONCLUSIONS

The experimental work related to the fluid-bed fluoride volatility processing of irradiated highly enriched uranium alloy on a bench scale has been completed. The results of this work show:

(1) The retention of uranium in the reactor bed and filter bed following the processing of irradiated uranium-Zircaloy or uranium-aluminum alloy was similar to that found in processing nonirradiated fuel alloys. It can be concluded that the results obtained regarding the removal and recovery of uranium in the bench-scale and pilot-plant work with nonirradiated uranium-alloy fuel materials can be validly applied to irradiated fuels.

(2) The uranium decontamination levels achieved in runs 3 and 4 were such that the preponderant gamma activity in the uranium product was due to the uranium isotope ^{237}U .

(3) The decontamination factors for the activities Ce, Sr, Cs, Ru, Sb, Zr, and Nb ranged from 3.5×10^5 to 1.0×10^8 for the final two experiments. A decontamination factor of 5.9×10^4 for tellurium was obtained for one run with 7-month cooled uranium-aluminum alloy. Decontamination factors of 44.6, 2.9, and 3.5 were obtained for molybdenum, technetium, and neptunium, respectively.

(4) Distribution of fission products following the hydrochlorination step showed the activities cerium, cesium, strontium, and ruthenium to be essentially nonvolatile. The activities which were slightly volatile

(<10%) were antimony, tellurium, and technetium. The activities which were found to be predominantly volatile (>50%) were zirconium, niobium, iodine, and krypton.

(5) Distribution of the fission products following the fluorination step showed that the activities cerium, cesium, and strontium are essentially nonvolatile and are not removed from the reactor bed or filter bed. Ruthenium was found to be essentially nonvolatile, with less than 1% volatilizing and collecting in the fission product trap. The activities which were found to be preponderantly volatile (>50%) were molybdenum,

technetium, and tellurium. Sufficient analyses were not performed to establish completely the behavior of neptunium; however, 21% of the charged neptunium was found with the uranium product, indicating a high volatilization.

(6) Iodine was found to volatilize essentially completely during the hydrochlorination step of the process. A caustic scrubber was successful in effecting the removal of iodine from the process off-gas stream.

(7) The complete removal of tellurium from the process off-gas during the fluorination step was effected by the use of an activated alumina trap.

C. BASIC STUDIES OF FLUIDIZED-BED BEHAVIOR RELATED TO PROCESS OPERATIONS (D. RAMASWAMI)

1. Behavior of Fluidized Beds Containing Large Quantities of Fines (J. D. GABOR, J. PHELPS⁴³)

In the reprocessing of low-enriched uranium dioxide fuels, the oxide pellets are reacted with oxygen to form U_3O_8 fines, 4 to 12 μ in mean diameter. These fines are subsequently reacted with fluorine gas to form UF_6 . Beds composed entirely of such fine particles are not fluidized readily, and the results from earlier exploratory studies (ANL-6687, p. 132; ANL-6900, p. 187; and ANL-7055, pp. 159-162) suggest that the addition of coarser alumina particles facilitates fluidization of these beds. During the current work, the scope of these studies was enlarged to determine the alumina particle size distribution and other process considerations which would maximize the residence time of the fines in the fluidized beds while maintaining good heat and mass transfer properties that are typical of gas-fluidized beds without fines.

In order to determine the optimum size distribution of the alumina particles, studies are being conducted to determine the elutriation rates of fines from fluid beds. Another objective of the overall program is to determine the conditions of filter blowback (filter blowback is used to return elutriated fines to the fluid bed) which would maximize the residence time of the fine particles in the fluidized bed.

a. ELUTRIATION STUDIES

The equipment and the operating procedure used for the elutriation studies are similar to those used previously (ANL-7055, pp. 159-162). The elutriation tests were conducted with a 6-ft long, 3-in. ID

brass column. To minimize the effects of static electricity, usually present in fluid beds, the fluidizing nitrogen was humidified and the brass column was grounded. The fluidizing gas was distributed by a porous metal plate at the bottom of the column. The fines elutriated from the fluidized bed were filtered from the off-gas in a secondary filter chamber containing a 9-in. long by 1 $\frac{3}{4}$ -in. wide sintered Inconel bayonet type filter (10- μ porosity). Elutriation rates were calculated from the weight of fines collected at periodic intervals (5 min) in the external filter chamber.

In the current work, -80+170 mesh alumina (Type T-61, Tabular alumina, manufactured by Alcoa) was used as the fluidized-bed material. A Coulter Counter size distribution analysis for this material indicates that the -80+170 mesh alumina has a smaller median diameter (130 μ) and a smaller spread in size distribution than the nominal 48 to 100 mesh alumina (165- μ dia., see ANL-7055, pp. 159-162) used in the previous work. For all tests, -500 mesh nickel shot, with an average particle diameter of 22 μ (see ANL-7055, p. 160), was used as the fines to simulate uranium oxide fines. The initial concentration of fines (C_0) in the alumina beds was varied between 4 and 50 w/o in the various tests.

The elutriation rate, defined as the rate of change of the ratio of the concentration of fines (C) at any time to the concentration of fines initially, decreased with increase in initial fines concentration in the bed (see Figure II-24). This behavior is similar to that noted previously with the 165- μ dia. alumina. Further, the

⁴³ Co-op student from Illinois Institute of Technology.

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FIG. II-24. Elutriation Rate as a Function of Initial Fines Concentration.

Gas velocity: 1.52 ft/sec
 -80+170 mesh alumina
 3-in. ID brass column
 13-in. static bed height

rate of fines elutriation from the 130- μ dia. alumina was less than from the 165- μ dia. alumina.

For the run with an initial fines concentration of 8.3 w/o in the 165- μ alumina, size distribution of the elutriated fines was determined after various time intervals of elutriation by Coulter Counter analysis. The average particle diameter of the elutriated fines increased with time. The description of the elutriated fines by the logarithmic normal distribution (i.e., the logarithm of the particle diameter is normally distributed) appears to be suitable and may be a useful means for characterizing the size distribution of these fines in the development of process kinetics.

b. FILTER BLOWBACK FREQUENCY

During fluorination, it is desired to have a maximum amount of uranium and/or plutonium oxide fines in the fluidized bed. This can be achieved by frequent filter blowback to return the fines collected on the filters. However, frequent filter blowbacks reduce the life of the blowback system and dilute the process gas if nitrogen is used for the blowback gas when the reactor is operating on recycle.

Calculations were made to determine the average concentration of fines in the reactor as a function of blowback frequency and elutriation rate. It was assumed that elutriation can be described by a first order rate law and that all elutriated fines are collected on the filter, being returned to the bed after a blowback. Depletion of fines by chemical reaction was neglected. From the first order rate law, the change in fines concentration with time, t , in the bed is described by

$$-\frac{dC}{dt} = kC \quad (1)$$

where k is the elutriation rate constant, min^{-1} .

Integrating with the boundary condition of $C = C_0$ at $t = 0$ yields:

$$\frac{C}{C_0} = e^{-kt} \quad (2)$$

At any time, t , the average fines concentration in the bed is found from

$$\bar{C} = \frac{\int_0^t C dt}{\int_0^t dt} = \frac{\int_0^t C_0 e^{-kt} dt}{t} = \frac{C_0}{kt} [1 - e^{-kt}] \quad (3)$$

108-9318

FIG. II-25. Dependence of Average Concentration of Fines in the Fluidized Bed on Blowback Interval.

The average fines concentration in the fluidized bed as a function of blowback interval and elutriation rate constants is shown in Figure II-25. It is seen, for example, that for low rate constants ($<0.02 \text{ min}^{-1}$), the average fines concentration in the bed would be $>87\%$ of the original amount with a blowback once every 15 min.

2. Particle Residence Times at Surfaces of a Gas-Fluidized Bed⁴⁴ (L. B. KOPPEL,⁴⁵ R. D. PATEL,⁴⁶ J. T. HOLMES)

A model⁴⁷ has been previously developed for prediction of heat transfer coefficients from solid surfaces (such as reactor walls) to gas-fluidized beds. This model requires knowledge of the distribution of residence times of particles at the heat-transfer surface (ANL-6925, p. 163). During the current work, theoretical and experimental efforts have been directed at development of computational and photographic techniques for estimating the residence time distribution statistically from limited observations. The residence time distribution, $f(\theta)$, is so defined that $f(\theta)d\theta$ is the fraction of those particles at the solid surface that reside there for the time between θ and $\theta + d\theta$.

The program consists of two parts. The first deals with the development of statistical methods to estimate particle residence times without actually tracking individual particles. The methods are based on experimental observation of only the total number of tagged particles at the surface with time, a procedure considerably simpler and less time consuming than tracking individual particles. Automatic scanning equipment may also be used to obtain these data.

The second part of the program involves an experimental verification of these methods for residence times of particles at the wall of a gas-fluidized bed. Motion pictures are taken of particles residing at the transparent wall of a fluidized-bed vessel. The film record is analyzed in two ways. The direct method consists of tracking individual particles from frame to frame to record their entrance and exit and thus obtain their residence times. This distribution is compared with that obtained by the indirect statistical techniques, employing only the total counts of tagged particles on each frame.

As a result of the current studies, a formula has been derived relating the residence time distribution directly to the autocorrelation (based on automatic processing of films) of the frame-to-frame fluctuations in total

Future Work. Studies will be continued on elutriation and filter blowback with the objectives of maximizing particle residence time in the reactor and describing the elutriation mechanism. Investigation will be made of heat transfer, solids mixing, segregation, channeling, and of gas contacting in fluidized beds containing high concentrations of fines.

counts of tagged (black) particles at the repeatedly photographed test surface. This formula is

$$f(\theta) = -k \frac{d^2\Omega}{d\theta^2} \quad (1)$$

where $\Omega(\theta)$ is the autocorrelation and k is a constant easily obtained from the total particle counts. This formula has been used to estimate average residence times and average Nusselt numbers in two systems.

In the first system, particle residence times were obtained from a known, theoretical distribution of residence times which was simulated on a digital computer. The computer then determined a sequence of particle counts from these residence times, and Eq. 1 was applied to back-estimate properties of the theoretical distribution. The theoretical distributions were of the gamma form

$$f(\theta) = \frac{1}{\alpha! \bar{\theta}} \left[(\alpha + 1) \frac{\theta}{\bar{\theta}} \exp\left(-\frac{\theta}{\bar{\theta}}\right) \right]^{(\alpha+1)}$$

which has a mean residence time $\bar{\theta}$, and for which α is a shape parameter. A number of cases were investigated; in each case the chosen mean was $\bar{\theta} = 1$. In the first twelve cases, the value of α was zero; in the last three cases, α took the values 1, 2, and 9. In each case the mean residence time and a mean Nusselt number (based on an instantaneous Nusselt number for individual particles given by $N_{Nu}(\theta) = 1/\sqrt{\pi\theta}$, a form typical of many heat transfer models including the one developed for fluidized beds) were computed from the autocorrelations and compared with the values for the

TABLE II-13. COMPARISON OF ESTIMATED AVERAGE RESIDENCE TIME AND NUSSLETT NUMBER WITH THEORETICAL VALUES

α	$\bar{\theta}$, theor.	$\bar{\theta}$, est.	N_{Nu} , theor.	N_{Nu} , est.
0	1	1.053 ^a	1.000	0.975 ^a
1	1	1.001	1.061	0.933
2	1	1.007	1.081	1.098
9	1	0.942	1.114	1.128

^a Average of 12 cases.

⁴⁴ Accepted for publication in AIChE Journal.

⁴⁵ Consultant, Purdue University.

⁴⁶ Resident Student Associate, Purdue University.

⁴⁷ E. N. Ziegler, L. B. Koppel, and W. T. Brazelton, Ind. Eng. Chem. Fundamentals **3**, 325 (1964).

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FIG. II-26. Experimental System for Photographic Analysis of Particle Residence Times at Solid Surfaces in Fluidized Beds.

theoretical distribution. The results are given in Table II-13.

The second system utilized a 4 in. dia. gas-fluidized bed (Figure II-26). The particles were $\frac{1}{8}$ -in. dia. cellulose acetate spheres, of which approximately 5% were black and the remainder white. A test area on a flat, Lucite window was photographed at 20 frames per second. The average residence time of the black particles was found, by direct analysis of the frames, to be between 58 and 70 frames, while for the autocorrelation method it was estimated to be 60 to 65 frames. Only ranges may be given in this case because of the small total number of particles involved; a significant increase in the number of particles analyzed was not feasible because of the excessive man-hour requirement for the direct analysis. In addition, the average Nusselt num-

bers computed for the directly observed distribution and for the autocorrelations, using the same method described for the computer-simulated counts, agreed within $\pm 10\%$.

On the basis of these results, it is concluded that the autocorrelation technique is sufficiently accurate for the prediction of heat transfer coefficients, as well as for other possible applications, such as mass transfer.

The next phase of the project concerns construction of a system in which both the residence times, by the autocorrelation method, and the heat transfer coefficients can be measured at the same surface. It is hoped that the data from this project will result in an accurate correlation for prediction of heat transfer coefficients from surfaces in fluidized beds.

III

Studies and Evaluations¹

(W. J. Mecham, V. G. Trice, Jr., M. Levenson)

The studies and evaluations are concerned with the feasibility and costs of projected applications of current research and developmental work. Such studies may show which step of a process should be modified in order that the process as a whole may be more economical. Or they may show that some particular step or technique has an economic advantage and that new ways of incorporating this step in other process applications should be sought. The scope and specific objectives of these studies and evaluations vary with the interests of the Division.

An analysis is being made of cost differentials among alternative cases in the processing of fast reactor fuels in conceptual facilities to be operated in about 1980. In this analysis costs are estimated for processing three types of fast reactor fuel (oxide, carbide, and metal) in

both close-coupled and central processing plants. Three alternative processing methods are considered: aqueous solvent extraction, fluid-bed volatility, and pyrochemical. Preliminary results of the analysis were presented previously (ANL-6925, pp. 259-263), and a summary of the entire study is presented in the report Research Highlights of the Chemical Engineering Division (ANL-7175). The full report of this study is to be published shortly.²

A portion of the larger study is presented in this report. Estimates are given of the cost of processing oxide fuel in a close-coupled processing plant serving a single 1000 Mw(e) fast reactor. Costs are estimated for aqueous, volatility, and pyrochemical processing.

² M. Levenson, V. G. Trice, Jr., and W. J. Mecham, Comparative Cost Study of the Processing of Metal, Oxide, and Carbide Fast Breeder Reactor Fuels by Aqueous, Volatility, and Pyrochemical Methods, ANL-7137, in press.

¹ A summary of this section is given on pages 9 to 10.

A. BASIS OF THE COMPARATIVE COST STUDY

1. Processing Requirements and Technical Ground Rules

The conceptual plant components on which the processing costs were based comprised the processing plant, ultimate waste disposal, analytical laboratory, and auxiliary facilities. Flowsheets and plant designs were specified and estimates made of capital and operating costs for each of the three alternative types of processes. A common set of technical and economic ground rules was adopted for the calculation of costs for the several cases:

(a) A common fuel processing load was adopted as a reference specification for all cases. This reference processing load is stated in Table III-1 in terms of average mass rate of fuel discharged from the reactor per day of full power operation. The specifications in the table were selected as typical ones, in the light of recent conceptual designs of 1000 Mw(e) oxide-fueled fast reactors.³ The average burnup of core fuel was

specified as 10%, the reference value which may be achievable in practice in 1980.

(b) A plant factor of 80% was adopted as the reference value for both reactor and processing plant operation. This is in keeping with the usual commercial standards and with AEC guidelines.⁴

(c) The products of the processes were uranium dioxide and plutonium dioxide in a form suitable as feed for fabrication operations without further chemical conversions.

(d) In the reference processes, fission product decontaminations were higher for the products of aqueous and volatility processing than for pyrochemical processing. In all processes, refabrication of the core fuel

Ceramic Fueled Fast Breeder Reactor. AEC Chicago Operations Office, COO-279, December 1, 1964.

⁴ AEC Guide to Nuclear Power Cost Evaluation, Kaiser Engineers, TID-7025, 1962.

³ An Evaluation of Four Design Studies of a 1000 Mw(e)

requires at least semi-remote techniques because of the hard radiation from the fuel actinides themselves. Although an estimate of the costs of refabrication is beyond the scope of this study, a preliminary analysis of possible cost penalties for low-decontamination blanket processing is included in the complete report.²

(e) Cladding was removed by either chop-leach or by chemical decladding, depending upon which of these was most favorable to the respective reference processes.

(f) The ultimate disposal of high-level radioactive waste as solids was taken as the reference method. However, because of present uncertainty as to the cost of solidification of aqueous waste, its disposal costs were calculated on the basis of perpetual on-site storage of concentrated waste solutions, with the expectation that technical developments in aqueous waste disposal would ultimately permit solid storage at an equal cost.

(g) As a preliminary assumption, a 1% processing loss was assumed for all cases.

(h) Two cost elements of processing were omitted from this study, namely, site acquisition and development costs and liability insurance. The magnitude of associated costs was expected to be of the order of only a few percent of the total cost and these cost items were assumed to be matters of economic indifference in the comparison of costs.

TABLE III-1. SPECIFICATIONS OF THE REFERENCE 1000 Mw(e) FAST REACTOR

All quantities stated as weights of elements

Total Thermal Power, Mw(t)	2500
Net Electrical Power, Mw(e)	1000
Fraction of Total Power Generated in Core	0.85
Total Breeding Ratio	1.4
<i>Initial Composition of Fuel, weight percent on metal basis:</i>	
<i>Core</i>	
Depleted Uranium	78.0
Plutonium (239, 241)	15.0
Plutonium (238, 240, 242)	7.0
<i>Blanket</i>	
Depleted Uranium	100.0
Core Fuel Burnup, Percent of Actinides	10.0
Blanket Fuel Burnup, Percent of Actinides	0.71
Plant Factor, Percent	80
<i>Average Daily Rate of Fuel Discharge, kg per full power day:</i>	
<i>Core</i>	
Depleted Uranium	15.66
Plutonium (239, 241)	2.91
Plutonium (238, 240, 242)	1.56
Fission Products	2.24
<i>Blanket</i>	
Depleted Uranium	53.90
Plutonium (239)	1.053
Plutonium (240)	0.058
Fission Products	0.39
Stainless Steel Cladding	12.0

2. Chemical Flowsheets

Conceptual flowsheets adopted in this study as a basis for developing cost estimates are considered representative of advanced aqueous, volatility, and pyrochemical processes that could be expected to be opera-

representative of advanced aqueous, volatility, and pyrochemical processes that could be expected to be opera-

FIG. III-1. Principal Steps of the Advanced Aqueous Process for Oxide Fast Reactor Fuel.

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FIG. III-2. Principal Steps in the First Generation Pyrochemical Process for Oxide Fast Reactor Fuel.

tional by about 1980. While each flowsheet is an assemblage of individual steps believed to be feasible in the light of laboratory and pilot plant data, none of the processes has been fully demonstrated with high-enrichment, high-burnup fuel.

The aqueous process adopted in this study is of the generic type referred to as a chop-leach solvent extraction method. However, many simplifications and optimistic assumptions were incorporated in this aqueous plant design compared to what is done in presently operating plants, particularly as regards the plutonium handling steps. An analysis of the process feasibility is included in the complete study.² The basic features of the aqueous process are shown in Figure III-1. The uranium and plutonium outputs from the solvent extraction system were converted to oxide in fluid-bed denitration and reduction units.

The pyrochemical process for oxide fuel is illustrated in Figure III-2. This process was adapted from the

melt refining and skull reclamation processes developed for the EBR-II Fuel Cycle Facility at Idaho. (A newer process concept, originally developed for oxide fuel, termed the salt transport process, holds promise for further cost reductions. However, this concept was not developed sufficiently to be selected as the reference process for the cost estimates in the present study.)

The fluid-bed volatility process is shown in Figure III-3. Fluoride-promoted oxidation was used to remove the stainless steel cladding. Bromine pentafluoride (BrF_5) was used as a selective fluorinating agent to separate volatile fluorides of uranium (UF_6) and fission products without converting plutonium into a volatile form. Elemental fluorine was used subsequently to form volatile plutonium hexafluoride (PuF_6) thereby effecting the separation of plutonium from both uranium and fission products. The process included fluid-bed conversion of uranium and plutonium hexafluorides to oxides.

3. Sources of Plant Designs and Costs

The plant design concept and cost sources for aqueous processing were mainly derived from the Idaho small-plant concept presented by Schneider et al.⁵ It

is considered that this process concept offers the lowest costs of aqueous plants for comparison with ad-

⁵ J. Schneider et al, A Study of the Feasibility of a Small-

Scale Reprocessing Plant for the Dresden Nuclear Power Station, IDO-14521, April 1961.

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FIG. III-3. Principal Steps in the Advanced Volatility Process for Oxide Fast Reactor Fuel.

vanced nonaqueous processes. The concept was modified to accommodate maintenance of the hot portion of the plant while retaining the requirement of an 80% plant factor.

The plant design concept and cost sources for the pyrochemical process were mainly derived from the EBR-II Fuel Cycle Facility now operating at Idaho.⁶

The volatility equipment design concepts and cost sources were derived from ANL pilot plant experience. Plant concepts were selected to conform to those for the aqueous or the pyrochemical plants as far as was appropriate.

Models relating costs to complexity and size were employed to estimate costs for the processing plant and its auxiliaries for the several cases (stated earlier) in a consistent manner. The chief models and factors of estimation were based on methods developed by Stockdale,⁷ Zevnik and Buchanan,⁸ and Bauman.⁹

⁶ J. C. Hesson, M. J. Feldman, and L. Burris, Description and Proposed Operation of the Fuel Cycle Facility for the Second Experimental Breeder Reactor (EBR-II), ANL-6605, 1963.

⁷ W. B. Stockdale, Estimating Costs for Radiochemical Plants, in *Cost Engineering in the Process Industries*, Edited by C. H. Chilton, McGraw-Hill Book Company, Inc., New York, 1960, p. 304.

⁸ F. C. Zevnik and R. L. Buchanan, Generalized Correlation of Process Investment, *Chem. Eng. Progr.*, **59**, No. 2, 70 (1963).

⁹ H. C. Bauman, *Fundamentals of Cost Engineering in the Chemical Industry*, Reinhold Publishing Corp., New York, 1964.

The basic design concepts and cost sources for interim storage of high-level-activity solid waste were taken from Blomeke et al.¹⁰ The shipping charge for the cooled waste was based on the study by Perona et al.,¹¹ and the charges for final burial on the study by Bradshaw et al.¹²

The provisional cost estimate of aqueous waste disposal by perpetual liquid care was patterned after the study by Stoller.¹³

Auxiliary facilities for which cost estimates were made in this study included "hot" and "cold" maintenance shops, warehouse, offices, and personnel convenience areas.

¹⁰ J. O. Blomeke, J. J. Perona, H. O. Weeren, and R. L. Bradshaw, Evaluation of Ultimate Disposal Methods for Liquid and Solid Radioactive Wastes. Part III. Interim Storage of Solidified Wastes, ORNL-3335, October 21, 1963.

¹¹ J. J. Perona, R. L. Bradshaw, J. O. Blomeke, and J. T. Roberts, Evaluation of Ultimate Waste Disposal Methods for Liquid and Solid Radioactive Wastes. Shipment of Calcined Solids, ORNL-3356, October 18, 1962.

¹² R. L. Bradshaw, W. J. Boegly, Jr., F. M. Empson, H. Kubata, F. L. Parker, J. J. Perona, and E. G. Struxness, Ultimate Storage of High-Level Waste Solids and Liquids in Salt Formations, in *Proceedings of the Symposium on Treatment and Storage of High-Level Radioactive Wastes* held by the IAEA in Vienna, October 1962, International Atomic Energy Agency, Vienna, 1963, pp. 153-175.

¹³ S. M. Stoller Associates, The Perpetual Care of High Level Radioactive Wastes in New York State, NP-12486, October 12, 1962.

4. Economic Ground Rules

For each reference plant, estimates were prepared of the investment in process equipment and building and in auxiliary facilities and spare equipment based on requirements established for the flowsheets and processing specifications. The following economic ground rules were used to calculate the total charges associated with capital investment:

(a) Twenty-five percent of the above investments in process plant and auxiliaries was added for construction overhead, including engineering. This overhead factor is based on the assumption that the plants as built are not the first of their type.

(b) A one-time charge associated with plant startup was added in an amount equal to 25% of the total annual operating cost.

(c) Working capital was added to the total investment as a nondepreciating item. It was charged as 5% of process building and equipment (including auxiliary facilities) plus 20% of the total annual operating cost.

(d) Annual charges on capital were calculated as the sum of two components, the return on capital and the repayment of capital. The return of capital was calculated as 13% of the total capital investment. The fixed charge rate of 13%/year applied to the non-depreciated portions of the capital investment was taken from the AEC Guide to Nuclear Power Cost Evaluation⁴ and is based on the practices of investor-owned electric utilities. The components are as follows:

Minimum return	6.75%
Property Insurance	0.40
Federal Income Taxes	3.40
State and Local Taxes	2.45
	<hr/>
	13.0%/year

(e) The out-of-reactor fuel inventory was charged as a separate nondepreciating item at the 13%/year rate. The fuel values employed were \$10/g for plutonium isotopes 239 and 241; no value was assigned to other actinides.

(f) The other component of capital cost, the repayment of capital, was calculated as the sum of annual charges on sinking funds at the 6.75%/year interest rate to recover the original amounts of depreciating capital items over their respective economic lifetimes. The economic lifetimes were assigned as follows:

(1) Process equipment operating in radioactive areas and for which decontamination was not considered practical: 2 years.

(2) Process equipment and mechanical equipment in radioactive areas maintained fully remotely or for which decontamination was practical: 5 years.

(3) Chemical and mechanical equipment in non-radioactive areas, including laboratory, office items, and mobile equipment: 15 years.

(4) Major building structures (including shielding windows in remote cells): 30 years.

(5) One-time charges associated with startup and construction overhead: 30 years.

(6) Spare processing equipment: 30 years.

Capital items not included in the above capital repayment assignment are plant working capital and out-of-reactor fuel inventory, which are nondepreciating items.

Estimates were made of the annual operating costs of direct labor, indirect labor for maintenance and analytical laboratory operations, and materials (including reagents and utilities) based on specific plant requirements. The following ground rules were used to calculate the total charges associated with operating costs.

(a) The above labor requirements were first established in man-hours per operating day. This man-hour requirement was then multiplied by 1.4 to obtain the quantity of man-hours per day for the actual payroll, which includes allowance for such benefits as vacations and sick leave. An average annual payroll cost per man of \$12,000 was used, which includes fringe benefits.

(b) Supervision and indirect labor (other than that specified above) was taken as 25% of direct labor.

(c) Maintenance materials cost was taken as 20% of the sum of (1) total labor costs and (2) the annual charge for capital replacement for process equipment and building items.

(d) An annual overhead charge for administration was taken as 15% of the sum of all the operating costs above.

Total annual costs were calculated for each alternative case as the sum of: (1) the total annual operating cost, (2) the annual amount for capital repayment, and (3) the annual return on capital investment. The electrical unit costs in mills/kw(e)-hr of fuel processed were calculated from the total annual costs for the annual electrical energy production at 80% plant factor for the reference reactor power.

B. DESCRIPTION OF PLANTS AND ESTIMATE OF INVESTMENT FOR PROCESSING OXIDE FUEL FROM A 1000 Mw(e) REACTOR

1. Aqueous Processing

Equipment and building requirements were based on the reference flowsheet described above for aqueous processing of oxide core and blanket of the reference fast reactor. A brief description of the plant design concept is given below.

Core and blanket fuel assemblies are received into a remote-handling inert-atmosphere cell via a transfer lock. In the remote-handling cell the assemblies are dismantled and the fuel is chopped into short segments. Batches are prepared and loaded into baskets, which are then transferred directly through a chute into the dissolver. Other operations conducted in the remote-handling cell include the hydrogen reduction of calcine produced in the fluid-bed denitration of the uranium-plutonium aqueous product and the packaging of UO_2 - PuO_2 refabrication feed material.

The following equipment is housed in the processing cell:

- 1) Dissolvers and most of the off-gas system.
- 2) Solvent extraction columns, feed tanks, surge tanks, and solvent purification mixer-settlers.
- 3) Aqueous waste and intercycle evaporators.

A decontamination pit, decontamination cell, and equipment disposal facility are provided. The decontamination pit accommodates rack-mounted assemblies of processing equipment from the processing cell. Defective equipment units are removed from the processing cell and a spare assembly is installed to replace the defective unit. After decontamination, the defective unit is repaired in hot maintenance facilities and then becomes a part of the spares inventory. The equipment disposal facility accommodates rack-mounted units from the processing cell and provides a remote-handling facility for the scrapping of equipment. It is also used to remove unsalvageable components from rack-mounted processing assemblies prior to decontamination. The decontamination cell is a separate facility that serves the remote-handling cell.

Intermediate-level-activity processing facilities are provided for process operations on uranium and plutonium product streams after primary removal of fission products in the co-decontamination step. The principal operations are the partition cycle of the solvent extraction and the fluid-bed denitration of the uranium-plutonium product solution. Facilities are also provided for storage of uranium product solutions to allow for decay of ^{237}U and for an acid recovery system.

TABLE III-2. ESTIMATED INVESTMENT IN BUILDING AND EQUIPMENT FOR AQUEOUS PROCESSING OF OXIDE FUEL FROM A 1000 Mw(e) FAST REACTOR

	Investment (thousands of dollars)
A. General Facilities	
1. Offices, storerooms, and personnel convenience areas	278
2. Warehouse	50
3. Analytical laboratory	338
4. Decontamination and maintenance facilities	550
5. Reagent preparation facilities	341
6. Equipment disposal facilities	836
	2393
B. Remote Handling Cell	
1. Building	467
2. Transfer locks	167
3. Windows	150
4. Cranes and manipulators	122
5. Installed processing equipment	123
6. Instrumentation	19
7. Welding station	15
	1063
C. Processing Cell	
1. Building	748
2. Installed equipment	507
3. Instrumentation	214
	1469
D. Intermediate-Activity-Level Processing Facilities	
1. Building	129
2. Installed equipment	28
3. Instrumentation	3
	160
E. Low-Activity-Level Processing Facilities	
1. Building	52
2. Installed equipment	194
3. Instrumentation	76
	322
F. Auxiliary Equipment	
1. Argon purification and cooling	63
2. Electrical substation and emergency generator	72
3. Spare equipment	349
4. Mobile equipment	35
	519
TOTAL	5926

Low-level-activity processing facilities are those for handling uranium product after cooling to allow decay of ^{237}U . The principal operation is the fluid-bed denitration of the uranium product solution.

The general facilities comprise, in addition to the equipment decontamination and disposal facilities

cited above, offices, personnel convenience areas, warehouse, analytical laboratory, and an inactive facility for preparation of process reagents.

The estimated investment in building and equipment for aqueous processing of oxide fuel from a 1000 Mw(e) fast reactor is summarized in Table III-2.

2. Pyrochemical Processing

Equipment and building requirements were based on the reference flowsheet described above for pyrochemical processing of oxide core and blanket of a 1000 Mw(e) fast reactor. In the case of pyrochemical processing, all operations are conducted fully remotely in

an inert-atmosphere cell. All operations are conducted batchwise and the operations concepts are patterned after those employed in the EBR-II Fuel Cycle Facility at Idaho.⁶

The remote cell is equipped with air locks for entry

TABLE III-3. ESTIMATED INVESTMENT IN BUILDING AND EQUIPMENT FOR PYROCHEMICAL PROCESSING OF OXIDE FUEL FROM A 1000 Mw(e) FAST REACTOR

	Investment (thousands of dollars)
A. General Facilities	
1. Offices, utility rooms, and personnel convenience areas	205
2. Warehouse	40
3. Analytical laboratory	370
4. Maintenance facilities	322
5. Reagent preparation facilities	53
	990
B. Processing Cell	
1. Building	2373
2. Transfer locks	151
3. Windows	200
4. Cranes and manipulators	307
	3031
C. Processing Equipment and Instrumentation	
1. Processing equipment	700
2. Instrumentation	192
3. Weighing stations	10
4. Service leadins and disconnects	94
5. Welding stations	15
	1011
D. Auxiliary Equipment	
1. Argon cooling and purification	140
2. Off-gas handling equipment	46
3. Electrical substation and emergency generator	167
4. Mobile equipment	35
	388
	5420
TOTAL	

of fuel and other materials and for exit of wastes. The processing area is of an annular configuration which allows a double row of shielded viewing windows for operation of manipulators and cranes.

Auxiliary facilities include a decontamination cell, analytical laboratory, hot and cold maintenance shops,

a facility for the preparation of process reagents, warehouse, office, and personnel convenience areas.

The estimated investment in building and equipment for pyrochemical processing of oxide fuel from a 1000 Mw (e) fast reactor is summarized in Table III-3.

3. Fluid-Bed Volatility Processing

Equipment and building requirements were based on the reference flowsheets described above for fluid-bed volatility processing of oxide core and blanket of the reference fast reactor. Combined core and blanket fuel are fed to the plant in batches limited in size to twice the daily load specified in Table III-1. This limitation is required for nuclear safety and is based on the plutonium content of the batch. The separated uranium blanket fuel is not subject to these batch limits, however, and larger processing equipment may be employed whenever appropriate.

The volatility plant operations are conducted in the conceptual plant with six subdivisions as follows:

(1) A remote-operations cell patterned after that used in the pyrochemical plant is provided. This cell contains equipment for dismantling and trimming the irradiated fuel assemblies and for preparing the batch charges to the fluorinator. It includes the disposable reactors for fluoride waste gas fixation, and facilities for packaging the alumina waste from the fluid-bed fluorinator. Plutonium-fuel processing equipment, including the fluid-bed converter for preparation of core oxide from hexafluorides, is located here. Facilities for solids-sampling of the fluid-bed reactors are included. The cell is outfitted with shielding windows, crane, manipulators, lighting, inert-atmosphere system, and other facilities for completely remote manipulations. Transfer locks are provided for introducing and removing equipment and materials. This cell operates at the full irradiation level of the incoming fuel and provides for remote maintenance of contained equipment.

(2) A decontamination cell is provided adjacent to the remote operation cell for the purpose of decontaminating containers or other items that are removed from the remote-operations cell.

(3) The processing cell contains the volatility separations equipment. The major equipment items in this cell are the fluid-bed fluorinator, the bromine trifluoride fluorinator, and the hexafluoride condensation and fractional distillation systems. Also located here are the systems for treatment of waste gas from the oxida-

tion step and for concentration of rare gases. In addition, intermediate product receivers and the hexafluoride converter feed boilers are located in this cell. The process equipment is preassembled in functional units on support racks in a manner similar to that used in the aqueous plant. Each equipment rack is designed to be removed and replaced as a unit. The racks are suspended from removable shielding plugs at the top of the cell. Connections to process and instrument lines are made semi-remotely from their positions above the shielding plugs.

(4) The equipment disposal cell is a remote-operations cell specifically designed for removal of equipment from the process hot cell and for disposing of this equipment by cutting it up and packaging it in waste containers. It provides access to the process hot cell, but no process operations are carried out in this cell.

(5) The intermediate-level-activity facility consists of UF_6 storage tanks for interim cooling of the uranium (containing ^{237}U) prior to the blanket conversion steps.

(6) The low-level-activity process area includes all nonradioactive chemical facilities. It includes reagent feed storage and metering tanks, a system for treatment of the converter off-gas, and a safety scrubber for the ventilation air of the process hot cell and of the process cold area. Uranium blanket conversion equipment is located here. Equipment for monitoring ventilation exhaust air is included. Direct modes of operation and maintenance are used in this area. The equipment is located in walk-in ventilated spaces. Normal operations are conducted by personnel stationed at panel-board operating areas outside the equipment spaces.

The conceptual plant also includes offices, utility rooms, personnel convenience areas, warehouse, analytical laboratory, and active and inactive maintenance shops.

A summary is given in Table III-4 of the estimated investment in building and equipment for the several portions of the volatility plant for processing oxide core and blanket of a 1000 Mw (e) fast reactor.

TABLE III-4. ESTIMATED INVESTMENT IN BUILDING AND
EQUIPMENT FOR VOLATILITY PROCESSING OF OXIDE
FUEL FROM A 1000 Mw(e) FAST REACTOR

	Investment (thousands of dollars)
A. General Facilities	
1. Offices, storerooms, and personnel convenience areas	156
2. Warehouse	40
3. Analytical laboratory	340
4. Decontamination and maintenance facilities	241
5. Equipment disposal facilities	640
	<hr/> 1417
B. Remote Handling Cell	
1. Building	309
2. Transfer locks	101
3. Windows	150
4. Cranes and manipulators	122
5. Equipment—processing	188
6. Equipment—non-processing	68
7. Instrumentation	43
	<hr/> 981
C. Processing Cell	
1. Building	140
2. Installed equipment	583
3. Installed instrumentation	152
	<hr/> 875
D. Intermediate-Level-Activity Processing Facilities (UF ₆ Storage)	
1. Building	12
2. Equipment	38
3. Instrumentation	18
	<hr/> 68
E. Low-Level-Activity Processing Facilities	
1. Building	16
2. Equipment	51
3. Instrumentation	58
	<hr/> 125
F. Auxiliary Equipment	
1. Argon purification and cooling	55
2. Refrigeration	24
3. Electrical substation	80
4. Spare equipment	496
5. Mobile equipment	35
	<hr/> 690
	<hr/> <hr/> 4156
TOTAL	

C. DESCRIPTION OF WASTE DISPOSAL FACILITIES AND ESTIMATE OF CAPITAL INVESTMENT

The basic need for disposal of radioactive fission product wastes is radiological safety. However, no attempt was made in this study to define complete criteria for safe and economical storage; it is expected that such criteria will be adequately developed for use in 1980. The reference concept adopted in this study was that substantially all the fission product activity be contained in a high-level-activity solid waste from the volatility and pyrochemical processes and be sealed in cylindrical metal containers. This packaged waste is given interim cooling in facilities providing adequate heat removal. After a period of time, the heat generation rate is reduced sufficiently to allow permanent burial under conditions that provide a high degree of safety against possible dispersion and that require minimum surveillance. It was assumed that the location of permanent storage would be separate from the

processing plant and, therefore, shipping of the contained waste would be required after interim cooling.

In the case of high-level-activity aqueous waste, however, present uncertainty in the cost of aqueous waste solidification led to the adoption in this study of an alternative scheme of cost evaluation for this case. The aqueous waste disposal costs were calculated on the basis of perpetual on-site storage of concentrated waste solutions, with the expectation that technical developments in aqueous waste disposal would ultimately permit solid storage at an equally low cost.

It was assumed, for all three processes in this study, that fission products ^{85}Kr and tritium could be safely dispersed to the environment under controlled conditions. This assumption follows present waste disposal practices, but may not be allowable when fission product generation is much larger at some future time.

1. Interim Storage of High-Level-Activity Solids Waste

The interim storage facility for the high-level-activity packaged waste consists of a water-filled canal. The canal, which is constructed of reinforced concrete with an epoxy resin coating, is housed in a light-construction steel building. The depth of the

water above the containers, which are stored upright in individual stands, provides biological shielding. Canal space is also provided for receiving and removing the cylinders; a service building contains the water cooling and purification equipment.

2. Perpetual Storage of High-Level-Activity Liquid Wastes from Aqueous Processing

The perpetual storage of liquids requires high-integrity tankage and allowance for everlasting surveillance and replacement in the future.¹³ In the plan adopted, one waste tank is being filled at all times, while a second empty tank is always on hand as a spare to receive waste transferred from any of the storage tanks that become defective. Each of the 200,000-gal tanks is filled in six years. The tank formerly serving as a spare is then put into service and a new

spare tank provided. Each tank put into active service has a lifetime of 50 years; at the end of this time a new tank is provided. Surveillance and operating charges for the storage period (after filling) must be provided for each tank put into service. Because the entire plant is given an economic lifetime of 30 years, all of the above tank replacements and operating expenses of perpetual storage have their charges funded over the 30-year economic lifetime.

3. Fission Product Gases and Tritium

The fission product gases krypton and xenon are not contained in the solid or liquid waste and are handled separately. In all three processes, the xenon and krypton emerge in a waste stream consisting chiefly of oxygen, which is removed by catalytic reaction with hydrogen, followed by drying of the gas. The concentrated fission product gases are stored in tanks under pressure for 100 to 150 days to allow the radioactive xenon to decay. The remaining krypton is diluted with

air and discharged from the 200-ft high stack of the waste facility. The discharge is performed only under satisfactory meteorological conditions.

Fission product tritium, although present in relatively small amounts (corresponding to a fission yield fraction of about 1×10^{-4}) is of concern because it has a moderately long half-life (12 years). Tritium in the form of condensed water can be a serious contaminant in the environment. In the reference plants, tritium

ium is oxidized to water and this water is evaporated and discharged under suitable meteorological conditions to the environment through the main 200-ft stack of the plant. The above plans for atmospheric

dispersal of krypton and tritium were adopted from the studies of Farrow¹⁴ and Oak Ridge National Laboratory.¹⁵

4. Other Wastes

Fission product iodine is removed from gas streams by sorption on charcoal. Because the principal activity has a short half-life (8 days), cooling time is used to advantage in the respective processes in iodine disposal. Spent charcoal is packaged and buried on site as low-activity waste.

Miscellaneous low-level activity solid wastes are

TABLE III-5. ESTIMATED INVESTMENT IN FACILITIES FOR DISPOSAL OF WASTE FROM AQUEOUS PROCESSING OF OXIDE FUEL FROM A 1000 Mw(e) FAST REACTOR

	Investment (thousands of dollars)
Exhaust stack and service building	458
Service building and tanks for interim storage of noble gas effluent from dissolvers	25
Service building and incinerator for disposal of waste solvent	59
Waste neutralization facilities (including spare equipment)	64
Two 200,000-gallon mild steel storage tanks with reflux condenser; installed underground in concrete vaults	950
Lagoon for disposal of evaporator overheads and other very low activity level wastes	117
Waste casks and transporters	27
Aqueous waste evaporators (including spare equipment)	716
TOTAL	2416

TABLE III-6. ESTIMATED INVESTMENT IN FACILITIES FOR DISPOSAL OF WASTE FROM VOLATILITY PROCESSING OF OXIDE FUEL FROM A 1000 Mw(e) FAST REACTOR

	Investment (thousands of dollars)
Exhaust stack and service building	458
Canal and building for interim storage of high-level-activity solid waste	483
Tanks and building for interim storage of noble gas fission products	25
Waste treatment facilities and building for converter scrubber waste solution	38
Tanks, evaporator, and lagoon for miscellaneous active aqueous waste	365
Waste casks and transporters	27
TOTAL	1396

TABLE III-7. ESTIMATED INVESTMENT IN FACILITIES FOR DISPOSAL OF WASTE FROM PYROCHEMICAL PROCESSING OF OXIDE FUEL FROM A 1000 Mw(e) FAST REACTOR

	Investment (thousands of dollars)
Exhaust stack and service building	458
Canal and building for interim storage of high-level-activity solid waste	393
Tanks and building for interim storage of noble gas fission products	25
Tanks, evaporator, and lagoon for miscellaneous active aqueous waste	365
Waste casks and transporters	27
TOTAL	1268

buried on site. Inactive liquid wastes are dispersed to the environment through a lagoon.

In the case of volatility and pyrochemical processing, miscellaneous waste from decontamination and laboratory operation are stored on site in stainless steel tanks.

In the case of solvent extraction processing, the kerosene solvent is washed with sodium carbonate solution to remove the products of solvent degradation that result from the high levels of irradiation. This spent washing solution is added to the high-level aqueous waste of the plant. The solvent is burned in an incinerator; the combustion gas is filtered and washed. The ash and wash are added to the main active waste storage tanks. Incineration of solvent is reasonably well developed.^{16, 17}

The estimated investment requirements for waste facilities are given in Tables III-5, III-6, and III-7 for the aqueous, volatility, and pyrochemical processing, respectively.

¹⁴ W. H. Farrow, Jr., Radiochemical Separations Plant Study. Part II. Design and Cost Estimates, DP-566, March 1961.

¹⁵ Oak Ridge National Laboratory, Chemical Technology Division Annual Progress Report for Period Ending May 31, 1964, ORNL-3625, October 1964, pp. 113-114.

¹⁶ R. R. Steins, Disposal of OMP High Boilers by Combustion, NAA-SR-5410, Nov. 15, 1961.

¹⁷ J. A. Harper and L. Lolly, Jr., A Method of Disposal of Large Quantities of Degraded and Low Level Contaminated Solvent, DPSPU 64-30-8B, May 1964.

D. ESTIMATE OF OPERATING COSTS AND ELECTRICAL UNIT COSTS

The estimates of the major categories of operating costs, namely, total labor and direct materials, are given in Table III-8 for the aqueous, volatility, and pyrochemical processing plants and their associated waste disposal facilities. The total annual operating costs calculated under the ground rules of this study are also shown in the tables.

The electrical unit costs for the respective processing

TABLE III-8. ESTIMATED OPERATING COSTS FOR AQUEOUS, VOLATILITY, AND PYROCHEMICAL PROCESSING OF OXIDE FUEL FROM A 1000 Mw(e) FAST REACTOR
Costs in thousands of dollars

	Aqueous	Volatility	Pyro-chemical
<i>Processing</i>			
Total labor	1,522	747	1,042
Direct materials	76	144	276
Total annual operating cost ^a	2,256	1,281	1,811
<i>Waste Disposal</i>			
Total labor	238	62	62
Direct materials	8	48	60
Total annual operating cost ^a	373	318	352

^a Calculated from the operating cost components shown according to the ground rules of this study.

TABLE III-9. SUMMARY OF ELECTRICAL UNIT COSTS FOR AQUEOUS, VOLATILITY, AND PYROCHEMICAL PROCESSING OF OXIDE FUEL FROM A 1000 Mw(e) FAST REACTOR

Unit costs are calculated in mills/kw(e)-hr according to the ground rules of this study

	Aqueous	Volatility	Pyro-chemical
Processing	0.53	0.35	0.44
Waste Disposal	0.15	0.09	0.09
Out-of-reactor fuel inventory	0.17	0.12	0.12
1% Loss	0.016	0.016	0.016
TOTAL	0.87	0.58	0.67

plants are shown in Table III-9. The total costs are shown for processing, waste disposal, out-of-reactor fuel inventory, and for an assumed 1% fuel loss. The costs in those categories were calculated for the economic ground rules of the study, which were summarized above. The out-of-reactor inventory charge is larger for aqueous than nonaqueous processing; this result is due principally to the longer cooling time required for discharged fuel before the beginning of solvent extraction operations.

E. INTERPRETATION OF RESULTS

The cost estimates presented here were developed to make cost comparisons of alternative cases of processing fast reactor fuel in a future nuclear economy. The estimates were not intended as estimates of actual construction costs. The electrical unit cost results given in this report furnish a comparison of three methods of processing of oxide fuel in close-coupled facilities associated with a single 1000 Mw(e) fast reactor. A substantial cost advantage is shown for both the volatility and pyrochemical processes as compared with the aqueous process. The cost difference between the volatility and pyrochemical processes is shown to

be smaller than that between either of these processes and the aqueous process; the cost difference between the two nonaqueous processes is considered to be insignificant because it is within the estimated uncertainty of the comparative unit costs.

The complete cost analysis² will compare the economics of processing oxide, carbide, and metal fast reactor fuels by each of the above types of processes. The study will also show the degree of saving in unit costs as plant size is increased to accommodate reactors having a total power of 10,000 Mw(e).

IV

Materials Chemistry and Thermodynamics¹

A. HIGH TEMPERATURE MATERIALS DEVELOPMENT

(R. K. EDWARDS, H. M. FEDER, M. ADER)

This program is directed toward the ultimate development of nuclear reactor materials for use at high temperatures (1500 to 3000°C). Its objective is to amass a fund of basic data which may be drawn on for guidance in materials selection. The studies are concerned with the vaporization and chemical stability of potential fuels, i.e., the oxides, carbides, phosphides, sulfides, arsenides, and nitrides of uranium, plutonium, and thorium, and their solid solutions; and with the reactions of these materials with supporting structural materials and coolant fluids. Experimentation will be done quantitatively so as to yield thermodynamic and phase-diagram information. Each selected system, comprising fuel, structural material, and coolant, is to be

studied in an integrated way, using several methods of investigation that are mutually supporting.

Current experimentation has emphasized the determination of the phase diagram of the condensed state of the uranium-urania² system, the equilibria between the vapor and condensed phases of this system, and the oxidation-reduction equilibria of urania. A detailed discussion of the expected behavior of this system and of the experimental approaches to its study was given in ANL-6925, pp. 165-173. Exploratory experimental work to extend the phase relations to cover the tungsten-uranium-urania triangle is in progress. A study³ of the uranium-uranium monosulfide phase diagram, initiated earlier, remains set aside temporarily.

1. Phase Diagram Studies

a. THE URANIUM-URANIA SYSTEM (A. E. MARTIN, F. C. MRAZEK)

Additional work on the uranium-urania phase diagram has added better definition to the uranium liquidus and has led to only minor changes in the diagram and information previously reported.⁴

The current "best" phase diagram⁵ is shown in Figure IV-1 and its essential features are summarized below.

¹ A summary of this section is given on pages 10 to 12.

² The term urania will be used in Section IV A to denote a solid phase of fluorite structure with composition unspecified; the symbol UO_2 will be used to denote stoichiometric uranium dioxide. The terms hyperstoichiometric and hypostoichiometric refer to the oxygen in UO_2 ; the symbols UO_{2-x} and UO_{2+x} denote hypostoichiometric and hyperstoichiometric urania, respectively.

³ ANL-6925, p. 173; ANL-6900, p. 219.

⁴ ANL-7055, p. 163; ANL-6925, p. 166.

⁵ A preliminary disclosure of the uranium-urania phase diagram was published in J. Phys. Chem. **69**, 1788 (1965). Also, a paper on this work was presented at the *Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic*

A wide, liquid miscibility gap exists at temperatures above $2470 \pm 25^\circ\text{C}$, which is the monotectic temperature in the system. At the monotectic temperature, the compositions in O/U atom ratio units of the three condensed phases in mutual equilibrium are: liquid uranium, 0.05 ± 0.01 ; monotectic liquid, 1.30 ± 0.10 ; and hypostoichiometric urania, 1.61 ± 0.02 .

Analysis of the combined results of oxide growth experiments and isopiestic equilibrations shows that between 1600 and 2470°C the hypostoichiometric urania phase boundary compositions can be expressed by the equation.

$$\log X_U = 1.335 - 5608/T \quad (1)$$

in which X_U is the mole fraction of uranium dissolved in UO_2 at saturation and T is temperature in degrees Kelvin. (Note that $2X_U$ is equal to the oxygen deficiency, x , in the formula UO_{2-x} .) Equation 1 repro-

Transport in Solids, IAEA, Vienna, Austria, July 22-27, 1965, SM-66/81. Changes apparent in the current report arise from the accumulation of more data and the consequent effect on the parameters in the equations fitted to the data.

108-8842

FIG. IV-1. Uranium-Urania Phase Diagram at Elevated Temperatures.

duces the values for X_U to within 8.6% (standard deviation). From Eq. 1, the heat of solution of uranium in the saturated solid is 26.5 kcal/mole. The strong upturn of the hypostoichiometric phase boundary above 2300°C, which was previously reported,⁴ no longer appears valid within the experimental uncertainty, and the implication that additional phase transformations occur in hypostoichiometric urania between 2300 and 2500°C is no longer warranted.

The liquidus data obtained between 1790 and 2436°C yields the equation

$$\log X_O = 6.267 - 2.820 \times \frac{10^4}{T} + 0.2021 \times \frac{10^8}{T^2} \quad (2)$$

in which X_O is the mole fraction of oxygen in oxygen-saturated liquid uranium. Equation 2 is in good agreement with the data obtained by Cleaves et al⁶ at 1810, 1900, and 2000°C, and its extrapolation gives fair agreement with their data at lower temperatures, 1400 to 1720°C. From Eq. 2, the composition of the uranium-rich liquid (L_1) at the monotectic temperature, 2470°C, is given by $X_O = 0.047$ or O/U atom ratio = 0.049.

The melting temperatures of urania which are indicated in Figure IV-1 are based on recent literature data. The melting point at the stoichiometric composition has been drawn to agree with the value $2805 \pm 15^\circ\text{C}$

obtained by H. Hausner.⁷ Within experimental error, this is equivalent to the value $2790 \pm 20^\circ\text{C}$ reported by J. A. Christensen.⁸ However, the maximum melting point of urania is shown at 2850°C at a slightly hypostoichiometric composition to conform with the indications of two recent studies.^{9, 10}

b. HYPOSTOICHIOMETRIC PHASE BOUNDARY OF URANIA: ISOPIESTIC MEASUREMENTS (M. S. CHANDRASEKHARAIAH¹¹)

The determination of the hypostoichiometric phase boundary of urania by isopiestic equilibration^{12a} in vacuo, rather than in helium as reported above, is essentially complete. The results obtained between 1600 and 2100°C are in very good agreement with those obtained by use of Eq. 1. However, as stated previously,^{12b} the results near 2200°C seem to yield O/U atom ratios that are higher by as much as 0.1. Efforts to pinpoint possible sources of discrepancy, e.g., contact of tantalum with urania, have not been fruitful. Only limited further work is planned.

c. THE URANIUM-URANIA-TUNGSTEN SYSTEM (A. E. MARTIN, F. C. MRAZEK)

A study of the uranium-uranium-tungsten system has been initiated because of its relevance to the use of tungsten as a cladding for very high temperature urania fuels, and because of the widespread use of tungsten supports in related experimentation. Some exploratory tests have been carried out in the ternary system. The liquid miscibility gap which has been found to exist in the U-UO₂ system at temperatures above the monotectic, 2470°C, was found to extend into the ternary system as well. Metallographic examination of the products of some tests indicate that the ternary monotectic may be as much as 300°C below the binary monotectic. The composition of the oxygen-rich ternary liquid at the monotectic temperature has not been established. Metallographic examinations also indicate that the solubility of tungsten in hypostoichiometric urania is less than 1% up to 2500°C.

⁷ H. Hausner, *J. Nucl. Mater.* **15**, 179 (1965).

⁸ J. A. Christensen, "Irradiation Effects on Uranium Dioxide Melting," HW-69234, March, 1962, p. 7.

⁹ J. L. Bates, in "Ceramics Research and Development Operation Quarterly Report, October-December, 1964," HW-81603, 1965, p. 2.21.

¹⁰ R. N. Duncan and H. M. Ferrari, *Trans. Am. Nucl. Soc.* **6**, 154 (1963).

¹¹ In collaboration with the High Temperature Group the Chemistry Division.

¹² (a) ANL-6925, p. 170; (b) ANL-7055, p. 164.

⁶ H. E. Cleaves, M. M. Cron, and J. T. Sterling, in "Progress Report for December, 1944," CT-2618, February, 1945, pp. 5-11.

2. Vapor Pressure Studies

a. TRANSPIRATION STUDIES OF TOTAL VAPOR PRESSURE OF URANIUM-BEARING SPECIES AND OF OXYGEN PARTIAL PRESSURE OVER URANIA (M. TETENBAUM, P. D. HUNT)

Transpiration measurements of the total pressure of uranium-bearing species and of the partial pressure of oxygen over hypostoichiometric urania have been made as a function of urania composition. The measurements were conducted with H_2 - H_2O buffering carrier gas mixtures which served to fix the oxygen partial pressures and thereby control the composition of the solid urania phases. The uranium content of the solid phases and of the uranium-bearing gaseous species (collected on a tungsten condenser¹³) were determined by conventional analytical methods. Oxygen partial pressures were calculated from the moisture content of the exit carrier gas streams which were monitored by an electrolytic moisture analyzer. The calculations were based on the equation

$$\log P_O(\text{atm}) = -\frac{26,240}{T} + \log \left(\frac{P_{H_2O}}{P_{H_2}} \right) + 6.38 \quad (3)$$

which is derivable from well-known thermodynamic data^{14, 15} on the equilibrium between water vapor and its elements.

Figure IV-2 shows the results of determinations of monatomic oxygen partial pressure over urania between 2185 and 2600°K. Included in Figure IV-2 are some calculated values corresponding to hypostoichiometric phase boundary compositions (taken from Figure IV-1). The oxygen partial pressures at the corresponding temperatures were estimated by an equation obtained by Ackermann, Chandrasekharaiah, and Rauh¹⁶ in their effusion and mass spectrometric studies of the urania-liquid uranium two-phase system. The trend in oxygen partial pressures obtained via the transpiration method appears to be consistent with expectations, namely, a rapid increase of oxygen partial pressure as the oxygen content of the solid is increased, with the most rapid increase taking place near the stoichiometric composition. The present results are in qualitative agreement with reasonable extrapolations of the lower tempera-

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FIG. IV-2. Monatomic Oxygen Partial Pressure as a Function of Urania Composition.

ture results of other investigations, such as the emf method of Markin and Bones.¹⁷ However, it should be noted that the pressures shown in Figure IV-2 are generally 2 to 10 times lower than those reported by Aitken, Brassfield, and Fryxell.¹⁸ We suspect that equilibrium was not reached in their experiments because they used a relatively high carrier gas flow rate of about four liters/min; in the present work, a flow rate of about 0.125 liter/min was used.

Figure IV-3 shows the results of measurements of the total vapor pressure of uranium-bearing species over urania. The results are consistent with the expected trend of an increase in total pressure of uranium-bearing species (primarily owing to the rapid increase in P_{UO}) as the solid is reduced. Between 2300 and 2600°K, a 2.5- to 3.5-fold increase in pressure of uranium-bearing gaseous species occurs on going from UO_2 to the hypostoichiometric phase boundary. The experimentally determined total pressure of uranium-bearing species over UO_2 at 2390°K was found to be in excellent agreement with the value derived from the extrapolated low-temperature effusion measurements of Ackermann et

¹³ ANL-6900, p. 214, Figure III-5.

¹⁴ O. Kubaschewski and E. LL. Evans, "Metallurgical Thermochimistry," Pergamon Press, New York, N. Y., 1958, p. 339.

¹⁵ D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series, No. 18, American Chemical Society, Washington, D. C., 1956, p. 144.

¹⁶ R. J. Ackermann, E. G. Rauh, and M. S. Chandrasekharaiah, ANL-7048, July, 1965.

¹⁷ T. L. Markin and R. J. Bones, "The Determination of Some Thermodynamic Properties of Uranium Oxides with O/U Ratios between 2.00 and 2.03 Using a High Temperature Galvanic Cell. Part II," AERE-R 4178, November 1962, pp. 23, 24.

¹⁸ E. A. Aitken, H. C. Brassfield, and R. E. Fryxell, *Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids*, IAEA, Vienna, Austria, July 22-27, 1965, SM-66/83.

FIG. IV-3. Total Pressure of Uranium-Bearing Species as a Function of Urania Composition.

al.¹⁹ Work to extend the temperature and composition range of the transpiration measurements is in progress.

b. EFFUSION STUDIES OF THE TOTAL VAPOR PRESSURE OF URANIUM-BEARING SPECIES OVER THE URANIUM-URANIA TWO-PHASE SYSTEM (M. S. CHANDRASEKHARAIHAH¹¹)

The measurements by the Knudsen effusion method of the total vapor pressure of uranium-bearing species over the two-phase system, uranium (liquid, saturated with UO_{2-x}) in equilibrium with UO_{2-x} (solid, saturated with uranium), have been completed in the range 1300 to 2000°C. The results may be expressed by the equation

$$\log P \text{ (atm)} = (7.25 \pm 0.14) - (27,024 \pm 255)/T, \quad (4)$$

where P is the total pressure of uranium-bearing species and T is the temperature in degrees Kelvin. The study for the temperature range noted is considered complete, and an ANL topical report on the work has been prepared.¹⁶ Beyond 2000°C, the vapor pressures are too high to permit the application of the effusion method, so any further measurements will be made by the transpiration method.

¹⁹ R. J. Ackermann, P. W. Gilles, and R. J. Thorn, J. Chem. Phys. 25, 1089 (1956).

c. THE CONGRUENTLY VAPORIZING COMPOSITION OF URANIA (M. S. CHANDRASEKHARAIHAH, P. M. DANIELSON)

It is possible that the congruently vaporizing composition of urania may not correspond to the stoichiometry, $O/U = 2$, but rather to hypostoichiometric urania. Fairly good evidence to this effect has recently been obtained.¹⁶ It has been pointed out²⁰ that the effusion observations of Ackermann et al.¹⁹ and of Ohse²¹ could also be attributed to a shift of the composition of the solid toward a congruently effusing composition. There is a need to establish firmly the congruently vaporizing composition of the solid in order to correlate vaporization data because, as previously indicated,²² the partial pressures of some gaseous species are very sensitive functions of composition in the vicinity of exact stoichiometry. The congruently vaporizing composition has a further importance, namely, that it can, in principle, be reproduced by other laboratories and hence serve as a reference composition for correlating thermodynamic data. For these reasons, an investigation to determine the congruently vaporizing composition of urania has been undertaken. It should be noted that the composition of congruent vaporization in a closed system at equilibrium may

²⁰ ANL-7055, p. 165.

²¹ R. W. Ohse, "High-Temperature Vapor Pressure Studies of UO_2 by the Effusion Method," EUR-2166.e, 1965.

²² ANL-6925, p. 169.

differ from the composition of congruent vaporization under effusion conditions; the latter was chosen, however, because it is capable of better experimental definition. The results of such measurements should also permit calculation of conditions for congruent equilibrium vaporization.

An ultrahigh-vacuum furnace system has been set up and is undergoing testing. In this furnace, tungsten effusion cells have been heated to the projected temperatures of experimentation while maintaining vacua corresponding to about 10^{-9} torr oxygen. (The residual gases are measured by a quadrupole-type analyzer.) This residual pressure is well below that of monatomic oxygen in equilibrium with hypostoichiometric urania above 2000°C. Consequently, urania subjected to vaporization by effusion should attain a congruent composition which is independent of the oxidation potential of the vacuum environment.

d. MASS SPECTROMETRIC, EFFUSION STUDIES OF THE PARTIAL PRESSURES OF URANIUM-BEARING SPECIES OVER THE URANIUM-URANIA TWO-PHASE SYSTEM
(J. W. REISHUS, J. E. BATTLES, G. E. GUNDERSEN)

Recent efforts have been directed toward finding and eliminating the cause of the nonreproducible heats of sublimation which were observed for $\text{UO}_2(\text{g})$ over urania, and for $\text{U}(\text{g})$, $\text{UO}(\text{g})$, and $\text{UO}_2(\text{g})$ over the uranium-urania system. It was first suspected that temperature gradients within the effusion cells might be responsible for the trouble.²³ Temperature gradients, rather than a defective pyrometer, were suspected at first because they are known²⁴ to have a significant effect on heats of sublimation, and because the existence of such gradients have been observed in our effusion cells. Thus, considerable effort was directed toward minimizing the temperature gradients in our effusion cells. It was found that with a single electron-bombard-

ment-heating filament (the present arrangement in our Knudsen effusion assembly) axial temperature gradients could be decreased to approximately 10°C, with the bottom of the cell cooler than the top. However, it became apparent that to reduce the gradients to 2 to 3°C and, more importantly, to be able to change a gradient during an experiment, two and perhaps three independent electron-bombardment-heating filaments would be necessary. Indeed, other workers have also recognized the necessity for more than one heating filament if temperature gradients are to be controlled in this type of experiment.^{24, 25} A power regulator for a second heating filament in our Knudsen effusion assembly is being procured.

When heats of sublimation²⁶ of UO_2 still could not be satisfactorily reproduced despite the reduction of the temperature gradient in our present system, the optical pyrometer in use, which had been calibrated earlier, was compared against another calibrated pyrometer. During this comparison it was found that the pyrometer in question had a defective tungsten lamp. After repairing the pyrometer, the heat of sublimation of UO_2 was again determined. The repaired pyrometer gave a heat of sublimation of 136.5 kcal/mole which is in good agreement with the accepted value¹⁹ of 137.4 kcal/mole. The repaired pyrometer differed by only a small constant amount—7 to 10°C over the range 1700 to 2100°C—from the other calibrated pyrometer; this difference has a negligible effect on the evaluation of the heat of sublimation.

It is now believed that the primary source of the reproducibility problem has been uncovered and corrected. In order to detect temperature determination troubles more rapidly in the future, all the optical pyrometers in the High Temperature Materials Group will be intercompared monthly to spot abnormalities in the performance of individual pyrometers.

Mass spectrometric effusion studies of the urania system can now be resumed.

²³ O. C. Trulson and H. W. Goldstein, *J. Phys. Chem.* **69**, 2531 (1965).

²³ ANL-7055, p. 166.

²⁴ E. K. Storms, in *Twelfth Annual Conference on Mass Spectroscopy and Allied Topics*, Montreal, Canada, June 7-12, 1964, p. 573.

²⁶ Evaluated from the slopes of the $\log IT$ vs. $1/T$ curves, where I is the ion intensity of a vaporizing species, and T is temperature in degrees Kelvin.

B. PREPARATION OF REACTOR MATERIALS (P. NELSON, A. D. TEVEBAUGH, J. D. BINGLE)

1. Ceramic Fuels

Refractory compounds of uranium and plutonium, such as carbides, nitrides, and sulfides, show promise as fast reactor fuels capable of withstanding high temperatures and high burnups. Methods are being investigated for the preparation of these fuel materials, and the more promising methods are being used to provide materials for fabricability evaluations and irradiation testing.

Various fluidized-bed processes are currently under study for synthesizing these fuel materials. These processes employ a reagent in the fluidizing gas which reacts with finely divided uranium or plutonium to yield the desired product. An example of such a process is the fluidized-bed carburization of hydrided uranium or hydrided uranium-plutonium alloy with hydrocarbon-hydrogen gas mixtures to form UC or (U,Pu)C, respectively, as described previously (ANL-7055, pp. 87-94). The present report discusses thermodynamic principles and processing techniques for the fluidized-bed method for preparing UC and (U,Pu)C; data on kinetics and product characteristics for these processes are also reported.

In the planning stage, and therefore not discussed in detail herein, are various other fluidized-bed processes for preparing UN, UC-UN, and UC-US from hydrided uranium and fluidizing gases containing nitrogen, methane or H₂S or combinations of these reagent gases. Preparation of UC and (U,Pu)C from the dioxides by a fluidized-bed process is also under consideration.

a. THERMODYNAMIC AND RATE CONSIDERATIONS IN CARBIDE SYNTHESIS BY THE METAL-HYDROCARBON REACTION (P. NELSON)

The equilibrium reactions of uranium and uranium monocarbide with methane at one atmosphere total pressure were discussed previously (ANL-7055, p. 87). That work has now been extended to include reactions at higher pressures, reactions involving plutonium, and the rate of approach to equilibrium.

The objectives in current work to produce UC or (U,Pu)C are to obtain (1) a satisfactory reaction rate and (2) a stoichiometric product. The first objective is partially met by hydriding the metal or alloy to obtain a fine powder which will react rapidly at carburizing temperatures of 600 to 900°C. A satisfactory reaction rate, such that the reaction will be complete in about 5 hr, can then be obtained in a fluidized bed if the hydrocarbon partial pressure is high enough at the maximum

fluidizing gas velocity to provide an adequate supply of carbon. Experience has shown that the maximum fluidizing gas velocity for hydrided uranium is about 0.5 ft/sec; above this velocity, loss of fines from the bed is excessive. This maximum velocity is rather insensitive to changes in gas pressure or composition.

The minimum partial pressure of hydrocarbon gas for reaction of the gas with uranium metal is very low ($\sim 10^{-6}$ atm of methane at 1 atm hydrogen pressure and 800°C) and thus does not pose a problem. However, if the partial pressure of hydrocarbon gas is too high, UC₂ and/or carbon are formed under equilibrium conditions by the reactions

In the case of U-Pu carbides, the sesquicarbide is formed:

The following general equations are useful in representing these reactions:

The standard free energy change for reaction 2, ΔG_2° , is well established¹ ($\Delta G_2^\circ = -21,550 + 26.16 T$ cal/mole). However, the free energy change for reaction 1 is not well established even for uranium carbides. In the temperature range of interest, ΔG_1° is about -1 kcal/mole of UC₂ but may be as low as -4 kcal/mole.² For the formation of (U,Pu)₂C₃, ΔG_1° is thought to be somewhat lower, perhaps -5 kcal/mole.

The effects of temperature, total pressure, and variation in the estimated values of ΔG_1° on the partial pressure of methane in hydrogen in equilibrium with actinide carbides are illustrated in Figure IV-4. Hydrocarbon gases other than methane would behave in a similar manner at equal overall hydrogen-to-carbon ratios if formation of higher carbides is not greatly favored by catalytic action.

¹ A. K. Biswas and G. R. Bashforth, *The Physical Chemistry of Metallurgical Processes*, Chapman and Hall, London (1962).

² "The Uranium-Carbon and Plutonium-Carbon Systems, A Thermochemical Assessment," Technical Report Series No. 14, International Atomic Energy Agency, Vienna, 1963.

108-9330 Corr.

FIG. IV-4. Methane-Hydrogen Mixture in Equilibrium with Actinide Carbides.

At methane partial pressures above values represented by an equilibrium line on this graph for an assumed value of ΔG_1° , the solid phase at equilibrium is the higher carbide; below values represented by this line, the solid phase is the monocarbide. Variation of the assumed values of ΔG_1° from 0 to -5 kcal/mole (the expected range) causes a pronounced variation in the calculated equilibrium methane pressure. However, increasing the total pressure of the fluidizing gas from 1 atm to 10 atm has an even larger effect, which is beneficial.

At a given temperature and a given fluidizing velocity, the methane throughput in a fluidized-bed reactor would be proportional to the partial pressure of methane (the ordinate in Figure IV-4). By operating at 800°C , 10 atm total pressure, 0.4 atm methane partial pressure, and 50% methane utilization efficiency, a carbide production rate of about 10 kg/hr could be attained in an 8-in. dia. reactor. If such a reactor contained 50 to 100 kg of material and the methane utilization efficiency was 50%, the total reaction time of 5 to 10 hr would be sufficient to complete the reaction (see below). It should be noted from Figure IV-4 that under the above operating conditions the product should be stoichiometric monocarbide.

In a fluidized-bed reactor, the formation of stoichiometric monocarbide is influenced by factors other than the proper methane-to-hydrogen ratio. It has been

shown (ANL-7055, p. 90) that in the carburization of uranium-plutonium alloys under conditions of high hydrocarbon (propane) concentrations (where higher carbides would be obtained at equilibrium), only small amounts of higher carbides are actually formed. The low rate of formation of UC_2 in the temperature range of interest has been attributed to a low rate of diffusion of carbon through UC_2 .³ The small amount of higher carbides which would be formed during carburization could be reduced by a final hydrogen treatment in the fluidized bed. Such a reaction has been shown by Harden et al⁴ to proceed rapidly at 850°C even at 1 atm hydrogen pressure.

In summary, thermodynamic and rate calculations indicate that stoichiometric UC and (U,Pu)C powders can be produced at high rates by the metal-hydrocarbon reaction in a fluidized bed.

b. THERMOBALANCE EXPERIMENTS ON CARBIDE SYNTHESIS (S. VOGLER, P. KRAUSE)

Thermobalance experiments are being continued in order to obtain preliminary data on the kinetics of the reactions of hydrocarbon gases with uranium and uranium-plutonium alloys. Another objective is to determine whether these reactions can be limited to formation of the monocarbides by the use of the proper gas composition, as expected from the thermodynamic calculations discussed above. A description of the thermobalance equipment and procedure has been reported previously (see ANL-7055, p. 90). Briefly, the procedure consists of reacting about 3 g of metal with hydrogen in the thermobalance to yield finely divided hydride, and then reacting the hydride with a hydrogen-hydrocarbon mixture. The carburizing gas flow is begun as soon as hydriding is complete in order to prevent sintering as the temperature is raised. The change in weight of the sample is recorded as a function of time.

In recent runs, both methane-hydrogen and propane-hydrogen gas mixtures were reacted with uranium and uranium-plutonium alloy. The operating conditions and the composition of the products resulting from these runs are shown in Table IV-1.

The sesquicarbide phase, which was usually not found in the product of previous experiments (see ANL-7055, p. 92), was observed in all the current experiments on preparation of (U,Pu)C. The explanation

³ S. Takeuchi, T. Honma, and T. Satow, The Reaction of Uranium with Graphite at High Temperatures, Trans. Japan Inst. Metals, 5(2), 111-115 (April 1964).

⁴ B. R. Harden, J. Read, and R. G. Sowden, The Reduction and Sintering of Hyperstoichiometric Carbides in Hydrogen, AERE-R 4877, Atomic Energy Research Establishment, Harwell, Berkshire, April 1965; also J. Nucl. Materials 17(3), 203 (1965).

TABLE IV-1. THERMOBALANCE EXPERIMENTS ON PREPARATION OF URANIUM-PLUTONIUM CARBIDE BY THE METAL-HYDROCARBON REACTION

Approximately 3 g of U-20 w/o Pu alloy hydrided, then reacted with hydrocarbon-hydrogen mixtures at a temperature of 750°C, a gas flow rate of 1.4 liters/min, and 1 atm pressure

Reaction Conditions			Weight Gain (% of Theor. ^c)	Product Composition					
Reagent Gas ^a	Reaction Time (min)			X-ray Analysis		Chemical Analysis (w/o)			
	To Completion ^b	Total		Major	Minor	Carbon ^d	Oxygen	Nitrogen	Hydrogen
1.0 v/o C ₃ H ₈	125	270	113	XC ^e	X ₂ C ₃	4.69	0.56	0.52	0.013
1.5 v/o C ₃ H ₈	—	215	102	XC	X ₂ C ₃ , XO ₂	4.26	0.18	0.40	0.009
1.5 v/o C ₃ H ₈	—	220	—	XC	X ₂ C ₃	4.23	0.23	0.81	0.006
1.0 v/o CH ₄	180	370	108	XC	X ₂ C ₃ , XO ₂	4.17	0.42	0.81	0.005
2.0 v/o CH ₄	85	290	114	XC	X ₂ C ₃	5.04	0.60	0.36	0.012

^a The balance is hydrogen.

^b Estimated time for completion of reaction, measured from the time temperature reached 500°C until the rate of change of weight became very low. The reaction was continued beyond this point for several hours.

^c Based on formation of pure (U,Pu)C.

^d Carbon content of pure (U,Pu)C is 4.80 w/o.

^e Face-centered cubic structure with lattice parameter of about 4.96 Å, a value which is within the range that might be expected for a uranium-plutonium monocarbide solid solution.

tion for this result lies in the manner in which the experiments were performed. In the early experiments, the reaction was terminated when the weight gain indicated that the reaction to the monocarbide had been completed. Thus the reaction to form the sesquicarbide was minimized, even though the hydrocarbon content was high enough for such a reaction to take place. In recent experiments, the goal was to obtain a monocarbide product by using a reacting gas of a composition such that the gas would be in equilibrium with the monocarbide. The experiments were continued beyond the point at which the weight gain had leveled off in order to determine if the reaction would terminate on completion of formation of the monocarbide phase. The fact that sesquicarbide formed with 1 v/o methane (the lowest hydrocarbon concentration used) indicates that even this concentration is too high for equilibrium of the gas with the monocarbide.

The standard free energy change, ΔG_1° , for the reaction

can be estimated from Figure IV-4 for assumed equilibrium conditions for the reaction:

If equilibrium conditions for the above reaction were the least carburizing conditions used in these experiments, namely, 1 v/o methane-hydrogen gas at 1 atm pressure and 750°C, then ΔG_1° would be about -4 kcal. Since some sesquicarbide was formed in the experi-

ment under these conditions, then ΔG_1° must be more negative than -4 kcal.

Another experiment with the thermobalance was devised to determine whether (U,Pu)₂C₃ which was formed during carbiding could, subsequently, be reduced to the monocarbide with pure hydrogen. In this experiment U-20 w/o Pu was carbided with a 1 v/o methane-hydrogen mixture at a temperature of 750°C to the point where the rate of change of weight had been very low for several hours. Then the methane flow was terminated but the hydrogen flow was continued. The response was a continuing decrease in the sample weight, indicating reaction of sesquicarbide with hydrogen to form methane. However, the X-ray diffraction pattern of the product showed that some sesquicarbide still remained, thus indicating that the back-reaction had not been carried to completion.

Further experiments are planned which should aid in determining the correct value of ΔG_1° for uranium-plutonium carbide mixtures. It is expected that much less contamination of the reacting material by oxygen and nitrogen will take place in these future experiments because of revisions in technique and equipment. Thus, equilibrium data will be more reliable. It should be noted that in runs reported previously (ANL-7055, p. 91) in which the total reaction times were usually shorter than in the more recent runs, the total amount of contamination was as low as 0.15 w/o.

Information on reaction rates was also obtained from the thermobalance experiments. Although data obtained in a fluidized-bed reactor would be more perti-

ment, the relative rates obtained in the thermobalance are of interest until facilities for preparing (U,Pu)C in a fluidized-bed reactor are ready for operation. In these thermobalance experiments, reaction rates were determined for hydriding and carbiding of unalloyed uranium and plutonium and U-20 w/o Pu alloy.

The behavior of uranium and plutonium metals during hydriding is markedly different. At a temperature of 250°C uranium reacts slowly, at a constant rate. Plutonium reacts very rapidly at room temperature after a short induction period; the reaction is usually complete in about 5 min for a 3-g sample. Uranium-20 w/o plutonium reacts with hydrogen in a manner similar to that of plutonium. However, occasionally it is necessary to heat the sample to approximately 200°C to start the reaction.

The relative rates of reaction of the metals with propane-hydrogen and methane-hydrogen gas mixtures were evaluated from the initial rate of weight change in the carbiding portion of the experiments. The data are summarized in Table IV-2. The alloy apparently reacts more rapidly than unalloyed uranium. Decreasing the concentration of either hydrocarbon decreases the reaction rate. It is difficult to compare the reaction rates of propane and methane because no two runs were made at the same carbon-to-hydrogen ratio. However, methane appears to react more rapidly than propane at a given carbon-to-hydrogen ratio.

c. PREPARATION OF CARBIDES IN FLUIDIZED BEDS (E. PETKUS, P. NELSON, C. PAYNE, C. LEHMANN)

The experimental program on preparation of UC and (U,Pu)C by the fluidized-bed technique is directed toward exploring the operating conditions which appear most likely to yield stoichiometric monocarbides at high production rates. The ranges of conditions to be studied are: temperature, 700 to 900°C; pressure, 5 to 10 atm; and fluidizing gas, 2-10 v/o methane in hydrogen. Installation of a 2½-in. dia. reactor which can be used with the above ranges of conditions for preparation of UC on a kilogram scale has just been completed. This reactor is constructed of type 304 stainless steel and has a jacketed heating section which will be pressurized with argon in order to balance the internal pressure and thus minimize the stress on the heated wall. The off-gas from the reactor will be discarded in initial tests, but, at a later date, equipment to recirculate the gas will be installed. A similar reactor is being designed for operation in a helium-atmosphere glovebox for preparation of (U,Pu)C.

During this period of equipment construction, UC has been prepared in a 1½-in. dia. fluidized-bed reactor

TABLE IV-2. RATES OF REACTION OF ACTINIDE METALS WITH HYDROCARBON-HYDROGEN GAS MIXTURES

The samples were hydrided before beginning the carbiding reaction

Temperature: 750°C
Sample weight: 3 to 3.5 g
Total pressure: 1 atm

Reactant Gas			Initial Rate of Reaction [mg/(g) (min)]		
Hydrocarbon	v/o	C:H Atom Ratio	Uranium	Pluto- nium	U-20 w/o Pu
Propane	1.5	0.0215	—	—	0.57
Propane	1.0	0.0147	0.22	—	0.52
Methane	2.0	0.0098	0.56	0.28	0.81
Methane	1.0	0.0050	0.27	—	0.30

that is capable of operation at near atmospheric pressure and at temperatures up to 750°C. The purpose of these experiments was to demonstrate that a stoichiometric monocarbide of low oxygen content could be obtained by the fluidized-bed technique. In these experiments 100 to 200 g of uranium rods were hydrided at 250°C to form fine UH_3 powder suitable for fluidization. This powder was dehydrided and converted to UC by heating at 600 to 750°C while fluidizing with a propane-hydrogen gas mixture. The temperature was maintained at the final level for 5 to 20 hr to complete the reaction.

In some of the early runs, oxygen impurity levels of 0.5 to 1.0 w/o were obtained. It is believed that the oxygen contamination was caused partly by oxygen leakage into the equipment and partly by oxidation of residual carbide left in the reactor from previous runs. The amount of oxygen contained in the fluidizing gas taken from the cylinders is not a serious source of contamination, even with the large amount used when the off-gas is discarded.

Stoichiometric UC with an oxygen content as low as 0.1 w/o was produced in recent experiments. Results from some of these runs are shown in Table IV-3. The carbon contents of the products from the first two runs in the table were very close to the stoichiometric value of 50 a/o (4.8 w/o) carbon. These runs were conducted under carburizing conditions which would be expected to yield the monocarbide (see footnote a, Table IV-3). The third run produced hyperstoichiometric carbide as was to be expected from the high propane concentration.

It is believed that UC or (U,Pu)C powder of low oxygen content and near-stoichiometric carbon content can be routinely prepared by the fluidized-bed process.

TABLE IV-3. PREPARATION OF URANIUM MONOCARBIDE
IN A FLUIDIZED BED

200-g scale; run duration, 10 hr.

Temperature (°C)	Propane in Fluidizing Gas ^a (v/o)	Product Composition				
		Carbon		Oxygen		Ura- nium ^b
		(a/o)	(w/o)	(a/o)	(w/o)	
600	3	47.2	4.5	2.5	0.32	50.3
700	1.5	48.6	4.6	0.8	0.10	50.6
700	9	56.5	6.2 ^c	0.5	0.08	43.0

^a The balance is hydrogen. The following C₃H₈ concentrations in hydrogen were calculated for C:H ratios equivalent to the equilibrium gas compositions in the systems CH₄-H₂-UC-UC₂ and CH₄-H₂-UC₂-C:

Temperature (°C)	C ₃ H ₈ Concentration (v/o)	
	UC-UC ₂	UC ₂ -C
600	5.5	8.6
700	2.0	3.6

^b Calculated by difference.

^c Carbon deposition on the reactor walls indicated the likelihood of a high free carbon content.

Such powder would be suitable for pressing and sintering into fuel pellets without further processing.

d. ELECTRON PROBE MICROANALYSIS OF (U,Pu)C PELLETS (S. VOGLER, P. KRAUSE)

In the preceding report (ANL-7055, p. 93), a description was given of the pressing and sintering of (U,Pu)C produced from U-20 w/o Pu alloy in thermobalance experiments. The metallographic study of the resulting pellets was also described in that report. Two of these pellets have now been studied under an electron probe microanalyzer.⁵ Photomicrographs of the specimens indicated the presence of a single phase. The objectives of the electron micro-probe examination were to ascertain the homogeneity of the sample and also to detect the presence of extraneous phases.

The samples (from runs 21 and 24) and standards of uranium, plutonium, and graphite were mounted in electrically conductive bakelite. The samples were then ground and polished, the final polish being made with 1/4-μ diamond paste. The lubricant in these operations was an ethyl alcohol-ethylene glycol solution.

The micro-probe procedure consisted of examining

several areas of the two pellets and measuring the uranium and plutonium contents simultaneously. In several instances, step scans across the field were made. Examination for carbon was on a more limited basis.

From the data, it is difficult to derive quantitative estimates of the plutonium and uranium content because of a lack of appropriate standards. Data are available which show that the use of a metal standard rather than a carbide standard results in a low value for the actual heavy metal content.⁶ Also, it is known that the carbon response is a function of the matrix material.⁷ The response for carbon in plutonium carbide is unknown, but is probably similar to the response in uranium carbide.

Initial evaluation of the data indicated that the uranium and plutonium contents were uniform. Further evaluation of the data consisted of comparing the standard deviation of the mean of a series of readings with the standard deviation to be expected from counting statistics alone. The standard deviation from the mean for the plutonium scans was usually within the expected value based on counting statistics. The standard deviation from the mean for the uranium scans was approximately twice the standard deviation based on counting statistics.

In addition, a series of readings was taken while the beam was focused on one spot on the sample. The standard deviation from the mean for the plutonium data conformed to statistical fluctuation. The standard deviation from the mean for the uranium results was 1½ times the statistically derived standard deviation.

On the basis of these results, it appears that the samples were homogeneous with respect to uranium and plutonium content.

The data for carbon analysis scatter more. This may be due to the fact that the emitted X-rays have a long wave length and so are more sensitive to matrix absorption. Imperfections in the surface may also interfere with the emission of the X-rays. Another difficulty is that N-series X-rays from uranium enhance the response from carbon atoms. Thus it is difficult to attempt a quantitative evaluation of the carbon data. The carbon appeared to be evenly distributed, but very small amounts of sesquicarbide may have been present, as indicated by the slight variations in the carbon content noted during scanning of the sample.

⁶ G. V. J. Ranzetta and V. D. Scott, Electron Probe Microanalysis of Actinide Ceramic Materials, AWRE Report 0-51/64.

⁷ A. V. Manzione and D. E. Formvalt, The Application of the Electron Microprobe to the Identification and Quantitative Determination of Carbon, Norelco Reporter, January-March, 1965.

⁵ The assistance of J. Sanecki, Metallurgy Division, who operated the electron probe microanalyzer, is gratefully acknowledged.

2. Mobile Blanket Fuels: Corrosion Testing (M. G. CHASANOV)

Paste-fueled reactors and paste blankets for breeder reactors show promise of reducing reactor downtime for fuel shuffling, improving power conversion efficiency through improved sodium coolant utilization, and decreasing fuel processing and fabrication costs. Development work on paste blanket fuels consisting of a ceramic fuel dispersed in a liquid metal was previously reported (see ANL-7055, p. 94). The corrosiveness of such paste fuels toward possible container materials has now been investigated.

Static corrosion tests were made to determine the compatibility of type 304 stainless steel with pastes of uranium mononitride, uranium dioxide, or uranium monocarbide and sodium. The pastes were prepared by heating ACS Reagent Grade sodium in a type 304 stainless steel corrosion capsule together with the ceramic fuel material until a thick paste was formed; all the manipulations were carried out in a helium glovebox. The ceramics used were: hydrogen-reduced UO_2 , UN prepared by high-temperature nitridation of uranium metal, and a hyperstoichiometric UC. A degreased coupon (5 mils thick) of type 304 stainless steel was inserted into the paste and the corrosion capsule was welded closed in the helium glovebox.

Six such capsules were prepared: one with each of the three paste fuels, a control capsule with sodium, a capsule with sodium containing 4000 ppm of Na_2O , and another capsule with a UN-Na paste to which 4000 ppm of a Na_2O had also been added. All the capsules were heated to 760°C , held at that temperature for

1000 hr, and then were allowed to cool in the furnace. The capsules were opened in a helium glovebox; the corrosion coupons were removed, washed with butanol, and examined. The results of physical and metallographic examination are presented in Table IV-4.

Visual examination of the coupons in contact with only sodium or with the UO_2 -Na paste showed no apparent etching or discoloration of the metal. The coupon in contact with the sodium containing sodium oxide had a greenish-gray deposit on the surface; X-ray diffraction examination indicated that this was probably α - NaFeO_2 . The coupons in contact with the UN-Na and UN-Na- Na_2O pastes showed some evidence of etching. The coupon from the UC-Na appeared quite grey and rough.

The coupon in contact with the UC-Na paste had become magnetic; the others remained nonmagnetic. Microhardness tests revealed a marked increase in the Knoop hardness number of the coupon in contact with the carbide paste; this coupon was so embrittled that it fractured on mounting in bakelite for metallographic examination. X-ray diffraction analysis of this coupon revealed its structure to be the α -Fe body-centered cubic structure, a finding which is in agreement with the magnetic character of the coupon.

Chemical analyses were performed on the coupons to determine nitrogen and carbon contents; the results are included in Table IV-4. In agreement with the metallographic observation of severe carburization of the coupon in contact with the UC-Na paste, chemical

TABLE IV-4. STATIC CORROSION TESTS OF TYPE 304 STAINLESS STEEL BY SODIUM-URANIUM CERAMIC PASTES

Time: 1000 hr
Temperature: 760°C

Contents of Capsule	Coupon Wt Change (mg/cm ²)	Thickness Change (mils)	Metallographic Observations	Chemical Analysis ^a	
				Nitrogen (w/o)	Carbon (w/o)
Na	+0.03	0	Sensitized structure. ^b	—	0.082
Na + Na_2O (4000 ppm)	+0.4	+0.5	Intergranular corrosion.	—	0.049
Na + UC ^c (34 v/o)	+0.9	+1	Heavy carbide precipitation throughout sample. Surface reaction layer visible.	—	1.6
Na + UO_2 ^d (42 v/o)	+0.2	0	Sensitized structure. ^b	—	0.071
Na + UN ^e (41 v/o)	-0.3	0	Sensitized structure. ^b	0.113	—
Na + UN ^e (40 v/o) + Na_2O (4000 ppm)	-0.3	0	Characteristic austenitic twinned structure.	0.028	—

^a Original coupon: nitrogen, 0.045 w/o; carbon, 0.056 w/o.

^b Carbides precipitated in grain boundaries.

^c Hyperstoichiometric UC (5.2 w/o C) prepared by the liquid metal process (Run UC-12, see ANL-6925, p. 98).

^d Hydrogen-reduced UO_2 .

^e High-density UN prepared by nitridation of uranium shot (Run UN-9A, see ANL-7055, pp. 94-97).

a. Specimen Current Image

b. Iron $K\alpha$ X-ray Image c. Chromium $K\alpha$ X-ray Image d. Nickel $K\alpha$ X-ray Image

FIG. IV-5. Electron Probe Images of an Area 45μ Square of Type 304 Stainless Steel Contacted with Hyperstoichiometric UC-Na Paste.

analysis indicated more than a twentyfold increase in its carbon content. An increase in the nitrogen content of the coupon in contact with the UN-Na was obtained. Analyses of the nickel and chromium content of the coupons were made. The only significant observation from these analyses was the indication that a preferential loss of chromium occurred in the case of the carburized coupon.

Electron probe microanalysis⁸ of the carburized coupon which had been contacted with the paste con-

⁸ The electron probe microanalysis and the interpretation of the results were carried out by N. Stalica.

taining hyperstoichiometric UC revealed segregation in the grain structure of the coupon. This grain structure can be readily seen in Figure IV-5a, a specimen current picture. The brightness in the specimen current image is inversely proportional to the mean atomic number of the elements present, i.e., chromium and chromium carbide areas (the grain structure) appear brightest and areas containing higher amounts of nickel darkest. The intense white area is a void.

The qualitative distribution of iron, chromium, and nickel can be seen in Figures IV-5b, IV-5c, and IV-5d. These are electron probe X-ray images of the same

area as Figure IV-5a. The relative brightness of the images in these photographs is greater as the concentration of the element present increases. These pictures have been biased to show contrast, that is, black does not correspond to 0 w/o but approximately to <60 w/o for iron, <10 w/o for chromium, and <8 w/o for nickel. (Analysis of an untested coupon of type 304 stainless steel showed 16.8 w/o chromium, 7.3 w/o nickel, and about 74 w/o iron.)

The band at the outer edge of the coupon is iron-rich (see Figure IV-5b). The chromium X-ray image (Figure IV-5c) and the nickel X-ray image (Figure IV-5d) show a deficiency of those elements in that layer. Analysis of the band showed that it contained over 90 w/o iron, up to 2-3 w/o nickel, and undetectable amounts of chromium. This band probably gave the coupon its magnetic character.

The particle on the surface next to the void is pure chromium. Other chromium-rich particles were found on the surface of the coupon, ranging in chromium content from 50 to 100 w/o. Some of these contain iron. Specimen current images indicate that they may possibly be mixed iron-chromium carbides. These particles correspond to the reaction layer observed on metallographic examination of the coupon.

The grain structure is rich in chromium (30-40 w/o). Specimen current images indicate that the material in the grain boundaries most likely is chromium carbide. The chromium concentration in the matrix within the grain boundaries averaged about 20-22 w/o and in some places was as low as 10 w/o. A slight deficiency

of iron and nickel in the grain boundaries is evident in the X-ray images. Iron, which was about 67 w/o in the matrix, dropped to about 40 to 60 w/o in the grain boundaries. The variation in nickel concentration was slight, dropping from 10 to 12 w/o in the matrix to 8 to 10 w/o in the grain boundaries.

The coupons in contact with sodium alone and with the Na-UN-Na₂O paste showed no significant variations of iron, chromium, or nickel content at the surface when examined with the electron probe micro-analyzer.

The overall results obtained in these corrosion studies are not unexpected. Intergranular corrosion of type 304 stainless steel in contact with Na₂O in sodium is well known.⁹ The compatibility of UN-Na and UO₂-Na with stainless steel under these conditions is not surprising, although the reason for lack of coupon sensitization in the experiment with the UN-Na-Na₂O paste is not clear. Carburization by the hyperstoichiometric UC was anticipated,¹⁰ although the extent of reaction was somewhat greater than expected. Interaction of type 304 stainless steel with pastes containing hypostoichiometric and stoichiometric UC should be less severe than the attack by the paste containing hyperstoichiometric UC. Corrosion experiments utilizing hypostoichiometric carbide pastes are now in progress.

⁹ F. L. LaQue and H. R. Copson, *Corrosion Resistance of Metals and Alloys*, 2nd Ed., Reinhold, N. Y., 1963, p. 432.

¹⁰ O. O. Gamba, *The Nature and Properties of the Carbides of Chromium*, NAA-SR-10929 (1965).

C. CALORIMETRY (W. N. HUBBARD, H. M. FEDER, M. ADER)

For many substances of interest in high temperature chemistry and nuclear technology, thermochemical data are lacking or they lack acceptable accuracy. These lacks may be due to difficulties of making the necessary measurements or of obtaining well-characterized samples. The present thermochemical program places equal emphasis on the procurement of well-characterized samples and on the development of adequate experimental techniques.

The determination of standard enthalpies of formation of substances is an essential foundation for further thermodynamic studies. Part of the program has been devoted to determinations of these enthalpies by oxygen bomb calorimetry, a technique which has been developed to a high degree of precision and accuracy. Many of the materials of interest are difficult to burn in oxygen, however, and can not be studied by this

method. To study these materials the techniques of the bomb calorimetric method have been modified so that fluorine may be used as an oxidant.

The accumulation of enthalpy-of-formation data for elemental fluorides is both a necessary preliminary to the general use of fluorine bomb calorimetry and a valuable program on its own merit. To date, enthalpy-of-formation values have been determined for 25 elemental fluorides. The enthalpies of formation of the following substances have also been determined by fluorine bomb calorimetry: boron nitride, quartz and vitreous silica, α - and β -silicon carbide, and the diborides of zirconium, hafnium, niobium, and tantalum.

In previous reports of this series, tables of calorimetric data have been presented as the research progressed. It has been decided to discontinue this practice for the sake of brevity. Instead, derived data will be

presented or, where appropriate, the abstract of the manuscript describing the research will be quoted. Occasionally, when an enthalpy of formation is published in its complete form in a journal article, it will be slightly different than the figure given in this report owing to minor refinements in calculation. Therefore, before the data are put to exacting use, the journal article should be checked. Detailed data may be obtained by request to the investigators.

To determine thermodynamic properties at high

temperatures, one combines values of enthalpies of formation at 25°C with values of the enthalpy increments up to the higher temperatures. A drop calorimeter for making enthalpy increment measurements to 1500°C has been assembled and tested with measurements on a standard sample of synthetic sapphire. It is now being used for measurements on a series of uranium compounds. A calorimeter for measuring enthalpy increments to 2500°C has also been designed and is being constructed.

1. The Enthalpy of Formation of Aqueous HF and of Alkali Metal Fluorides

(E. RUDZITIS, E. H. VAN DEVENTER)

The enthalpy of formation of aqueous HF is a basic quantity in the solution calorimetry of fluorine-containing compounds. In addition, it may be used to link thermochemical measurements on aqueous and non-aqueous systems. Unfortunately, $\Delta H_f^\circ(\text{HF}, \text{aq})$ is very

(where $M = \text{Li, Na, K}$) according to the scheme below. The heats of reactions 1 to 4 are well established;² only the heat of reaction 5 remains to be determined experimentally. An attractive by-product of this scheme will be the acquisition of the enthalpy-of-formation

uncertain.¹ To help resolve this uncertainty, it is proposed to combine existing solution calorimetric data for the fluorides and hydroxides of lithium, sodium, and potassium with bomb calorimetric values for $\Delta H_f^\circ(\text{MF})$

data for alkali metal fluorides. Preliminary experiments have shown that bomb combustions of alkali metals in fluorine are feasible.

2. The Enthalpies of Formation of Boron Trifluoride and Some Boron Compounds

(G. K. JOHNSON)

a. BORON TRIFLUORIDE

A paper entitled "Fluorine Bomb Calorimetry. XV. The Enthalpy of Formation of Boron Trifluoride" was published.³ The experimental detail and discussion of this work was presented previously.⁴ The abstract of the paper is as follows:

"The energy of formation of boron trifluoride was measured by direct combination of the elements in a combustion bomb calorimeter. Two different com-

bustion techniques on the same specimen of zone-refined boron yielded a value for the standard enthalpy of formation, $\Delta H_{f,298.15}^\circ(\text{BF}_3, \text{g})$ of -271.6 ± 0.2 kcal mole⁻¹. This value is more negative (by 1.77 kcal mole⁻¹) than one previously determined by a similar method in the same laboratory. Reanalysis of the specimen of Moissan boron used in the previous work uncovered additional impurities which account for the difference."

b. BORON NITRIDE

The revision of the value for $\Delta H_f^\circ(\text{BF}_3)$ affects our earlier value⁵ for $\Delta H_f^\circ(\text{BN})$ which was derived from fluorine combustion data several years ago. A paper entitled "Fluorine Bomb Calorimetry. XVI. The

¹ ANL-6725, p. 197.

² (a) S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.*, **80**, 4782 (1958); (b) V. B. Parker, "Thermal Properties of Univalent Electrolytes," NSRDS-NBS 2, U. S. Government Printing Office, Washington, D. C., April, 1965.

³ G. K. Johnson, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.*, **70**, 1 (1966).

⁴ ANL-7055, p. 172; *J. Phys. Chem.*, **65**, 2157 (1961).

⁵ ANL-6477, p. 159.

"Enthalpy of Formation of Boron Nitride" discusses the results of this study.⁶ The abstract of the paper is as follows:

"The energy of combustion of boron nitride in fluorine was measured in a combustion bomb calorimeter. This value was combined with the enthalpy of formation of BF_3 , determined by a similar method, to give the standard enthalpy of formation, ΔH_f° , of hexagonal BN. The value obtained, -59.97 ± 0.37 kcal mole⁻¹, is in excellent agreement with several recent determinations by other methods."

c. THE DIBORIDES OF ZIRCONIUM, HAFNIUM, NIOBIUM, AND TANTALUM

Combustions in fluorine of the diborides of zirconium, hafnium, niobium, and tantalum have been discussed previously.⁷ The derived enthalpies of formation are also affected by the revision of the enthalpy of formation of boron trifluoride. The revised values of ΔH_f° in kcal mol⁻¹ are: -77.8 ± 1.5 ($\text{ZrB}_{1.996 \pm 0.006}$); -78.9 ± 2.5 ($\text{HfB}_{2.009 \pm 0.007}$); -59.0 ± 1.8 ($\text{NbB}_{1.880 \pm 0.007}$); and -44.5 ± 1.7 ($\text{TaB}_{1.925 \pm 0.006}$).

d. BORIC OXIDE

The enthalpy of formation of boric oxide is of basic importance in the thermochemistry of boron compounds. Unfortunately, determination by direct combination of boron and oxygen in a combustion bomb has led to ΔH_f° values which disagree by as much as 80 kcal mol⁻¹. In order to overcome the difficulties en-

countered in the direct reaction of boron with oxygen, namely, incomplete combustions and poorly defined products, modern investigators have resorted to solution calorimetric methods. However, the solution work is indirect and depends heavily on the accuracy of several auxiliary measurements. An uncertainty of 2 kcal mol⁻¹ still exists in the value for $\Delta H_f^\circ(\text{B}_2\text{O}_3)$.

The combustion of boric oxide in fluorine according to eq. 7

would offer a method of determining $\Delta H_f^\circ(\text{B}_2\text{O}_3)$ that depends only on the enthalpy of formation of BF_3 as an auxiliary datum. Trial experiments indicate that, upon ignition, the combustion of B_2O_3 in high pressure fluorine goes to completion, and that the infrared spectrum of the combustion products shows no absorption attributable to boron oxyfluoride compounds. Therefore, present indications are that the reaction proceeds as shown in eq. 7.

The standard state for B_2O_3 is the crystalline state. However, the most common form is the amorphous (glassy) form. Both forms will be studied. Attempts to obtain crystalline B_2O_3 commercially have been unsuccessful; hence, a crystalline specimen of B_2O_3 that appears to be suitable for calorimetric study has been prepared in this laboratory. The glassy form will be obtained by melting a portion of the crystalline specimen.

3. The Enthalpy of Formation of Carbon Tetrafluoride (Tetrafluoromethane) (E. GREENBERG)

The interest in the enthalpy of formation of CF_4 and some of the modern thermochemical studies on this subject have been discussed previously in ANL-6687, p. 160. To the previous summary can be added a number of additional determinations^{8, 9, 10} and a new provisional value.¹¹ Resolution of the value for the enthalpy of formation of CF_4 is complicated by the fact that most of the reported determinations involve, as an

auxiliary datum, the use of the still somewhat uncertain value for the enthalpy of formation of hydrofluoric acid. A summary of the modern thermochemical literature on CF_4 by Cox and coworkers¹⁰ shows a spread of about 8 kcal mol⁻¹ for $\Delta H_f^\circ(\text{CF}_4)$. Therefore, a direct determination of $\Delta H_f^\circ(\text{CF}_4)$ by combustion of carbon in fluorine would be desirable.

Exploratory experiments¹² had shown that the most satisfactory combustions were achieved with thin graphite flakes supported on a nickel dish. Continuation of these experiments was deferred in favor of calorimetric combustion studies on silicon carbide which have since been completed. Work on the combustion of carbon in fluorine has now been resumed with emphasis on the preparation and procurement of high-purity samples, and on the further development of a suitable combustion technique.

Because of the variations in stacking order of pure

⁶ S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.* **70**, 7 (1966).

⁷ ANL-6925, p. 181; ANL-6900, p. 221; ANL-6800, p. 310.

⁸ A. F. Vorob'ev and S. M. Skuratov, *Russ. J. Inorg. Chem.*, **5**, 679 (1960).

⁹ (a) V. F. Baibuz, *Dokl. Akad. Nauk. SSSR.*, **140**, 1359 (1961); (b) V. F. Baibuz and Medvedev, *Tr. Gos. Inst. Prikl. Khim.*, **84**, No. 49 (1962).

¹⁰ J. D. Cox, H. A. Gundry, and A. J. Head, *Trans. Faraday Soc.*, **61**, 1594 (1965).

¹¹ E. S. Domalski, National Bureau of Standards, Washington, D. C., private communication. Provisional value is -222.8 ± 0.3 kcal mol⁻¹.

¹² ANL-6800, p. 314; ANL-6725, p. 194; ANL-6687, p. 161.

graphites, it would be desirable to burn both natural and synthetic samples and to compare the combustion results. Samples of pyrolytic graphite, in the form of flakes approximately $\frac{1}{32}$ to $\frac{1}{16}$ in. in diameter, have been received from Pyrogenics, Inc., Woodside, N. Y. This material appears to have the desired purity. In trial experiments, greater than 99.8 % combustions have been achieved with 0.4-g samples (~ 7200 cal).

Starting material for the preparation of the natural graphite sample was 50 lb of Ticonderoga graphite-rock material. The crushed rock was leached alternately with aqueous HCl and HF to remove the siliceous matrix in which the graphite was embedded. After extensive leaching, there still remained a rather large residue of sandy material and rock. This residue was thoroughly washed with water, dried with acetone, and treated with methyl iodide in a series of fractionation operations to selectively float the graphite away from the denser constituents. After another wash with acetone, the graphite content of the product was 97 % or more. Arrangements have been made with the Union

Carbide Corp. to carry out the final purification of this sample. The purification process will involve heating the sample to a temperature of 2000°C or higher in the presence of a chlorinating agent. After removal of impurities and graphitization, the sample will be cooled in an inert atmosphere (probably nitrogen). In order to minimize the effect of any unforeseen difficulties, the purification process will be carried out twice, using half the sample for each run, with suitable analyses to demonstrate the effectiveness of the treatment before committing the second half of the sample. It is expected that the level of residual impurities will be about 10 ppm.

Exploratory experiments with natural graphite flakes have demonstrated the feasibility of burning about 98 % of a 0.4-g sample. Fluorine pressures of 20 atm did not appear to effect any greater degree of combustion than was obtained in earlier experiments with 15 atm pressure. The prospects of obtaining more complete combustions of the sample do not appear to be very good.

4. The Enthalpies of Formation of Pnictogen Pentafluorides (P. A. G. O'HARE¹³)

a. PHOSPHORUS PENTAFLUORIDE AND THE ENTHALPY OF FORMATION OF TWO MODIFICATIONS OF RED PHOSPHORUS

The technique previously described¹⁴ for the measurement of the enthalpy of combustion of red(IV) phosphorus in fluorine has been used to study the combustion of a sample of red(V) phosphorus, of amorphous red(I) phosphorus, and of α -white phosphorus. The standard enthalpy of formation, $\Delta H_f^{\circ}_{298}$, (PF_5 , g), based on the combustions of α -white phosphorus is -380.71 ± 0.31 kcal mol⁻¹. This is in good agreement with the only previously published value¹⁵ of -381.4 ± 0.4 kcal mol⁻¹. The values derived for the enthalpies of transition are:

5. The Enthalpies of Formation of Chalcogen Hexafluorides (P. A. G. O'HARE,¹³ J. L. SETTLE)

A paper on this subject has been accepted for publication in the Transactions of the Faraday Society. The

¹³ Postdoctoral Fellow.

¹⁴ ANL-6925, p. 175.

¹⁵ P. Gross, C. Hayman, D. L. Levi, and M. C. Stuart, Final Technical Report. R.146/4/23, Fulmer Research Institute Limited, Stoke Poges, England, November, 1960.

The latter value is considered tentative owing to the large and uncertain calorimetric correction term for the oxygen impurity in red(V) phosphorus.

b. ARSENIC PENTAFLUORIDE

High purity arsenic was burned in fluorine to give arsenic pentafluoride. The standard energy of the reaction was measured and a value for $\Delta H_f^{\circ}_{298}$ (AsF_5 , g) derived. The following abstract is from a paper¹⁶ based on this work:

"The energy of formation of arsenic pentafluoride was measured by direct combination of the elements in a bomb calorimeter. From these measurements the standard enthalpy of formation, $\Delta H_f^{\circ}_{298.15}$ (AsF_5 , g), was calculated to be -295.59 ± 0.19 kcal mole⁻¹. The average bond strength in AsF_5 (92.4 kcal mole⁻¹) is about 20 kcal mole⁻¹ less than it is in AsF_3 ."

abstract is as follows:

"The energies of formation of the hexafluorides of sulfur, selenium, and tellurium were measured by direct combination of the elements in a bomb calorim-

¹⁶ P. A. G. O'Hare and W. N. Hubbard, J. Phys. Chem. **69**, 4358 (1965).

eter. From these measurements the standard enthalpies of formation ΔH_f° (gas), were calculated (in kcal mol⁻¹): SF₆, -291.77 ± 0.24; SeF₆, -266.95 ± 0.14; TeF₆, -327.20 ± 0.56. These

values are substantially more negative than those reported by Yost and Claussen in 1933. The thermodynamic properties of these compounds have been computed and tabulated from 0 to 1500°K."

6. The Bond Energies of the Chalcogen Hexafluorides (P. A. G. O'HARE,¹³ H. M. FEDER)

The average bond energy, $\bar{D}(A-X)$, in a molecule, AX_n, with *n* equivalent bonds is defined as 1/*n*th of the atomization energy. Average bond energy values are usually calculated by the thermochemical relationship:

$$\bar{D}(A-X)_{AX_n} = \frac{1}{n} [\Delta H_f^\circ(A, g) + n\Delta H_f^\circ(X, g) - \Delta H_f^\circ(AX_n, g)]. \quad (9)$$

Another type of relationship, akin to eq. 9, is used in conjunction with electron impact studies to measure the strength of a specified bond:

$$D(M-N) = A_o(N^-) + E_a(N) - \phi_{total} \quad (10)$$

where $A_o(N^-)$ is the appearance potential of the N⁻ ion, $E_a(N)$ is the electron affinity of N, and ϕ_{total} is the total excitation energy of the two fragments, M and N⁻, above their ground states. Equations 9 and 10 may be used to derive values for bond energies in the hexafluorides of sulfur, selenium, and tellurium and related compounds. Comparisons of these values with each other and with the predictions of current theories are of considerable interest.

a. SULFUR HEXAFLUORIDE

For the electron impact dissociation reaction

Curran¹⁷ has measured $\phi_{kinetic} = 0.23 \pm 0.05$ ev and $A_o(F^-) = 0_{-0.00}^{+0.05}$ ev. This result, when combined with $E_a(F) = 3.50 \pm 0.15$ ev,¹⁸ and the reasonable assumption that the internal excitation of the SF₅ fragment is small, yields

$$D(SF_5-F) = 3.27 \pm 0.17 \text{ ev} = 75.5 \pm 4.0 \text{ kcal mol}^{-1}.$$

For the average dissociation energy of the S—F bonds in SF₆ we insert into eq. 9 the values (in kcal mol⁻¹) $\Delta H_f^\circ(S, g) = 65.9$,¹⁹ $\Delta H_f^\circ(F, g) = 18.9$,²⁰ and $\Delta H_f^\circ(SF_6, g) = -291.8$ (this work) and obtain

$$\bar{D}(S-F)_{SF_6} = 78.5 \pm 1 \text{ kcal mol}^{-1}.$$

¹⁷ R. K. Curran, J. Chem. Phys., **38**, 780 (1963).

¹⁸ (a) H. O. Pritchard, Chem. Rev., **52**, 529 (1953); (b) D. Cubicciotti, J. Chem. Phys., **31**, 1646 (1959).

¹⁹ H. Mackle and P. A. G. O'Hare, Tetrahedron, **19**, 961 (1963).

²⁰ "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Michigan, June, 1961.

It is somewhat unusual to find the primary bond dissociation energy in a polyatomic molecule equal to or less than the average bond dissociation energy. The enthalpy of formation of the SF₅ fragment, $\Delta H_f^\circ(SF_5, g)$, may be calculated as follows:

$$\begin{aligned} D(SF_5-F) &= 75.5 \pm 4 \text{ kcal} \\ &= \Delta H_f^\circ(SF_5, g) + 18.9 + 291.8 \end{aligned}$$

$$\Delta H_f^\circ(SF_5, g) = -235 \pm 4 \text{ kcal mol}^{-1}.$$

This quantity, in conjunction with accurate values for $\Delta H_f^\circ(S_2F_{10}, g)$ and $\Delta H_f^\circ(SF_4, g)$ would give values for the interesting quantities $D(S-S)_{S_2F_{10}}$ and $D(SF_4-F)$.

b. SELENIUM HEXAFLUORIDE

For calculation of the average dissociation energy of the Se—F bonds in SeF₆, $\Delta H_f^\circ(Se, g)$ is needed. This quantity may be deduced from eq. 12:

$$\Delta H_f^\circ(Se, g) = \frac{1}{2}[D(Se_2, g) + \Delta H_f^\circ(Se_2, g)] \quad (12)$$

Gaydon²¹ gives a value of 64.6 kcal mol⁻¹ for $D(Se_2, g)$. Denison²² has found $\Delta H_f^\circ(Se_2, g) = 33$ kcal mol⁻¹. From eq. 12, $\Delta H_f^\circ(Se, g) = 48.8 \pm 1.0$ kcal mol⁻¹. (Recent vaporization studies²³ on SrSe give a confirming value of about 50 kcal mol⁻¹ for $\Delta H_f^\circ(Se, g)$.) This value, along with $\Delta H_f^\circ(F, g) = 18.9$ kcal mol⁻¹²⁰ and $\Delta H_f^\circ(SeF_6, g) = -266.8$ kcal mol⁻¹ (this work), when inserted in eq. 9, yields

$$\bar{D}(Se-F)_{SeF_6} = 71.5 \pm 2.0 \text{ kcal mol}^{-1}.$$

c. TELLURIUM HEXAFLUORIDE

For calculation of the average dissociation energy of the Te—F bonds in TeF₆, $\Delta H_f^\circ(Te, g)$ is needed. This quantity may be deduced from eq. 13:

$$\Delta H_f^\circ(Te, g) = \frac{1}{2}[D(Te_2, g) + \Delta H_f^\circ(Te_2, g)] \quad (13)$$

Inserting in eq. 13 the values $D(Te_2, g) = 53.0$ kcal mol⁻¹²¹ and $\Delta H_f^\circ(Te_2, g) = 40.2$ kcal mol⁻¹²⁴ yields

²¹ A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Edition, Chapman Hall, London, 1953.

²² G. W. Denison, Ph.D. Thesis, University of Oklahoma, 1962.

²³ J. Berkowitz, Argonne National Laboratory, private communication.

²⁴ D. D. Wagman et al, "Selected Values of Chemical Thermodynamic Properties, Part I," NBS Technical Note 270-1,

$\Delta H_f^\circ(\text{Te}, \text{g}) = 46.6 \text{ kcal mol}^{-1}$. This value, when inserted in eq. 9 along with $\Delta H_f^\circ(\text{F}, \text{g}) = 18.9 \text{ kcal mol}^{-1}$ ²⁰ and $\Delta H_f^\circ(\text{TeF}_6, \text{g}) = -327.2 \text{ kcal mol}^{-1}$ (this work), yields

$$\bar{D}(\text{Te}-\text{F})_{\text{TeF}_6} = 81.2 \pm 2 \text{ kcal mol}^{-1}.$$

d. DISCUSSION

The average M—F bond dissociation energy (in kcal mol⁻¹) is 78.5 in SF₆, 71.5 in SeF₆ and 81.2 in TeF₆. This nonmonotonic variation does not have any obvious explanation. Its rationalization is therefore a challenge to current theories of bonding.

(1) *d*-Orbital Hybridization in SF₆, SeF₆, and TeF₆

In their ground states S, Se, and Te atoms have the outer electronic configuration ns^2np^4 . In accordance with this, these elements form many bivalent compounds, e.g., SCl₂, SO, etc. The *d*-orbitals of principal quantum number *n* are vacant and lie only slightly higher in energy than the *s*- and *p*-orbitals. If the necessary promotion energy is supplied, molecule formation involving the *d*-orbitals can occur. Koch and Moffitt²⁵ were the first to make quantitative calculations to show that bonding involving sulfur *d*-orbitals was required to explain certain unusual physical and chemical properties of sulfones and sulfoxides.

In the formation of the hexafluorides, two electrons of the chalcogen atom are promoted to *d*-orbitals to form six equivalent sp^3d^2 hybrid orbitals having an octahedral configuration. These hybrid orbitals overlap with the ligand fluorine orbitals to form six equivalent σ bonds. The extent to which sulfur orbitals overlap with fluorine orbitals is a measure of the strength of the S—F bonds (or Se—F or Te—F bonds, as the case may be). However, application of Slater's atomic orbitals²⁶ to sulfur, selenium, and tellurium shows²⁷ that their unperturbed *d*-orbitals are much too diffuse to be capable of forming useful bonds. Craig and Magnusson²⁸ have proposed a type of polarization in which the *d*-orbitals of the central atom, under the perturbing effect of the ligand atoms, contract and are made more useful for bonding. Such an effect would be greatest for atoms held together by relatively short bonds and would decrease as bond lengths increase. This aspect of molecular orbital theory implies, *ceteris paribus*, that *d*-orbital contraction (and consequent

overlap) will be greatest for SF₆, with its comparatively short bonds, and least for TeF₆, with its comparatively long bonds; i.e.,

$$\bar{D}(\text{S}-\text{F})_{\text{SF}_6} > \bar{D}(\text{Se}-\text{F})_{\text{SeF}_6} > \bar{D}(\text{Te}-\text{F})_{\text{TeF}_6}.$$

Craig and Zauli²⁹ have concluded that *d*-orbital contraction is not, per se, influenced by the electronegativity of the ligands; however, electronegativity must play a part in determining the strengths of bonds (i.e., $D(\text{S}-\text{F}) > D(\text{S}-\text{Cl})$), via its influence on the *s*- and *p*-orbitals.

(2) Resonance Stabilization of Bonds in SF₆, SeF₆ and TeF₆

The chalcogen atoms and fluorine have greatly different electronegativities; as a result, it is to be expected that S—F, Se—F, and Te—F bonds will exhibit some ionic character. Using Pauling's values³⁰ for the electronegativities of the atoms ($\chi_{\text{F}} = 4.0$, $\chi_{\text{S}} = 2.5$, $\chi_{\text{Se}} = 2.4$, and $\chi_{\text{Te}} = 2.1$) and his suggested relation between electronegativity differences and ionic character, one calculates about 45 % ionic character in the S—F and Se—F bonds, and about 60 % ionic character in the Te—F bond. Partial transfer of positive charge to the central atom and hybridization will decrease these percentages, but the relative amounts of ionic character should be essentially unchanged. Further transfer of charge to the peripheral atoms can lead to numerous structures, such as (a) and (b), which are stabilized by resonance. (The full double bond is,

of course, an extreme case provided by complete removal of a *p*-electron from fluorine, making a second orbital available.) Resonance stabilization can be diagnosed by the shortening and strengthening of bonds.

The Schomaker and Stevenson equation³¹ has been widely used to predict the lengths of single bonds in molecules:

$$\ell(\text{M}-\text{F}) = r_{\text{M}} + r_{\text{F}} + 0.08 |\chi_{\text{F}} - \chi_{\text{M}}| \quad (14)$$

In eq. 14 $\ell(\text{M}-\text{F})$ is the predicted single-bond length (M = S, Se, or Te), r_{M} and r_{F} are the covalent atomic radii of M and F, respectively, and $|\chi_{\text{F}} - \chi_{\text{M}}|$ is the

U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., October, 1965.

²⁵ P. H. Koch and W. E. Moffitt, J. Chem. Soc., 47 (1951).

²⁶ J. C. Slater, Phys. Rev., **36**, 57 (1930).

²⁷ D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, J. Chem. Soc., 332 (1954).

²⁸ D. P. Craig and E. A. Magnusson, J. Chem. Soc., 4895 (1956).

²⁹ D. P. Craig and C. Zauli, J. Chem. Phys., **37**, 601 (1962).

³⁰ L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, N. Y., 1960.

³¹ V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc., **63**, 37 (1941).

absolute value of the difference in electronegativity of the two atoms. Table IV-5 lists the single-bond length predicted by means of eq. 14; the experimentally measured bond lengths; Δ , the bond shortening; θ , the corresponding percentage double-bond character in the bond M—F, calculated according to Pauling;³² and $\bar{D}$, the average bond dissociation energy. There is an obvious, direct parallel between the bond dissociation energies and the calculated percentage double-bond characters. It seems likely, therefore, that in the series SF₆, SeF₆, TeF₆ the strengths of the bonds (and also their contractions relative to ideal single bonds) sensitively reflect two opposing factors: weakening due to greater *d*-orbital diffuseness and strengthening due to enhanced differences in electronegativity.

The "resonance energy" of a molecule, $\Delta H_{\text{res.}}$, can be defined³³ by

$$\Delta H_{\text{res.}} = \Delta H a^{\circ}(\text{obs.}) - \Delta H a^{\circ}(\text{calc.}) \quad (15)$$

where $\Delta H a^{\circ}(\text{obs.})$ is the observed enthalpy of atomization and $\Delta H a^{\circ}(\text{calc.})$ is the enthalpy of atomization calculated from the sum of all the bond energy terms for the molecule. These bond energy terms can be calculated from the enthalpies of formation of model molecules formed from the same atoms but having structures such that resonance stabilization or steric repulsion would not be expected to occur. For SF₆ the model molecules are SF₂ and, possibly S₂F₂. The need for systematization of the important effects of resonance is one of several reasons why thermodynamic data for simple, lower fluorides are so vital.

(3) Replacement Effects

It is interesting to inquire about the effects of replacing fluorine atoms in a molecule such as SF₆. The bond dissociation energy, $D(\text{SF}_5\text{—Cl})$, in sulfur chloride pentafluoride can be calculated from eq. 16:

$$D(\text{SF}_5\text{—Cl}) = \Delta H f^{\circ}(\text{SF}_5, \text{g}) + \Delta H f^{\circ}(\text{Cl, g}) - \Delta H f^{\circ}(\text{SF}_5\text{Cl, g}) \quad (16)$$

Inserting in eq. 16 the values (in kcal mol⁻¹) $\Delta H f^{\circ}(\text{SF}_5, \text{g}) = -235$ (this work), $\Delta H f^{\circ}(\text{Cl, g}) =$

TABLE IV-5. BOND SHORTENING IN CHALCOGEN HEXAFLUORIDES

Bond	$\ell(\text{M—F})$ (Å)		Δ (Å)	θ	$\bar{D}$ (kcal mol ⁻¹)
	Calc.	Obs.			
S—F	1.64	1.56	0.08	18%	78.5
Se—F	1.76	1.69	0.07	13%	71.5
Te—F	1.94	1.84 ^a	0.10	35%	81.2

^a I. G. Ryss, "The Chemistry of Fluorine and Its Inorganic Compounds," USAEC Report AEC-tr-3927 (Pt. I), 1960.

28.9,²⁰ and $\Delta H f^{\circ}(\text{SF}_5\text{Cl, g}) = -250.5^{24}$ yields

$$D(\text{SF}_5\text{—Cl}) = 44 \pm 4 \text{ kcal mol}^{-1}.$$

This value may be compared with the average S—Cl bond energy of SCl₄, $\bar{D}(\text{S—Cl}_4)$, which is calculated as follows. NBS Circular 500³⁴ gives $\Delta H f^{\circ}(\text{SCl}_4, \ell) = -13.6 \text{ kcal mol}^{-1}$. Using the estimate $\Delta H v^{\circ}(\text{SCl}_4, \ell) = 7.5 \pm 1 \text{ kcal mol}^{-1}$, we find (for the hypothetical gas state of SCl₄) $\Delta H f^{\circ}(\text{SCl}_4, \text{g}) = -6.1 \pm 2 \text{ kcal mol}^{-1}$. By inserting the appropriate values into eq. 9, we obtain $\bar{D}(\text{S—Cl}_4) = 47 \pm 2 \text{ kcal mol}^{-1}$. Thus, the S—Cl bond in SF₅Cl is seen to be of about normal strength.

The application of eq. 17,

$$\begin{aligned} D(\text{SF}_5\text{—Cl}) + 5\bar{D}(\text{S—F})_{\text{SF}_5\text{Cl}} \\ = \Delta H f^{\circ}(\text{S, g}) + 5\Delta H f^{\circ}(\text{F, g}) \\ + \Delta H f^{\circ}(\text{Cl, g}) - \Delta H f^{\circ}(\text{SF}_5\text{Cl, g}), \end{aligned} \quad (17)$$

gives

$$\bar{D}(\text{S—F})_{\text{SF}_5\text{Cl}} = 79.1 \pm 1.5 \text{ kcal mol}^{-1}.$$

The S—F bonds in SF₅Cl are therefore virtually of equal strength with those in SF₆. The S—F bond length in SF₅Cl is 1.58 Å,³⁵ which may be compared to 1.564 Å³⁶ in SF₆; thus, within the experimental uncertainty, these bonds are also of equal length. This equality of bond strength is not consistent with the theoretical work of Craig and Magnusson²⁸ who predicted that the effect of replacing fluorine by a larger atom would be to weaken all the bonds in the molecule.

7. The Enthalpy of Formation of Nickel Difluoride and of Thorium Tetrafluoride (E. RUDZITIS, E. H. VAN DEVENTER)

The calorimetric combustion of nickel in fluorine has been one of the most difficult fluorine bomb calorimetric studies carried out to date. Combustion yields have usually been about 50%. In addition to poor

combustion yields, considerable difficulties have also been encountered in devising analytical procedures

³⁴ "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

³⁵ R. Kewley, K. S. R. Morty, and T. M. Sugden, Trans. Faraday Soc., **56**, 1732 (1960).

³⁶ V. C. Ewing and L. E. Sutton, *ibid.*, **59**, 1241 (1963).

³² L. Pauling, J. Phys. Chem., **56**, 361 (1952).

³³ H. Mackle and P. A. G. O'Hare, Trans. Faraday Soc., **57**, 1070 (1961).

for the determination of fluoride present in unburned residues. Despite these major problems, a precision of $\pm 0.2\%$ has been obtained.

The combustion technique employed was similar to that previously described for metals forming nonvolatile fluorides.³⁷ Nickel foil of 2-mil thickness was perforated with a punch and formed into a basket. The basket was filled with cuttings of the 2-mil foil. After pretreatment of the sample with fluorine to obtain prefluorination rates, the basket was suspended from the bomb head with nickel wire. Discs of nickel foil, slightly larger than the NiF_2 liner, were stacked to catch the burning nickel after ignition. A cadmium fuse was inserted among the cuttings to initiate the reaction. Ignition proceeded smoothly, with the reaction gradually being quenched as the molten nickel coalesced into spheres and melted its way down into the liner. Following combustion, the bomb was disassembled and the residues, nickel beads encased in a matrix of melted NiF_2 , were removed. The major portion of NiF_2 was mechanically removed, and the beads were then washed in water to remove most of the surface fluoride. The dried residues were weighed and chemically analyzed to determine the amounts of occluded NiF_2 . Amounts ranging from 1 to 18 mg were found. The amount of nickel burned was calculated by

subtracting both the prefluorinated and unburned portions from the initial sample weight. Standard corrections were applied in the usual manner.

Eight calibration experiments were performed with benzoic acid, which yielded $\varepsilon(\text{Calor.}) = 3437.38 \pm 0.94 \text{ cal deg}^{-1}$. The standard thermal data (in kcal mol^{-1}) derived from the combustion data for the reaction

are $\Delta E_f^\circ = -156.7$, $\Delta H_f^\circ = -157.3$, and $\Delta G_f^\circ = -146.0$, all $\pm 0.6 \text{ kcal mol}^{-1}$.

The currently accepted value³⁴ for $\Delta H_f^\circ_{298.15}(\text{NiF}_2, \text{c})$ is $-159.5 \text{ kcal mol}^{-1}$. The uncertainty of $\pm 0.6 \text{ kcal mol}^{-1}$ attached to the present result is equal to twice the combined standard deviations arising from the scatter of $\Delta E_c^\circ/M$ values, the impurity correction, and the calibration data.

Work on determination of the enthalpy of formation of thorium tetrafluoride is in progress. Preliminary combustion experiments with thorium show that the combustion behavior is very similar to that of nickel but that greater combustion yields are to be expected. Analytical methods for the determination of fluoride in the presence of thorium are being developed.

8. The Enthalpy of Formation of Uranium Compounds (J. L. SETTLE)

The considerations leading to the construction of a trial apparatus for testing the combustion behavior of fluorine-sensitive substances, e.g., uranium compounds, in a fluorine flow calorimeter were discussed in ANL-6925, p. 182. Satisfactory combustions of uranium monosulfide were obtained without encountering the

problems associated with combustions in a bomb calorimeter. During the present report period, the analytical part of the calorimetric system has been completed and tests of the analytical techniques are in progress. The calorimeter is in place and nearly ready for use in trial combustions.

9. 1500°C Drop Calorimeter (J. E. BRUGGER, A. T. HU,¹³ A. CHAUDHURI³⁸)

Experimental work has been completed on the determination of enthalpy increments between 800 and 1200°C in the 1500°C drop calorimeter for the Calorimetry Conference-National Bureau of Standards sample of alumina (synthetic sapphire). Inspection of the computed results reveals an apparent temperature-scale bias toward low values at the extremes. Further work on the temperature scale is required.

A series of drops of a sample of uranium monophosphide (containing about 1% uranium dioxide) in a thick-walled tantalum capsule has been completed. A second series in a thin-walled capsule is under way. A thorough discussion of the alumina and the uranium monophosphide data will be included in a subsequent report.

Assembly of the adiabatic calorimeter is progressing rapidly. It is anticipated that testing will soon begin. The adiabatic calorimeter will eventually replace the copper-block calorimeter now in use.

³⁷ ANL-6925, p. 179; ANL-6900, p. 227.

³⁸ Graduate Student, Rice University.

10. 2500°C Electron-Beam-Heated Calorimetric System (D. R. FREDERICKSON, R. KLEB,³⁹ J. BREWER⁴⁰)

108-8922A

FIG. IV-6. Furnace for the 2500°C Calorimetric System.

system is unconventional in that it employs an electron-beam-heated, rotating tantalum target as a constant-temperature furnace. All subassemblies have been fabricated, except for a copper-block calorimeter which will be built soon. Most of the components, in various stages of assembly, of the calorimetric system have been mounted on the support posts. The electron beam guns have been tested and the furnace subassembly, whose proper operation is critical, is being tested.

The electron beam furnace⁴² consists of the furnace proper and two electron beam guns. Figure IV-6 shows the furnace proper with its beam locator plates, spiral tantalum radiation shield, and cavity for the tantalum target. Prior to hitting the target, the beam must pass through a slot which is determined by the relative positions of the four locator plates. This slot, as now set, approximates the $\frac{3}{32}$ -in. by $2\frac{3}{4}$ -in. opening in the radiation shield. Each locator plate individually indicates a current (via a milliammeter to ground) when the electron beam strikes it. Optimum conditions are being established for passing beam power through the slot and to the target without excessive heating of the locator plates and radiation shield.

The electron beam guns and their power supply make up the other half of the furnace system. Figure IV-7 is a block diagram of this system. The Pierce-type, grid-controlled, electron guns can be supplied with an ac-

108-9296

FIG. IV-7. Block Diagram of Electron Beam Gun and Power Supply.

A calorimetric system⁴¹ for determining enthalpy increments up to 2500°C is under construction. This

celerating voltage up to 20 kv. The emission level is determined by the temperature of the hot cathode and by the grid bias voltage. In normal operation, gun emission is maintained at a set level by a magnetically

³⁹ Central Shops.⁴⁰ Electronics Division.⁴¹ ANL-7055, p. 175, Fig. IV-1.⁴² Ibid, p. 176, Fig. IV-2.

amplified feedback loop whose sensing element is the grid. The electron beams may be made to sweep vertically by means of an audio oscillator connected to the deflection coils.

A comprehensive testing and evaluation of the electronic portion of the furnace system is being conducted.

So far the tests have shown a need for a sturdier filament support, more focus current, and a longer beam sweep. Appropriate modifications are being made. That the guns have adequate power capability is evidenced by their ability to heat a solid 75-g tungsten rod to its melting point (3410°C).

D. LIQUID SODIUM COOLANT CHEMISTRY

(A. COSGAREA, JR., H. M. FEDER, M. ADER)

The chemistry of liquid sodium is being studied to obtain fundamental information on the equilibria and kinetics of chemical reactions that can affect its use as a heat transfer fluid in nuclear reactors. The studies are mainly directed toward understanding the influence of sodium's common contaminants—carbon, oxygen, hydrogen, and nitrogen—on corrosion phenomena. Investigations carried out during this report period were devoted entirely to the contaminant carbon and, in particular, to its characterization and removal.

Various mechanisms for the observed carbon transport in loops containing liquid sodium have been proposed, but the problem remains unresolved. Elucidation of the nature of the carbon-containing species in liquid sodium is being sought since such information would furnish a logical basis for the understanding of

carburization and decarburization phenomena. Generally, corrosion studies are based on a carburization potential measurement with metal coupons; they are empirical in nature and do not identify the transported carbon species. Both identification and control of the stable carbon-containing species that are present in sodium are essential to the understanding of the basic corrosion mechanism(s) involved.

The studies of carbon in sodium carried out during this report period can be divided for purposes of discussion into three categories: determination of the nature of carbon species in sodium, ultrapurification of sodium, and total carbon analysis. The breakdown is somewhat artificial since the studies in each section are interrelated.

1. Nature of Carbon Species in Sodium

Experience in this laboratory has confirmed the heterogeneity of carbon in sodium and has shown that a significant part of the variability of carbon analyses arises from this fact. Efforts are being made to determine the composition of the carbon-bearing species and, if possible, their origins.

a. MASS SPECTROMETRIC OBSERVATIONS

(C. LUNER, I. JOHNSON, J. W. REISHUS¹)

Previous work at this and other laboratories has shown that distillation of sodium does not reduce its carbon content below 50 to 75 ppm. One plausible explanation for this observation is the presence of carbon compounds whose volatilities are similar to that of sodium. Mass spectrometric detection of high molecular weight ($m/e \geq 207$), presumably organic compounds in various samples of sodium heated to $\sim 300^\circ\text{C}$ was reported previously.² However, the combined results, although not entirely conclusive, suggested that most sodium does not contain significant amounts of volatile carbon compounds except when

mold-coating fluids have been employed during casting. Such fluids (kerosene or mineral oil base) are used in the manufacture of commercial and reagent-grade sodium, but not reactor-grade sodium. Hence, the failure of distillation to remove carbon-bearing impurities may be caused by the entrainment of particulate matter.

Two graphite electrodes of the type employed in the electrolytic manufacture of sodium were also examined mass spectrometrically. Only low-mass species (< 103) were evolved up to 900°C , and these gradually disappeared with time; at about 1025°C , no peaks above background were observed. These results indicate that volatile organic compounds of high molecular weight are not likely to be introduced into sodium during its manufacture.

b. REACTIONS OF CARBON COMPOUNDS WITH LIQUID SODIUM (C. LUNER, K. ANDERSON)

The reactions of common carbon compounds with sodium at elevated temperatures are being investigated. Identification of the reaction products may, in addition

¹ High Temperature Materials Development Group.

² ANL-7055, p. 85.

to elucidating the course of reaction, provide clues as to the chemical forms in which carbon can exist in relatively pure sodium. The reaction products—solid, liquid, and gaseous—are identified and analyzed by gas chromatography and other chemical techniques. In order to gain experience with these techniques, several preliminary experiments were performed with sodium- Na_2CO_3 , a previously investigated reaction, and with sodium-lampblack and sodium-graphite.

The experiments consisted of heating two grams of United States Industrial Co. (U.S.I.) reactor-grade sodium (containing 30 to 40 ppm carbon) with 0.1 g of the carbon-containing material for 2 to 16 hr at 700°C in stainless steel or nickel capsules in a helium atmosphere. After cooling, a portion of the unfiltered reaction products was treated with dilute sulfuric acid; the gases evolved were collected on a liquid-nitrogen-cooled, demountable, silica gel trap, and analyzed by gas chromatography. The results may be summarized as follows:

1. Na_2CO_3 is unstable in liquid sodium at 700°C , yielding decomposition products whose relative amounts vary with heating time. A carbide or carbide-like compound is formed as shown by the evolution of acetylene on dissolution of the sodium. The final product of Na_2CO_3 decomposition ap-

pears to be carbon, which is observed as insoluble, black particles after the dissolution.

2. Lampblack and graphite do not react with sodium at 700°C to give carbides, as indicated by the absence of any significant amounts of carbon-containing gaseous products on dissolution.

These results are in qualitative agreement with the findings of Hobart (Pratt and Whitney Aircraft, CANEL) who studied the effect of temperature on the sodium- Na_2CO_3 reaction at constant time (2 hours).

Experiments similar to those above were made in which sodium was heated (500 to 700°C) in various metal capsules (Ni, Ta, Mo, SS 304, SS 316) in the presence of nitrogen, nitrogen and Na_2CO_3 , or $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. In all cases cyanide was found in the aqueous dissolution products as previously reported.³

An equilibration apparatus for use up to 800°C has been constructed and will be tested shortly. It should be possible to determine whether various carbon compounds react with or dissolve in liquid sodium since provision has been made to filter the mixture *in situ* at high temperatures. Appropriate chemical analyses will be performed on the filtered solutions and residues. Carbon-14-labeled compounds will be used to facilitate the analytical work when necessary.

2. Ultrapurification of Sodium

Ultrapurification of sodium from impurities present at the ppm level, such as oxygen, hydrogen, and carbon, is of interest for several reasons. The study of reactions between liquid sodium and impurities would be greatly simplified if ultrapure sodium were available. The reliability and accuracy of analytical methods for impurities could also be tested if sodium requiring a negligible blank correction were available. Furthermore, the development of economical, on-line, ultrapurification methods would be of considerable interest for reactor loops.

With respect to carbon, previous studies⁴ have shown that a considerable fraction of the carbon in sodium is present as submicron-sized particles. An effective means of ridding sodium of such carbon might be one whereby sodium atoms or ions are made to migrate through an electrolyte. Two techniques using this concept were tested. Removal of carbon from sodium by transport of carbon-containing impurities through liquid sodium was also attempted.

a. ELECTROMIGRATION (R. M. YONCO)

Electromigration of sodium through a molten sodium halide electrolyte is being studied as a method of re-

moval of carbon present at the ppm level. A cell to accomplish the purpose can be represented by

Since there is no plausible means by which positively charged carbon species can be formed and transported in such an arrangement, the removal of carbon should, in principle, be feasible. About a dozen such cells using various cell configurations and electrolytes have been operated. A schematic diagram of the last design, and the most successful to date, is shown in Figure IV-8. The procedure and results are discussed below.

The cell reagents and equipment were handled and assembled in a helium-atmosphere glovebox to avoid contamination of the sodium by environmental carbon. In this manner, any change in carbon concentration could be attributed to the electrolytic process only. The crude sodium had been filtered through a Pyrex glass frit. The electrolyte, a ternary mixture of 15 m/o NaF, 32 m/o NaCl, and 53 m/o NaI, had been dried under vacuum at 400°C , melted (m.p. $\sim 535^\circ\text{C}$) under helium, and filtered. The cell was enclosed by a stainless steel furnace tube and operated under these conditions: sodium, 52 g; ternary salt, 102 g; current, 1 amp; time, 27 hr; temperature, $\sim 550^\circ\text{C}$; atmosphere, 1300 torr He.

At the end of the experiment, the cell was disassembled.

³ E. W. Hobart and R. G. Bjork, Nucl. Appl. **1**, 490 (1965).

⁴ ANL-7055, pp. 84, 85; ANL-6925, p. 92.

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FIG. IV-8. Electromigration Cell for Purification of Sodium.

bled in the glovebox for examination and sampling. Approximately half the crude sodium had been transported. Samples of sodium for carbon analysis were removed from the mid-regions of the anode pool (dregs) and cathode pool (pure). The results of numerous analyses of these fractions and of the original crude sodium are shown below:

Fraction	Ppm Carbon
Crude	35.4 ± 4.3
Cathode	27.4 ± 4.0
Anode	38.6 ± 6.6

The uncertainty given is the standard error. The data indicate that at the 80% confidence level, a significant difference in carbon content exists between the crude and pure sodium (also between the pure and dregs). Thus, it appears that some reduction in carbon content was effected by the electromigration process. The reason for the appearance of carbon in the purified product is not known at present. Further electromigration experiments are planned.

b. THERMOELECTRODIFFUSION (C. E. JOHNSON,⁵ R. A. BLOMQUIST)

The concept of purification by thermoelectrodiffusion may be explained as follows. An emf is developed between two similar metal electrodes when a temperature difference exists between them. If an electrolyte containing this metal is interposed between them, the metal can, in principle, be transported through the electrolyte and be deposited at one temperature while being dissolved at a different temperature. (A return path of low electrical resistance must be provided.)

The utility of thermoelectrodiffusion is dependent on the rate of transport of the metal and was evaluated by conducting an experiment with lithium. (Lithium, instead of sodium, was used because its lower vapor pressure permitted simplification of the apparatus.) A gradient of 119°C was maintained for about six hours between the lithium at 663°C and a stainless steel collector sponge immersed in a LiF-LiCl electrolyte. No lithium was transported to the collector region. Further thermoelectrodiffusion experiments are not planned at the present time.

c. ELECTRODIFFUSION (R. M. YONCO)

It was reported⁶ that oxygen migrates through liquid sodium at ~600°C under the influence of high-density direct current. A liquid-state electrodiffusion apparatus was constructed to determine if carbon, as well as oxygen, would migrate preferentially toward either electrode under the influence of high-density, direct current. The apparatus consisted of a 9-mm dia. Pyrex U-tube that was filled with sodium and fitted with aluminum electrodes. The U-tube was heated in an oil bath at 100 to 110°C while a direct current density of ~140 amps/cm² was maintained. Analyses of the sodium after one week of operation indicated that preferential migration of carbon and oxygen had not occurred.

d. DIRECTIONAL FREEZING (R. M. YONCO)

An experiment was performed to determine if slow freezing of liquid sodium would lead to segregation of carbon-containing impurities. About 75 g of filtered U.S.I. sodium was sealed in a 1.7-cm dia. by 60-cm. long Pyrex tube. The sodium was melted in a horizontal position (filling about 75% of the tube) in a furnace having a temperature gradient of about 20°C from end to end. After 24 hours, the molten sodium was slowly cooled so that it froze progressively from one end of the tube to the other over a period of about six hours. Anal-

⁵ Energy Conversion Group.

⁶ B. A. Nevzorov, "The Nature of Oxygen in Liquid Sodium," USAEC Report AEC-tr-5412, November 28, 1962.

sis of several fractions of the sodium for total carbon indicated that significant segregation had not occurred.

Multicycle directional freezing (analogous to zone refining) will be tested in a future experiment.

3. Carbon Analysis (P. PELTON)

A series of experiments related to determination of graphitic carbon in sodium has been completed. Graphite thread (Union Carbide, Grade WCB, 99.96 % graphitic carbon) was added to samples of U.S.I. sodium which were then carried through the analytical procedure.⁷ The results, shown in Table IV-6, indicate that elemental carbon in sodium can be determined by our usual analytical procedure. However, the variability in recovery found at the higher carbon concentrations is somewhat surprising.

Recent analytical results for carbon in reactor-grade sodium have been erratic. Our previous results with U.S.I. sodium had indicated that a linear correlation between carbon content and sample size existed. Recently, however, the results of analyses of the same sodium have varied above and below this correlation line in a nonrandom manner. Apparently a nonsystematic

⁷ Combustion in an alumina boat with pure oxygen, followed by dissolution in dilute sulfuric acid and manometric measurement of liberated CO₂.

variable exists in our determination. Possible sources of variability being investigated are: (a) contamination of the sample via the helium atmosphere of the glove-box and by mechanical handling, and (b) nonuniform distribution of carbon species in the sodium.

TABLE IV-6. RECOVERY OF GRAPHITIC CARBON ADDED TO SODIUM

Weight of Sodium (g)	Carbon (μg)				% Recovery
	In Sodium	In Graphite Thread	Total	Found	
0.71	20	44	64	67	105
0.94	27	38	65	52	80
0.97	28	189	217	187	86
0.57	16	224	240	245	102
1.09	31	337	368	324	88
1.01	29	275	304	289	95
0	0	86	86	92	108

E. CHEMISTRY OF LIQUID METALS (I. JOHNSON, H. M. FEDER, M. ADER)

The physical chemistry of liquid metal solutions and alloys is being investigated to provide basic data for the testing of theories of metallic liquids and for the development of compact pyrochemical processes.

The following experimental studies are under way:

(a) Thermodynamic properties of binary liquid solutions of alkali metals are being measured by an atomic absorption spectrophotometric method. The data obtained will be used to test theoretical calculations of the properties of the simplest metallic solutions.

(b) Studies of the solubilities of inert gases in liquid metals are being made. The primary purpose of these studies is to assess the importance of the size and polarizability factors in metallic solutions; however, the data may also have some practical use in fast reactor technology. These studies are continuing on a part-time basis.

(c) Thermodynamic properties of binary metallic systems are being obtained by Knudsen effusion and

high temperature galvanic-cell measurements. These studies have been extended to obtain data suitable for the empirical correlation of thermodynamic properties with the atomic parameters of the metallic constituents. While such correlations are of obvious practical utility, they may also furnish a guide to the development of theory for alloy systems which cannot, at present, be treated theoretically.

(d) Experiments have recently begun on the measurement of velocity and absorption of high frequency sound in liquid metal solutions. It is hoped that unambiguous evidence will be obtained for the existence or nonexistence of distinct atomic complexes in liquid metal solutions.

(e) The magnetic susceptibility of selected alloys is being studied. These studies often yield useful information on the electronic configuration of the constituents in metallic systems.

1. Thermodynamic Properties of Liquid Binary Alkali Metal Solutions

(F. CAFASSO, V. KHANNA¹)

Thermodynamic activities of alkali metals in their binary liquid solutions are being measured to enable testing of theoretical methods² for calculating these activities. The experimental method,³ which is based on the principles of atomic absorption spectrophotometry, has been shown⁴ to be effective for the determination of the thermodynamic activities of both sodium and potassium in their binary liquid solutions. These activities were determined by comparing the absorption of resonance radiation (5890 Å sodium or 7665 Å potassium lines) by vapor above the Na-K solutions with that above pure sodium or pure potassium. In such a computation very little error is introduced by the assumption that the absorption coefficients of the absorbing

(4) Stark effect broadening—due to perturbations induced by the electric fields of electrons or ions;

(5) Nuclear hyperfine splitting (NHFS)—due to the existence of a nonzero nuclear spin and/or the presence of isotopes.

Of these factors, (2), (3), and (4) are negligible. Holtzmark and Lorentzian broadening effects become important only when the pressure of the absorbing system approaches 10^{-5} atm. Over the temperature range of this study (405 to 420°K), the partial pressures of sodium never exceeded 10^{-8} atm. Stark effects are ruled out since the temperatures were too low to induce any significant ionization of the vapor. Another factor considered in this study was the width of the emission line produced by the hollow cathode source.

Equations 1 and 2 below relate the transmission of the 5890 Å sodium line to the pressure of monatomic sodium. Equation 1 incorporates line broadening by the Doppler effect only; Eq. 2 incorporates line broadening by both the Doppler effect and nuclear hyperfine splitting.

$$I/I_o = \exp(-\ell K_o) \quad (1)$$

$$I/I_o = \frac{3}{8} \exp(-0.3900 \ell K_o) \quad (2)$$

$$+ \frac{5}{8} \exp(-0.6316 \ell K_o)$$

where $K_o = \frac{1.563 \times 10^{12} P \alpha}{T^{3/2}}$ (constant based on a

value of 0.65 for the oscillator strength),

P = partial pressure of monatomic sodium, atm,

T = absolute temperature, °K,

ℓ = optical path length (2.54 cm),

α = emission line width factor.

species are independent of experimental conditions. However, the determination of absolute values of partial pressures from absorbance measurements is much more sensitive to the factors which influence absorption coefficients. In the following, the experimental data which have been obtained for pure sodium have been examined in terms of absolute pressures. To do this one must examine the factors which influence line width and shape. The absorption line-broadening factors considered in this study are:

(1) Doppler effect broadening—due to the thermal motion of the excited atoms;

(2) Holtzmark or self-broadening—due to collisions between atoms of the same kind;

(3) Lorentz broadening—due to collisions with foreign gas atoms;

¹ Postdoctoral Fellow.

² J. R. Christman and H. B. Huntington, *J. Phys. Rev.* **139**, A83 (1965).

³ ANL-6725, p. 107.

⁴ ANL-6925, p. 97; ANL-7055, p. 80.

The partial pressures of monatomic sodium determined from some representative absorption measurements for pure sodium are shown in Table IV-7 and compared with values based on an equation in the monograph by Sittig.⁵ When Doppler broadening and nuclear hyperfine splitting are considered, but the width of the emission line is neglected (i.e., $\alpha = 1$), the observed pressures are consistently lower than the literature-based values by 18 to 26 %. (If only Doppler broadening were included, the values would be about 60 % too low.) The correct value of α is difficult to determine without

⁵ M. Sittig, "Sodium, Its Manufacture, Properties and Uses," Rheinhold Publishing Corp., New York, N. Y., 1956, p. 428.

high-resolution scan of the profile of the 5890 Å line, but by a method outlined by Mitchell and Zemansky⁶ and Vidale,⁷ a value of 0.80 to 0.85 can be estimated. The observed pressures would accordingly increase by 15 to 20 %. The uncertainty in the partial pressure of sodium based on the equation in Sittig's monograph is about 10 %. Thus, it may be concluded that substantial agreement exists among our partial pressure values, the values from Sittig, and values reported by Vidale.⁷

The activities, a_{Na} , of sodium in Na-K alloys can be determined by use of the relationship $a_{\text{Na}} = P/P^0$ where P is the partial pressure of monatomic sodium in equilibrium with the Na-K solution, and P^0 is the partial pressure of monatomic sodium in equilibrium with pure liquid sodium at the same temperature. One could equate P/P^0 to $\ln(I_{\text{NaK}}/I_0)/\ln(I_{\text{Na}}/I_0)$ of Doppler broadening alone were effective. The effect of nuclear hyperfine splitting makes the calculation less simple, but it can be performed by means of Eq. 2. The influence of NHFS on the activities of sodium in Na-K solutions is shown in Table IV-8. The activities obtained by including the effect of NHFS are all smaller than when this effect is ignored, the differences varying between 0.2

TABLE IV-8. INFLUENCE OF THE NUCLEAR HYPERFINE STRUCTURE (NHFS) OF THE 5890 Å SODIUM LINE ON CALCULATED SODIUM ACTIVITIES (a_{Na})

405 to 420°K

Atom Fraction Na in Na-K Sol'n	a_{Na} , NHFS Factor Not Included	a_{Na} , NHFS Factor Included
0.826	0.855	0.853
0.654	0.745	0.742
0.594	0.688	0.684
0.320	0.505	0.500
0.180	0.322	0.315
0.125	0.225	0.219

and 2.6 %. These differences are within the experimental uncertainty but, because of their trend with composition, they cannot be ignored in the refined thermodynamic treatment of the data now in progress.

The 7665 Å potassium resonance line also possesses nuclear hyperfine structure. Calculations of the absolute partial pressures of potassium are under way. The influence of NHFS on the activity of potassium in Na-K alloys appears negligible.

2. Decomposition Pressures of CeCd and PrCd (E. VELECKIS, R. MURRAY)

The stoichiometry, stability, and structure of inter-metallic phases formed by lanthanons (rare earths) and cadmium or zinc have received considerable attention in recent years at this laboratory. As a part of these studies, we reported⁸ the decomposition pressures and standard free energies of formation of eight selected LnCd compounds (Ln = La, Nd, Sm, Gd, Tb, Ho, Tm, and Lu). The present report is concerned with similar data obtained by the effusion technique for two additional compounds, CeCd and PrCd.

Alloys having approximately the composition Ln-Cd_{0.85} were prepared by heating mixtures of the component metals in sealed tantalum capsules for about 1 hr at 1200°C. The resulting ingots were crushed to 100- to 200-mesh powder in a helium-atmosphere glovebox. Because of the high reactivity of the powders, the effusion cell was filled in the glovebox and transported to the effusion apparatus without exposure of its contents to air.

Continuous weight loss (cadmium vaporization)

⁶ A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, London, 1961, p. 122.

⁷ G. L. Vidale, "The Measurement of the Vapor Pressure of Atomic Species from Spectrophotometric Measurements of the Absorption of Resonance Lines," Gen. Elec. Co., Phila., Pa., TIS-R60SD330, May 1960.

⁸ ANL-7055, p. 81.

measurements under isothermal effusion conditions were made at several temperatures for each alloy specimen. After each isothermal period, the temperature was re-adjusted without interrupting the effusion. The series

TABLE IV-9. DECOMPOSITION PRESSURE AND STANDARD FREE ENERGY OF FORMATION OF CeCd

Experiment Number ^a	Temperature (°C)	Decomposition Pressure (microtorr)	$-\Delta G_f^0$ (kcal/mole)
I-2	376.0	5.0	15.1
II-5	379.8	4.9	15.4
I-4	385.6	10.8	14.7
II-7	389.5	7.2	15.4
I-6	390.3	11.8	14.8
II-9	394.7	10.1	15.3
I-8	395.3	15.0	14.8
I-1	400.4	27.1	14.3
II-4	404.2	17.9	15.1
II-8	404.9	17.5	15.2
I-5	405.1	28.6	14.5
II-3	407.1	24.3	14.9
II-2	410.0	30.2	14.7
II-10	410.2	21.9	15.2
I-3	410.7	47.3	14.2
II-6	413.5	29.9	15.0
II-1	413.7	29.9	15.0
I-7	415.6	48.0	14.4

^a Two series of experiments, I and II, were made. The second number gives the chronological order in each series.

TABLE IV-10. DECOMPOSITION PRESSURE AND STANDARD FREE ENERGY OF FORMATION OF PrCd

Experiment Number ^a	Temperature (°C)	Decomposition Pressure (microtorr)	$-\Delta G_f^\circ$ (kcal/mole)
II-1	395.0	13.3	15.0
I-3	395.4	13.7	14.9
II-4	398.2	14.7	15.0
III-2	399.9	14.5	15.1
III-4	404.5	17.5	15.2
II-3	414.9	35.1	14.8
III-5	419.8	40.7	14.9
I-2	419.9	48.8	14.6
III-1	425.0	54.0	14.8
I-1	425.4	68.7	14.5
II-2	428.0	74.4	14.5
III-3	429.8	63.3	14.8

^a Three series of experiments, I, II, and III, were made. The second number gives the chronological order in each series.

was terminated when the initial effusion rate at a particular temperature was observed to decrease owing to the surface depletion effect. Decomposition pressures were calculated by means of the Knudsen equation. The

corresponding standard free energies of formation, ΔG_f° , were calculated using the relation

$$\Delta G_f^\circ = RT \ln (P/P^\circ),$$

where P is the decomposition pressure at temperature T in °K, and P° is the corresponding vapor pressure of pure liquid cadmium. The results are listed in Tables IV-9 and -10.

In comparison with the heavier⁹ Ln-Cd systems, the eutectic temperatures of the Ce-Cd and Pr-Cd systems are particularly low, 417 and 435°C, respectively. In order to assure the presence of solid alloys during effusion, the effusion temperatures were kept below these values. Consequently, very low effusion rates (0.5 to 1 mg per 10 hr) were obtained which led to erratic and scattered decomposition pressures and, hence, to a loss of accuracy.

The free energies of formation, extrapolated to 450°C, were estimated to be -14.3 and -14.4 kcal/mole for CeCd and PrCd, respectively. These values are essentially identical to the -14.4 kcal/mole previously found for LaCd.¹⁰ Because of the uncertainties in the present decomposition pressure data, extrapolations to higher temperatures should be avoided.

3. Plutonium Activity in Liquid Magnesium Solutions (I. JOHNSON, J. B. KNIGHTON,¹¹ R. K. STEUNENBERG¹¹)

The activity coefficient of plutonium dissolved in liquid magnesium can be estimated from the results of two recently completed experimental studies made in connection with pyrochemical processing of irradiated nuclear fuels. In the first of these studies, the distribution of plutonium between a liquid MgCl_2 -NaCl-KCl salt mixture and various liquid Mg-Zn alloys was measured;¹² in the second, the liquid miscibility gap in the plutonium-magnesium system was determined.¹³ The following shows how this information can be used to calculate plutonium activity coefficients in dilute solutions of plutonium in magnesium.

The distribution of plutonium between the molten ternary salt mixture and liquid zinc-magnesium alloy can be represented by the equilibrium

Equation 3 leads to the thermodynamic (activity) equilibrium constant relation

⁹ ANL-6925, p. 96.

¹⁰ ANL-7055, p. 82, Fig. I-36.

¹¹ Pyrochemical Research Group.

¹² ANL-6925, pp. 35, 36.

¹³ Ibid, pp. 48, 49.

$$K_a = \frac{(a_{\text{Pu}})(a_{\text{MgCl}_2})^{3/2}}{(a_{\text{PuCl}_3})(a_{\text{Mg}})^{3/2}}. \quad (4)$$

Equation 4 may be rearranged to

$$\gamma_{\text{Pu}} = (D) (x_{\text{Mg}})^{3/2} (\gamma_{\text{Mg}})^{3/2} (K_s) \quad (5)$$

where γ_{Pu} = activity coefficient of Pu in the metal phase,

$D = x_{\text{PuCl}_3}/x_{\text{Pu}}$, distribution coefficient of Pu,

x_{PuCl_3} = mole fraction of PuCl_3 in the salt phase,

x_{Pu} = atom fraction of Pu in the metal phase,

x_{Mg} = atom fraction of Mg in the metal phase,

γ_{Mg} = activity coefficient of Mg in the metal phase,

$K_s = (K_a) (\gamma_{\text{PuCl}_3}) / (a_{\text{MgCl}_2})^{3/2}$,

γ_{PuCl_3} = activity coefficient of PuCl_3 in the salt phase,

a_{MgCl_2} = activity of MgCl_2 in the salt phase.

Under the experimental conditions of the distribution studies, K_s remained essentially constant in all experiments done at a constant temperature. Knowledge of the value of K_s is not required; it may be eliminated from Eq. 5 in the following way. First, the limiting value of the quantity $(D) (x_{\text{Mg}})^{3/2}$ is determined $\lim x_{\text{Mg}} \rightarrow 0$. Under these conditions,

$$\gamma_{\text{Pu(Zn)}} = [(D) (x_{\text{Mg}})^{3/2}]_0 (\gamma_{\text{Mg(Zn)}}^\circ)^{3/2} (K_s), \quad (6)$$

where $\gamma_{\text{Pu}(\text{Zn})}$ is the activity coefficient of plutonium dissolved in liquid zinc, and $\gamma_{\text{Mg}(\text{Zn})}^0$ is the limiting value of the activity coefficient of magnesium in liquid zinc (containing a small amount of plutonium) as

$$\lim x_{\text{Mg}} \rightarrow 0.$$

Second, the limiting value of the quantity $(D)(x_{\text{Mg}})^{3/2}$ is determined as $\lim x_{\text{Mg}} \rightarrow 1$. Under these conditions,

$$\gamma_{\text{Pu}(\text{Mg})} = [(D)(x_{\text{Mg}})^{3/2}]_1 (K_s), \quad (7)$$

where $\gamma_{\text{Pu}(\text{Mg})}$ is the activity coefficient of plutonium dissolved in liquid magnesium. [The term $(\gamma_{\text{Mg}(\text{Mg})})^{3/2}$ has been set equal to unity since the metal solution is greater than 99.9₂ a/o magnesium.] Combining Eq. 6 and 7 to eliminate K_s , the equation

$$\gamma_{\text{Pu}(\text{Mg})} = \frac{[(D)(x_{\text{Mg}})^{3/2}]_1 (\gamma_{\text{Pu}(\text{Zn})})}{[(D)(x_{\text{Mg}})^{3/2}]_0 (\gamma_{\text{Mg}}^0)^{3/2}} \quad (8)$$

is obtained. Provided that the appropriate distribution coefficients are known, this equation permits the determination of the activity coefficient of a metal in one solvent in terms of the activity coefficient of the same metal in another solvent and the limiting value of the activity coefficient of the first solvent in the second solvent. Although the method depends on an oxidation-reduction reaction in which the thermodynamic properties of a molten salt play an important role, quantitative data for the properties of the molten salt are not required.

By use of the distribution data previously reported¹² and the thermodynamic data for the Pu-Zn¹⁴ and Mg-Zn¹⁵ systems, values of $\gamma_{\text{Pu}(\text{Mg})}$ were computed for temperatures of 650, 700, 750, and 800°C. The determination of the limiting values of the quantity $[(D)(x_{\text{Mg}})^{3/2}]$ as $\lim x_{\text{Mg}} \rightarrow 0$ and 1 was simplified by the fact that the logarithm of $[(D)(x_{\text{Mg}})^{3/2}]$ was found to be a linear function of x_{Mg} as $\lim x_{\text{Mg}} \rightarrow 0$ and 1. The calculated plutonium activity coefficients are shown graphically in Figure IV-9.

4. Pu-Cd System: Thermodynamics And Partial Phase Diagram¹⁶ (I. JOHNSON, M. G. CHASANOV, R. M. YONCO)

A paper entitled "Pu-Cd System: Thermodynamics and Partial Phase Diagram," by I. Johnson, M. G. Chasanov, and R. M. Yonco, was published in *Trans. Met. Soc. AIME* **233**, 1408 (1965). The abstract of the

108-9477

FIG. IV-9. Activity Coefficient of Plutonium in Magnesium versus Temperature ($\sim 8 \times 10^{-4}$ atom fraction Pu).

The activity coefficient of plutonium in magnesium was also estimated from liquid miscibility-gap data by means of an assumption regarding the mathematical form of the activity coefficient-concentration relation. Since the miscibility-gap data furnish only two independent relations, i.e., $a'_{\text{Pu}} = a''_{\text{Pu}}$ and $a'_{\text{Mg}} = a''_{\text{Mg}}$ (' and '' refer to the two equilibrium liquid phases), the assumed mathematical relation may involve only two adjustable parameters. It was assumed that the activity coefficient of plutonium in liquid magnesium depends on concentration in the following way:

$$\log \gamma_{\text{Pu}(\text{Mg})} = (x_{\text{Mg}})^2 (A + Bx_{\text{Pu}}) \quad (9)$$

where A and B are functions of temperature only. Values of A and B were computed from the miscibility-gap data previously reported.¹³ For this computation, the experimental phase-composition data were smoothed by the assumption of a linear variation of the logarithm of the solubility with the reciprocal of the absolute temperature below 900°C. The activity coefficient of plutonium for $x_{\text{Pu}} \simeq 8 \times 10^{-4}$, the average value of the plutonium concentration in the distribution studies, is shown graphically in Figure IV-9. It is seen that the two series of experimental results agree to within 10%, which is well within their combined uncertainties.

paper follows:

"The thermodynamics of the cadmium-rich portion of the Pu-Cd system has been studied with a high-temperature galvanic-cell method. The partial phase diagram of the Pu-Cd system was determined. The existence of the intermediate phases PuCd_{11} (cubic, BaHg_{11} structure, $a_0 = 9.282$) and PuCd_6 (cubic, CeCd_6 structure, $a_0 = 15.59$) was established. The existence of at least one other intermediate phase

¹⁴ I. Johnson and M. G. Chasanov, *J. Inorg. Nucl. Chem.* **2059** (1964).

¹⁵ P. Chiotti and E. R. Stevens, *Trans. Met. Soc. AIME* **233**, 198 (1965).

¹⁶ ANL-6725, p. 105; ANL-6800, p. 179.

richer in plutonium was indicated. PuCd_{11} was found to peritectically decompose into PuCd_6 and liquid at $406^\circ\text{C} \pm 2^\circ\text{C}$. The solubility of plutonium in liquid cadmium may be represented by the equations:

$$(355^\circ \text{ to } 399^\circ\text{C}) \log (\text{at. pct Pu}) = 6.223 - 4282T^{-1}$$

$$(399^\circ \text{ to } 632^\circ\text{C}) \log (\text{at. pct Pu}) = 5.148 - 5277T^{-1} + 1.156 \times 10^6 T^{-2}$$

The free energy of formation values (kcal per mole) of the two intermetallic phases are given by the equations:

$$(\text{PuCd}_{11}), \Delta G_f^\circ = -45.9 + 35.7 \times 10^{-3}T$$

$$(\text{PuCd}_6), \Delta G_f^\circ = -39.27 + 25.86 \times 10^{-3}T$$

The excess free energy (kcal per mole) of plutonium in liquid cadmium may be represented by the equation:

$$\bar{G}_{\text{Pu}}^{\text{xs}}/N_{\text{Cd}}^2 = -26.57 + 41.56N_{\text{Pu}} - (-16.72 + 29.54N_{\text{Pu}})10^{-3}T$$

in which N_{Pu} and N_{Cd} are the atom fractions of plutonium and cadmium. The thermodynamics of the U-Cd and Pu-Cd systems are compared."

5. Magnetic Susceptibilities of US-ThS Solid Solutions

(F. CAFASSO, D. GRUEN,¹⁷ C. THALMAYER¹⁷)

Measurement of the magnetic susceptibilities of a series of US-ThS solid solutions ranging from 100 to 27 % US was previously reported.¹⁸ Pure US was found to have a linear (Curie-Weiss) dependence on temperature and a Curie temperature of 181°K . The magnetic moment, susceptibility at room temperature, and Curie temperature of pure US obtained by other investigators¹⁹⁻²³ and in this study are listed in Table IV-11. It can be seen that there is a considerable spread in both the magnetic moment and absolute susceptibility values. Our value for the magnetic moment of US (2.51 Bohr magnetons) agrees well with that reported by Didschenko and Gortsema,¹⁹ (2.46 Bohr magnetons) but differs significantly from the moments reported by Trzebiatowski and Suski²⁰ (2.22 Bohr magnetons) and Allbutt et al²¹ (2.25 Bohr magnetons). In view of the difficulties associated with the preparation of pure US, much of the discrepancy can probably be associated with sample purity.

Dilution of US with ThS induced a complex series of changes in magnetic behavior. The χ_M^{-1} vs. T (reciprocal molar susceptibility versus absolute temperature) curves¹⁸ for the solutions were not linear, as for pure US, but were concave toward the temperature axis. The degree of concavity increased as the solutions became

TABLE IV-11. MAGNETIC MOMENT, ROOM-TEMPERATURE MOLAR SUSCEPTIBILITY, AND CURIE TEMPERATURE OF URANIUM IN URANIUM MONOSULFIDE

Investigators	Magnetic Moment, μ_B (Bohr magnetons)	Molar Susceptibility, $\chi_M \times 10^6$ at 298°K (emu)	Curie Temp. ($^\circ\text{K}$)
This study	2.51	6667	181
Didschenko and Gortsema ¹⁹	2.46	6280	180
Trzebiatowski and Suski ²⁰	2.22	5773	185
Allbutt et al ²¹	2.25	5022	178
Picon and Flahaut ²²	2.09 ^a	4603	—
Eastman et al ²³	1.99 ^a	4180	—

^a Calculated from the measured room-temperature susceptibility by assuming that the system follows a Curie-Weiss law with $\Delta = 180^\circ\text{K}$.

more dilute in US. The Curie temperature was progressively lowered with dilution, changing from 181°K for 100 % US to close to 0°K for a 37 % US solution. Our finding that the Curie temperature of US is gradually lowered by dilution with ThS contradicts the results reported by Allbutt et al,²¹ namely, that the Curie temperature is invariant with dilution. These investigators reported that the Curie temperature remained unchanged even at 10 m/o US. They contend that ferromagnetism is an intrinsic property of the solid solutions. Our data, however, indicate that the addition of ThS to US so significantly reduces the exchange forces responsible for ferromagnetism that they are rendered essentially negligible by the addition of 63 % ThS. The most probable explanation of the results of Allbutt et al is their failure to attain complete solid solution in the US-ThS preparations.

A tentative interpretation of the results in terms of electronic structure is as follows. These alloys may be

¹⁷ Chemistry Division.

¹⁸ ANL-7055, p. 83.

¹⁹ R. Didschenko and F. P. Gortsema, *J. Inorg. Chem.* **2**, 1079 (1963).

²⁰ W. Trzebiatowski and W. Suski, *Roczn. Chem. Pol.* **37**, 117 (1963).

²¹ M. Allbutt, A. R. Junkison, and R. M. Dell, *International Symposium on Compounds of Interest in Nuclear Reactor Technology, 1964 Nuclear Metallurgy Symposium AIME*, Edwards Bros., Inc., Ann Arbor, Michigan, p. 65.

²² M. Picon and I. Flahaut, *Compt. Rend.* **241**, 655 (1955).

²³ E. D. Eastman, L. Brewer, L. A. Bromley, P. Gilles, and H. L. Lofgren, *J. Am. Chem. Soc.* **72**, 4019 (1950).

regarded from the tight-binding point of view as composed of S^{2-} ions, Th^{4+} (Rn core) ions, and U^{5+} ($5f^1$ outside Rn core) ions. The remaining electrons populate a $s-d$ conduction band. The curvature of the magnetic susceptibility of the 27 % US solution may be interpreted in terms of the influence of a crystal field of cubic symmetry on a single $5f$ electron.²⁴ Preliminary calcula-

tions reveal that an overall splitting of the $^2F_{5/2}$ multiplet of approximately 660 cm^{-1} provides a reasonable single-parameter fit to the experimental susceptibility curve.

²⁴ D. M. Gruen and C. A. Hutchison, Jr., J. Chem. Phys. **22**, 386 (1954).

V

Reactor Safety¹

(L. Baker, Jr., A. D. Tevebaugh, J. D. Bingle)

The main areas of research in the reactor safety program are: (1) the study of metal-water reactions, and (2) studies relating to the safety of fast 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. As a result of the chemical reactions between the metals and water, a release of energy approaching or exceeding the energy released by the fission process during a nuclear excursion could occur. These chemical reactions are being studied so that realistic estimates can be made of the rates and extents of reactions during hypothetical reactor accidents.

Several methods are being employed to study the reactions of the metals of interest with water. These include isothermal reaction rate determinations, non-isothermal studies of the reactions with fine metal particles, in-pile meltdown experiments with specimens of typical reactor fuel materials, and heating experiments designed to simulate the conditions experienced by fuel elements during a loss-of-coolant accident. Calculational studies in which experimental results obtained by several methods are correlated and methods of accident analysis are developed have been yielding important information.

¹ A summary of this section is given on pages 13 to 15.

Studies relating to the safety of fast reactors are being made; these include a survey study of chemical and physical interactions of fuel and cladding materials at high temperature with molten sodium. Emphasis is given to detecting and evaluating exothermic alloying reactions and interactions which result in extensive break-up or frothing.

The transient boiling of water or liquid sodium resulting from sudden contact with fragmented or molten core materials is under study. This work will provide data needed for the analysis of the transient pressures generated by the violent disruption of reactor cores in nuclear excursion accidents. The first experiments are being carried out in water.

A third study is the measurement of high-temperature physical properties of fast reactor materials. The initial effort is concentrated on determining the specific heat of molten UO_2 for use in accident calculations. Samples of UO_2 in sealed tungsten crucibles have been inductively heated and melted at $>3000^\circ\text{C}$. Further development of apparatus is proceeding.

Two other fast reactor safety studies are the determination of the extent of fuel migration and segregation in mixed uranium-plutonium fuels, and experimental studies of the sodium-air reaction. The migration study is in the apparatus development stage, whereas the sodium-air study is in the planning stage.

A. METAL-WATER REACTIONS

1. Isothermal Studies of the Stainless Steel-Steam Reaction (R. E. WILSON, C. BARNES, L. BAKER, JR., R. O. IVINS)

Studies of the isothermal reactions between molten metals and steam are needed to provide kinetic rate data for predicting, by means of mathematical models, the chemical behavior of core materials during hypothetical reactor incidents. The reaction of molten stainless steel with steam is of particular interest because

of the large number of power reactors which employ stainless steel-clad fuels.

The reaction of stainless steel with steam has been studied previously by an induction heating method (ANL-6900, p. 239) over the temperature range 1100 to 1300°C . However, samples heated to 1400°C under-

went rapid swelling and foaming, and, as the sample disintegrated, all control of temperature was lost because of changes in inductive coupling between the induction coil and the sample. It was concluded that the reaction rate data for temperatures above 1300°C were questionable and that another method of heating the samples was needed.

The high-pressure furnace, which is designed to operate at a maximum pressure of 1000 psi and at temperatures up to 1700°C, allows heating of a sample by a method unaffected by sample disintegration. The furnace, which has been previously described (see ANL-6900, p. 242; ANL-6925, p. 187; and ANL-7055, p. 177), is contained in a steel pressure vessel and consists of two zones: an internal steam-filled zone that is surrounded by an alumina tube and an external zone that is argon-filled. The argon-filled zone contains molybdenum heater windings and insulation. The pressures in the two zones are automatically matched to avoid stresses on the alumina tube. Water is introduced into the lower part of the steam zone by a positive-displacement pump and is converted to steam. At the start of an experiment, the sample is elevated from a moderate-temperature section, where reaction with steam is negligible, into the high-temperature section. Some unreacted steam and the hydrogen produced by the metal-steam reaction are continuously removed from the upper part of the steam zone (high-temperature section) through an outlet valve. The extent and the rate of metal-steam reaction are determined by continuously monitoring the amount of hydrogen collected. Upon completion of the experiment, the sample is lowered to its initial position.

The high-pressure furnace was used in experiments

designed to determine the rate and the stoichiometry of the reaction of steam with stainless steel. A study of the thermodynamics of the reaction and a calculation of the heat of reaction were also carried out. The results of these studies are reported in the following paragraphs.

a. MEASUREMENT OF THE RATE OF THE STAINLESS STEEL-STEAM REACTION AT 1400°C

The isothermal experiments to determine the rate of reaction of steam with stainless steel were performed at 1400°C and at various steam pressures. The samples were type 304 stainless steel (16.8 w/o Cr, 8.3 w/o Ni, 1.7 w/o Mn, 73.2 w/o Fe) discs, $\frac{3}{4}$ in. in dia. and $\frac{1}{4}$ in. thick, and had a nominal weight of 13 g. Steam flow rate through the furnace was 5 ml of water/min, which is equivalent to a linear flow rate of steam past the sample of approximately 2 ft/sec. At the steam flow rate employed, enough steam passed through the furnace every minute so that the sample could have been oxidized to completion.

The results of two experiments in the high-pressure furnace at 1-atm pressure are plotted in Figure V-1. For comparison, Figure V-1 also includes a typical rate curve obtained by the induction heating method. The extent of reaction is expressed in terms of hydrogen generation per gram of sample, instead of in the more usual terms of hydrogen generation per square centimeter of sample surface area; this is necessary because of the swelling and foaming, which result in a rapidly changing surface area.

The effect of pressure on the stainless steel-steam reaction at 1400°C was examined. The results of typi-

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FIG. V-1. Hydrogen Evolution from the Reaction between Type 304 Stainless Steel and Steam at 1400°C and One Atmosphere Pressure. (Sample size: $\frac{3}{4}$ in. dia. by $\frac{1}{4}$ in. thick.)

108-9415

FIG. V-2. Hydrogen Evolution from the Reaction between Type 304 Stainless Steel and Steam at 1400°C and Various Pressures. (High-pressure furnace apparatus. Sample size: $\frac{3}{4}$ in. dia. by $\frac{1}{4}$ in. thick.)

cal experiments performed at 1, 2, and 12 atm (15, 30, and 176 psia) are compared in Figure V-2, where it can be seen that the reaction rate is independent of steam pressure. These results are in agreement with the results of nonisothermal experiments by the condenser discharge method (ANL-6648, p. 194) in which the pressure was varied from atmospheric to 1500 psia, and also with the results of experiments in the high-pressure furnace under conditions simulating a loss-of-coolant accident (see Section V.A.2. of this report).

The results expressed in Figures V-1 and V-2 indicate that approximately one-third of a sample had reacted in about 15 min. The nature of the reaction (swelling and foaming) prevents a simple interpretation by means of a reaction rate law expressed in terms of original sample surface area. It seems clear that the reaction rate will be a function of sample size and

shape and that the overall rate of consumption of metal may be higher with thinner sample sections.

b. STOICHIOMETRY OF THE STAINLESS STEEL-STEAM REACTION

To determine the stoichiometry of the stainless steel-steam reaction, a series of four experiments was performed in which small samples of type 304 stainless steel were completely reacted with steam at 1500°C. The results of the experiments are given in Table V-1. The average yield of hydrogen is 0.51 ± 0.01 liter (STP)/g, which is somewhat greater than values calculated previously. These calculations, which were based on the assumptions that the reaction products are Cr_2O_3 and FeO and that nickel does not react, yield a value for hydrogen generation of 0.40 liter (STP)/g. If it is assumed that the nickel forms NiO , a value of 0.44 liter (STP)/g is obtained. The experimental value of 0.51 liter (STP)/g indicates that higher oxides are formed.

X-ray diffraction studies² were made of the oxidation products of the four experiments and showed that the major phase was of the Fe_3O_4 or spinel type. Other likely spinels, FeCr_2O_4 , NiFe_2O_4 , and NiCr_2O_4 , could not be distinguished from Fe_3O_4 by X-ray analysis. Calculation of the hydrogen yield on the basis of complete conversion to spinel compounds of the type M_3O_4 results in a value of 0.54 liter (STP)/g, which is only slightly greater than the observed value. It was therefore concluded that the oxidation by steam type 304 stainless steel leads primarily to the formation

TABLE V-1. DETERMINATION OF THE TOTAL HYDROGEN GENERATED BY THE REACTION OF TYPE 304 STAINLESS STEEL WITH STEAM AT 1500°C AND ONE-ATM PRESSURE
Steam flow rate: 10 ml water/min.

Sample Weight (g)	Approximate Time to Completion of Reaction (min)	Total Exposure Time (min)	Hydrogen Generated [liters (STP)/g of SS]
4.83609	60	100	0.522
3.87858	45	90	0.516
1.14582	12	26	0.510
2.34223	16	25	0.492
			Av. 0.510

² Performed by R. Schablaske of the Chemical Engineering Division Analytical Laboratory.

tion of spinel type oxides in which the nickel and chromium atoms substitute freely into the Fe_3O_4 lattice.

c. THERMODYNAMICS OF THE STAINLESS STEEL-STEAM REACTION

Because of the experimental finding that spinel-type oxides are the products of the stainless steel-steam reaction, it was of interest to examine the existing thermodynamic data concerning these compounds. Thermodynamic data are available for Fe_3O_4 at temperatures from 298 to 1800°K,³ for FeCr_2O_4 at 298°K,⁴ for the heat content and entropy of FeCr_2O_4 between 298 and 1900°K,⁵ and for the free energy of FeCr_2O_4 and NiCr_2O_4 between 1000 and 1400°K.⁶ No data could be found for NiFe_2O_4 . Because of the greater availability of data at 1200°K, free energies of the reactions of the metals with steam are reported at 1200°K. At 1200°K, all metals and oxides are solids. Table V-2 is arranged so that total free energy of the oxides forming each spinel can be compared with the value for the spinel. The stabilization energy of the spinel is obtained by difference and is listed in the final column of the table.

The results given in Table V-2 indicate that the spinel compounds are stabilized relative to the constituent oxides by amounts varying from 4.8 to 8.1 kcal/mole. If the stabilization energy were the same for each of the spinel compounds, then it could be shown that the overall free energy of the reaction of stainless steel with steam is independent of which spinels are formed. However, it is likely that all four spinels are formed, in spite of the indicated positive free energy value for NiFe_2O_4 .

Calculations of the heat of reaction to form Fe_3O_4 and NiCr_2O_4 indicate that about 6 kcal/mole of en-

TABLE V-2. FREE ENERGY OF REACTIONS OF METALS WITH STEAM AT 1200°K TO FORM VARIOUS OXIDES AND SPINELS

Free Energy (kcal/mole)				Difference ^a
FeO -1.4	Fe_2O_3 +7.3	$\text{FeO} + \text{Fe}_2\text{O}_3$ +5.9	Fe_3O_4 -2.2	-8.1
FeO -1.4	Cr_2O_3 -66.8	$\text{FeO} + \text{Cr}_2\text{O}_3$ -68.2	FeCr_2O_4 -73.0	-4.8
NiO +12.6	Cr_2O_3 -66.8	$\text{NiO} + \text{Cr}_2\text{O}_3$ -54.2	NiCr_2O_4 -61.3	-7.1
NiO +12.6	Fe_2O_3 +7.3	$\text{NiO} + \text{Fe}_2\text{O}_3$ +19.9	NiFe_2O_4 —	—

^a Difference equals the free energy of spinel minus the sum of free energies of the constituent oxides.

ergy is released beyond that released in forming the constituent oxides. Assuming that this excess energy applies to the formation of FeCr_2O_4 and NiFe_2O_4 as well, one can calculate an overall heat of reaction. Calculating on the basis of 18% chromium, 8% nickel, and 74% iron reacting to form solid spinel compounds at 1600°K (1327°C), the heat of reaction of solid stainless steel with steam is determined to be 254 cal/g steel. Uncertainties in the calculation of the heat of reaction develop at higher temperatures where the metals and the oxides are molten, because of uncertainties in the melting points of the mixtures and in the heats of fusion. Steel begins to melt at about 1370°C and the oxide mixture is formed in a molten state. The heat of reaction of liquid metal to form liquid oxide is of greatest interest since, at lower temperatures, the reaction rate is low. The desired heat of reaction is obtained from the heat required to form solid oxide from solid metal by subtracting from this heat the heats of fusion of the oxides and adding to it the heats of fusion of the metals. The heats of fusion of the metals appear to be well known; however, considerable uncertainty exists in the values for the oxides. The heat of fusion of Cr_2O_3 is reported as 4.2 kcal/mole, that of FeO as 7.5 kcal/mole, and that of Fe_3O_4 as 33 kcal/mole.³ Using these values, the heat of reaction of molten stainless steel to form a molten oxide was calculated to be 155 cal/g of steel.

2. Reaction of Flowing Steam with Stainless Steel and Zircaloy-2-Clad UO_2 Fuel Elements (R. E. WILSON, C. BARNES)

A series of experiments has been designed to simulate the environment of the fuel in a water-cooled power reactor following a loss-of-coolant accident. In such a situation, the fuel would be subjected to a slowly

rising temperature because of decay heat. Typical accident calculations have indicated that, in the absence of effective countermeasures, fuel temperatures would reach the melting point of the metal cladding

³ C. E. Wicks and F. E. Block, "Thermodynamic Properties of 65 Elements—Their Oxides, Halides, Carbides and Nitrides," U. S. Bureau of Mines Bulletin 605 (1963).

⁴ F. D. Rossini et al, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500 (1952).

⁵ K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy," U. S. Bureau of Mines Bulletin 584 (1960).

⁶ W. Kunnman, D. B. Rogers, and A. Wold, The Use of CO-CO₂ Atmospheres for the Preparation and Free Energy Determinations of Several Oxide Systems, J. Phys. Chem. Solids **24**, 1535 (1963).

in about 10 min. The experiments were performed in the high-pressure furnace described in the previous section of this report.

Each sample (8 in. long by 0.4-in. OD) consists of a number of high-density UO_2 pellets clad with either type 304 stainless steel or Zircaloy-2 tubing having a 27-mil wall thickness. The top and bottom of the tube are closed with $\frac{3}{16}$ -in. thick welded plugs. The 2.5-mil radial gap between the UO_2 and the cladding is filled with helium at a pressure of 20 psia. A sample is

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FIG. V-3. Type 304 Stainless Steel-Clad, UO_2 -Core Simulated Fuel Element before and after Exposure to One Atm Steam at 1600°C for 10 Minutes.

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FIG. V-4. Hydrogen Evolution and Temperature of Top End of Sample during Exposure of Type 304 Stainless Steel-Clad Fuel Element to Steam at 1600°C in High-Pressure Furnace.

raised into the high temperature section of the furnace at the rate of 1 in./min, thus requiring a total of 8 min for complete insertion.

a. REACTION OF STAINLESS STEEL-CLAD FUEL ELEMENTS WITH STEAM

A preliminary experiment with a type 304 stainless steel-clad fuel element was described in ANL-6925, p. 187. In that experiment, which utilized a steam flow rate of about 1 ml of water/min, the fuel element remained in the hottest part of the furnace for 180 min. The upper two-thirds (hottest portion) of the cladding appeared to be reacted completely, most of the reaction occurring in the first 90 min. It was apparent from these results that the reaction rate was limited by the low flow rate of steam past the sample.

Recent experiments were performed, therefore, with higher steam flow rates. In the first several of these experiments, the flow rate was set at 10 ml of water/min with a nominal linear velocity of steam past the sample of 3.2 ft/sec; the steam pressure was maintained at 1 atm. The residence time of the fuel element in the hottest part of the furnace was greatly reduced. The total time of reaction with steam was 10 min. During the first 8 min, the fuel element was being elevated into the high temperature section. The fuel element was maintained in the high temperature section at 1600°C for an additional 2 min and was then rapidly withdrawn to the original position in the cooler part of the furnace.

The typical appearance of a fuel element which was exposed to steam under the conditions described above is shown, together with an unexposed element, in Figure V-3. The temperature-time history of the top (hottest) end of this fuel element and a plot of the hydrogen evolution are given in Figure V-4. The top

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FIG. V-5. Radial Cross Section near the Top of a Type 304 Stainless Steel-Clad, UO_2 -Core Simulated Fuel Element exposed to One Atm Steam at 1600°C for 10 Minutes.

of the fuel element reached a maximum temperature of about 1600°C and the bottom, a maximum of about 900°C , thereby creating an axial temperature gradient of about 700°C . The top one-third of the stainless steel cladding appeared to be completely reacted, whereas the remainder had reacted only slightly. The demarcation between the two reaction zones can be readily seen in Figure V-3. The maximum temperature at the demarcation has been estimated to be about 1400°C from the results of other experiments (see ANL-6900, p. 239, and section V.A.1. of this report). The total hydrogen evolved corresponded to 37% reaction of the stainless steel present in the fuel element.

A photomicrograph of a radial cross section near the top of the fuel element (Figure V-5) shows areas of interaction between the UO_2 and the stainless steel oxides. The foamy appearance of the oxidized stainless steel is also apparent in the photomicrograph. A photomicrograph of an axial cross section of the top UO_2 pellet in this experiment is shown in Figure V-6. X-ray analysis of the stainless steel oxides showed a structure of the $\gamma\text{-Fe}_3\text{O}_4$ type.

Additional experiments were conducted to determine the effects of both steam flow rate and steam pressure. the first of these experiments, an increased steam flow rate of 20 ml of water/min was employed, with a steam pressure of 1 atm. In the second and third experiments, increased steam pressures of 4 and 11

atm, respectively, were used with a steam flow rate of 10 ml of water/min. The results of these experiments are summarized in Table V-3 where it is apparent that neither the rate nor the extent of stainless steel-steam reaction were significantly affected by the changes in steam flow rate or pressure.

b. REACTION OF ZIRCALOY-2-CLAD FUEL ELEMENTS WITH STEAM

A preliminary experiment with a Zircaloy-2-clad fuel element was also described in ANL-6925, p. 187. The conditions of the experiment were identical with those of the first experiment with the stainless steel-clad fuel element, i.e., low steam flow rate and long residence time. The upper two-thirds of the Zircaloy-2 cladding appeared to be reacted completely, forming a tube of ZrO_2 which retained the original shape of the metal cladding. The lower (cooler) portion of the cladding reacted only slightly. Most of the reaction occurred during the first 2 hr of the exposure. Again, it was apparent that the low steam flow rate had limited the rate of reaction.

Additional experiments with Zircaloy-2-clad fuel elements were performed with an increased steam flow rate of 10 ml/min of water and the shortened residence time used in the studies with the stainless steel-clad elements (described above).

The typical appearance of a Zircaloy-2-clad fuel ele-

ment which was exposed to steam under these conditions is shown together with an unexposed element in Figure V-7. The temperature-time history of the top (hottest) end of the element is given in Figure V-8

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FIG. V-6. Axial Cross Section of the Top Pellet of a Type 304 Stainless Steel-Clad, UO_2 -Core Simulated Fuel Element after Exposure to One Atm Steam at 1600°C for 10 Minutes.

TABLE V-3. REACTION OF STAINLESS STEEL-CLAD FUEL ELEMENTS WITH STEAM IN THE HIGH-PRESSURE FURNACE
Total exposure time: 10 min.^a

Steam Pressure (atm)	Steam Flow Rate		Hydrogen Generated [liters (STP)]	Extent of Stainless Steel-Steam Reaction ^b (% of Total Metal)
	(ml H_2O / min)	(ft/sec)		
1	10	3.2	7.52	37.0
1	20	6.4	7.25	35.7
4	10	0.8	5.57	27.4
11	10	0.3	7.14	35.2

^a Sample elevated into hottest ($\sim 1600^\circ\text{C}$) part of furnace over an 8-min period, maintained there for 2 min, and then rapidly withdrawn.

^b Based on 0.51 liter of H_2 (STP)/g of SS (see Table V-1).

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FIG. V-7. Zircaloy-2-Clad, UO_2 -Core Simulated Fuel Element before and after Exposure to One Atm Steam at 1600°C for 10 Minutes.

together with a plot of the hydrogen evolution. The top and the bottom of the fuel element reached maximum temperatures of 1600 and about 900°C , respectively, resulting again in an axial temperature gradient of about 700°C . The hot upper end of the sample was embrittled, and only the outer surface was converted to ZrO_2 . There was no apparent interaction between the UO_2 and the cladding. In the case of Zircaloy-2-clad fuel pin, there was no sharp demarcation between reaction zones; however, the attack on the

cladding was more severe at the hotter end than at the cooler end. Figure V-9 shows a cross section of the top cap of the fuel pin. Measurements made on the photomicrograph indicated that a 14-mil thick layer of tubing wall remained as metal, and there was an oxide film which was also about 14 mils thick (original tubing wall thickness, 27 mils). Measurements of the

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FIG. V-8. Hydrogen Evolution and Temperature of Top End of Sample during Exposure of Zircaloy-2-Clad Fuel Element to Steam at 1600°C in High-Pressure Furnace.

TABLE V-4. REACTION OF ZIRCALOY-2-CLAD FUEL ELEMENTS WITH STEAM IN THE HIGH-PRESSURE FURNACE
Total exposure time: 10 min.^a

Steam Pressure (atm)	Steam Flow Rate		Hydrogen Generated [liters (STP)]	Extent of Zircaloy-2-Steam Reaction (% of Total Metal)
	(ml H ₂ O/min)	(ft/sec)		
1	10	3.2	2.96 (3.40 ^b)	18.5 (21.3 ^b)
4	10	0.8	3.30	20.6
11	10	0.3	2.52 ^c	15.8 ^c

^a Sample elevated into hottest (~1600°C) part of furnace over an 8-min period, maintained there for 2 min, and rapidly withdrawn.

^b Value calculated from experimental temperature-time history for 1 atm experiment and from the parabolic rate law.

^c Low values due to slightly lower temperatures reached during experiment.

evolved hydrogen indicated that the overall extent of reaction of Zircaloy-2 in the fuel element was 18%.

Experiments with Zircaloy-2-clad fuel elements were also performed at pressures of 4 atm and 11 atm. The results of these experiments are given in Table V-4. As in the case of the experiments with stainless steel, there was no significant effect of pressure on either

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FIG. V-9. Cross Section of the Top Cap of a Zircaloy-2-Clad, UO₂-Core Simulated Fuel Element after Exposure to One Atm Steam at 1600°C for 10 Minutes.

the rate or the extent of the Zircaloy-2-steam reaction.

The parabolic oxidation law, reported previously for zirconium (see ANL-6548), was used to calculate the rate and extent of reaction of the fuel element. The parabolic oxidation law can be expressed as follows:

$$-\frac{dr}{dt} = \frac{K}{(r_o - r)} \exp\left(-\frac{\Delta E}{RT}\right) \quad (1)$$

where r = the radius of unreacted metal in the pin, cm,

r_o = the original radius of unreacted metal, cm,

K = the rate law constant, $0.3937 \text{ cm}^2/\text{sec}$,

ΔE = the activation energy, 45.5 kcal/mole ,

R = the gas constant, $1.987 \text{ cal/(mole)} (^\circ\text{K})$,
and

T = temperature, $^\circ\text{K}$.

The equation was programmed on the CDC3600 digital computer for integration using small time intervals. An arbitrary temperature-time function could be inserted into the calculation. Temperature-time functions programmed into the computer are plotted in Figure V-10 and represent the approximate temperature history experienced by various portions of the Zircaloy-2 cladding on the fuel element. The corresponding calculated reaction rates for these regions, expressed in terms of the mils of cladding reacted during the course of the exposure, are also plotted in Figure V-10.

The amount of cladding reacted at the top (hottest) region of the fuel rod is calculated to be 13.1 mils (see uppermost curve in Figure V-10). The calculated reaction compares favorably with the measured thickness of the oxide film in the photomicrograph in Figure V-9. The measured oxide film thickness (~ 14 mils) is equivalent to the reaction of about 10 mils of Zircaloy; however, considerable additional reaction is represented by oxygen dissolved in a sublayer of α -zirconium. The total calculated reaction of each region of surface was summed over the seven regions and the total hydrogen evolution and percent reaction for the entire fuel rod calculated. This calculated result is included in Table V-4. The calculated extent of reaction was 3.40 liters H_2 (21.3% reaction) compared with measured values of 2.96 liters H_2 (18.5% reaction). Thus, the extent of reaction calculated from the parabolic rate law is only about 15% higher than that observed.

c. COMPARISON OF THE STAINLESS STEEL-STEAM REACTION WITH THE ZIRCALOY-2-STEAM REACTION

The results of the experiments with stainless steel-clad and Zircaloy-2-clad fuel elements indicate that above 1400°C the reaction of stainless steel with steam is more rapid than the reaction of Zircaloy-2 with steam. The rapidity of the stainless steel reaction under these conditions is due to the melting and foaming (and the subsequent large increase in surface area) of the mixture of stainless steel oxides. The rapidity of the oxidation of the stainless steel as it reaches about 1400°C results in observable self-heating of the cladding, as indicated in the temperature-time history in Figure V-4. Neither Zircaloy nor ZrO_2 is melted under the conditions of these experiments. However, the overall heat of reaction of Zircaloy with steam is

* Region 1, lowest 15.9% of surface; Region 2, 12.2% of surface; Region 3, 10% of surface; Region 4, 11.1% of surface; Region 5, 13.0% of surface; Region 6, 17.3% of surface; and Region 7, upper 20.5% of surface.

108-9419

FIG. V-10. Calculation of Reaction Rate with Steam of Zircaloy-2 Cladding of Fuel Element in High-Pressure Furnace Experiment.

much greater than the heat of reaction of stainless steel with steam.

Calculations presented in a recent analysis of a loss-of-coolant accident in a reactor which utilizes zirconium-clad fuel have indicated that the reaction at temperatures greater than 1000°C will probably be limited by the availability of steam to the reactor core (ANL-6925, p. 215 and ANL-7055, p. 192; see also Ref. 7). These calculations were performed using the

⁷ L. Baker, Jr. and R. O. Ivins, *Nucleonics* **23**(7), 70 (1965).

3. Studies of the UO_2 -Steam Reaction (R. E. WILSON, C. BARNES, L. BAKER, JR.)

A reaction between UO_2 and water to form UO_{2+x} and hydrogen was reported (see ANL-6925, p. 204) to occur during a pulsed heating cycle in the Transient Reactor Test Facility (TREAT). Three experiments were performed in TREAT using unclad high density UO_2 pellets. In the experiments, the samples received 223, 409, and 775 cal/g UO_2 of fission energy, resulting in the corresponding production of 5.7, 17.7, and 16.9 ml (STP) hydrogen/g UO_2 . The hydrogen evolution was equivalent to the conversion of the $\text{UO}_{2.0}$ to $\text{UO}_{2.07}$, $\text{UO}_{2.20}$, and $\text{UO}_{2.19}$, respectively. The finding of a significant reaction in TREAT prompted a study of the thermodynamics of the reaction and an experimental study of the reaction of UO_2 with flowing steam under isothermal conditions. The purpose of the studies was to verify the existence of a significant reaction and to determine the extent and rate of the reaction with typical high density UO_2 fuel pellets.

a. THERMODYNAMICS OF THE UO_2 -STEAM REACTION

A discussion of the oxygen potential of UO_{2+x} is given in a paper by Aukrust et al.⁸ The data in Figure V-11, taken from the paper by Aukrust, show the results of several series of investigations of the partial pressure of O_2 in equilibrium with UO_{2+x} . The method of evaluating the oxide composition in equilibrium with steam involves the calculation of the partial pressure of oxygen in equilibrium with steam and noting the points of coincidence of oxygen partial pressure in Figure V-11.

The method of calculating the partial pressure of oxygen in equilibrium with steam assumes that the

parabolic oxidation rate law for the zirconium-steam reaction. A rate law for the stainless steel-steam reaction has not yet been established because of the spontaneous disintegration of stainless steel at 1400°C, which results in a changing surface area. The sharp increase in reaction rate resulting from the increased surface area suggests that similar reactor calculations can be performed for stainless steel-clad fuel using the approximation that the reaction rate is negligible below 1400°C and is limited by the availability of steam above 1400°C (see Section V.A.7. of this report).

oxygen and the hydrogen are derived only from the steam, hence

$$P_{\text{H}_2} = 2 P_{\text{O}_2} \quad (2)$$

where P = partial pressure, atm. In using Equation 2, it is assumed that:

- (1) no significant concentration of hydrogen or oxygen is present in the incoming steam except that produced by water decomposition,
- (2) enough excess steam is employed so that any hydrogen or oxygen produced by the UO_2 -steam reaction will not significantly change the equilibrium, and
- (3) other species produced by steam decomposition, i.e., OH, H, and O, are not present in such quantity as to significantly upset the H_2/O_2 ratio.

Values for the equilibrium constant for steam decomposition are obtained from the JANAF tables.⁹ The equilibrium constant is expressed as follows:

$$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}} \quad (3)$$

It is now assumed that the total pressure is 1 atm and that the total extent of decomposition is small so that $P_{\text{H}_2\text{O}} = 1$ atm. It follows from Equations 2 and 3 that:

$$P_{\text{O}_2} = \left(\frac{1}{2K_p} \right)^{2/3} \quad (4)$$

The partial molar free energy of the O_2 can also be calculated as:

$$\Delta \bar{F}_{\text{O}_2} = RT \ln P_{\text{O}_2} \quad (5)$$

The results of the calculation are given in Table V-5.

It is apparent from Table V-5 that, at low temperatures, a few ppm of oxygen present initially in the steam could seriously upset the equilibrium, i.e., $P_{\text{O}_2} =$

⁸ C. Aukrust, T. Farland, and K. Hogemark, "Equilibrium Measurements and Interpretation of Non-Stoichiometry in UO_{2+x} " in *Thermodynamics of Nuclear Materials*, Proceedings of Symposium, Vienna, May 21, 1960, p. 713.

⁹ JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, 1965.

108-9593

FIG. V-11. Partial Pressure of O_2 in Equilibrium with H_2O , Superimposed on Plot of Partial Pressure of O_2 in Equilibrium with UO_{2+x} . (O_2 - UO_{2+x} data from Aukrust et al.⁸)

TABLE V-5. CALCULATION OF THE PARTIAL PRESSURE OF OXYGEN AND THE PARTIAL MOLAR FREE ENERGY OF OXYGEN IN PURE STEAM AT ONE ATMOSPHERE

$T(^{\circ}K)$	$\log K_p^a$	$\log P_{O_2}$	$\Delta \bar{F}_{O_2} = RT \ln P_{O_2}$ (kcal/mole)
1000	10.062	-6.91	-31.6
1100	8.883	-6.12	-30.8
1200	7.899	-5.47	-30.0
1300	7.064	-4.91	-29.2
1400	6.347	-4.43	-28.4
1500	5.725	-4.02	-27.6
1600	5.180	-3.65	-26.8
1700	4.699	-3.33	-25.9
1800	4.270	-3.07	-25.3
1900	3.886	-2.79	-24.3
2000	3.540	-2.56	-23.4
2500	2.224	-1.68	-19.3
3000	1.343	-1.10	-15.0

^a Data from the JANAF Tables.

$\sim 10^{-7}$ or 0.1 ppm at $727^{\circ}C$. At $1000^{\circ}C$, P_{O_2} is about 10^{-5} or 10 ppm so that significant oxygen contamination would be required to affect the equilibrium. At very high temperatures, the effect of other species cannot be ignored. Reference is made to the note by

Friel and Goetz¹⁰ where the compositions of steam to about $5000^{\circ}K$ ($4727^{\circ}C$) are plotted. From their calculations, H_2O at $3000^{\circ}K$ ($2727^{\circ}C$) and 1 atm pressure is in equilibrium with O_2 at 0.04 atm, H_2 at 0.14 atm, OH at 0.09 atm, H at 0.06 atm, and O at 0.02 atm. Their value of P_{O_2} of 0.04 atm compares favorably with the value of 0.08 atm given in Table V-5 where the presence of other decomposition products was ignored.

Points of coincidence (equal P_{O_2}) between oxygen in equilibrium with UO_{2+x} and oxygen in equilibrium with H_2O were superimposed on Figure V-11. Values of x corresponding to the equilibrium between UO_{2+x} and H_2O are thus concluded to be about 0.27 at $1000^{\circ}C$, 0.21 at $1200^{\circ}C$, 0.18 at $1400^{\circ}C$, and 0.17 at $1500^{\circ}C$.

The results of the calculation of the equilibrium composition of uranium oxide in a steam environment, expressed in Figure V-11, indicate that the oxygen content is decreasing continuously with increasing temperature. It was of interest, therefore, to attempt an extrapolation of the thermodynamic data for UO_{2+x} in an attempt to estimate the degree of oxidation to be expected at very high temperature. The extrapolation

¹⁰ P. J. Friel, and R. C. Goetz, J. Phys. Chem. **64**, 175 (1960).

is based on discussion given in a paper by Markin et al.¹¹ which showed that a plot of the function

$$\Delta \bar{F}_{O_2} + \Delta \bar{C}_p T (2.3 \log T - 1) \text{ vs } T \quad (6)$$

was accurately linear over a temperature range from 600 to 1100°C for $UO_{2.012}$, $UO_{2.053}$, and $UO_{2.116}$. The plot for the latter composition, $UO_{2.116}$, was extended to 3000°K (2727°C) using the equation:

$$\Delta \bar{F}_{O_2} + \Delta \bar{C}_p T (2.3 \log T - 1) = \Delta \bar{H}_o - T \Delta \bar{S}_o \quad (7)$$

where $\Delta \bar{C}_p = 11$ e.u.,
 $\Delta \bar{H}_o = -87.4$ kcal/mole, and
 $\Delta \bar{S}_o = 100.5$ e.u.

Values of $\Delta \bar{F}$ that were calculated using this extrapolation are listed in Table V-6. Also listed in Table V-6 are the values of $\Delta \bar{F}_{O_2}$ for water from Table V-5. Since the $\Delta \bar{F}$ values for $UO_{2.116}$ are consistently more negative than those for water, it is concluded that x in the equilibrium between UO_{2+x} and H_2O is greater than 0.116 over the entire temperature range, although it is clear that the equilibrium value is not much greater than 0.116 at 3000°K.

The heat of the reaction can also be estimated from the data of Markin et al.¹¹ The heat of oxidation of UO_2 to $UO_{2.25}$ (U_4O_9) is given as -9.8 kcal/mole at 850 and 1000°C and as -9.4 kcal/mole at 1100°C. The heat of oxidation of hydrogen to form water is found to be more negative, so that the overall reaction of UO_2 with steam is endothermic. The reaction

is calculated to absorb about 20 cal/g UO_2 at temperatures in the range 850 to 1100°C. To a first approximation, a lesser degree of oxidation is accompanied by a proportionally lesser energy absorption. It is concluded, therefore, that the heat of the UO_2 -steam reaction is very small.

b. ISOTHERMAL UO_2 -STEAM REACTION AT 1500°C

The UO_2 -steam reaction was studied in the high-pressure furnace apparatus which has been described in previous reports (see ANL-6900, p. 242; ANL-6925, p. 187) and sections V.A.1. and V.A.2. of this report. The furnace is designed for a maximum pressure of 1000 psig and sample temperatures as high as 1700°C. The experiments with unclad UO_2 , however, were performed at 1 atm pressure and 1500°C.

TABLE V-6. CALCULATION OF THE PARTIAL MOLAR FREE ENERGY OF O_2 IN $UO_{2.116}$ AND IN H_2O AT VARIOUS TEMPERATURES

T(°K)	$\Delta \bar{F}_{O_2}$ (kcal/mole)	
	$UO_{2.116}$	H_2O
1000	-51.8	-31.6
1200	-47.1	-30.0
1400	-42.8	-28.4
1600	-38.8	-26.8
1800	-35.2	-25.3
2000	-31.6	-23.4
2500	-23.1	-19.3
3000	-16.9	-15.0

The samples consisted of $\frac{1}{2}$ in. dia. by $\frac{1}{2}$ in. high pressed and sintered cylinders of UO_2 of greater than 95% theoretical density. Each cylinder weighed about 19.2 g. The samples, contained in alumina crucibles, were washed with alcohol and dried to constant weight before use.

The usual experimental procedure employed for studies with the high pressure furnace was altered for these experiments with UO_2 in order to avoid contact between UO_2 and air at elevated temperature. In the experiments, the UO_2 was inserted into the lower region of the furnace at room temperature, and the air replaced by argon. The furnace was then heated to the operating temperature, bringing the sample to about 650°C. Steam flow, generated from degassed distilled water, was then started. After steam had replaced the argon, a blank for the experiment was obtained, i.e., noncondensable gas was collected from the outlet of the furnace for a period of time to determine whether a reaction of UO_2 with steam occurred at 650°C. The sample was then elevated into the hottest portion of the furnace (1500°C). At this time, collection of a second gas sample was begun and continued throughout the duration of the experiment. After a predetermined period of time, the UO_2 sample was lowered to the 650°C position; gas collection was continued for an additional 30 min. Argon flow then replaced steam flow while the entire furnace was cooled to room temperature. The UO_2 samples were again dried to constant weight.

The amount of oxidation was determined by four independent methods: sample weight gain during an experiment, gravimetric analysis (subsequent controlled oxidation of sample residues to U_3O_8), X-ray diffraction, and hydrogen evolution. In the latter technique, the two gas samples described above were collected, sampled separately, and analyzed by means of a mass spectrometer. The gas samples contained a small amount of N_2 and O_2 from air contamination, H_2

¹¹ T. L. Markin, L. E. J. Roberts, and A. Walter, "Thermodynamic Data for Uranium Oxides Between UO_2 and U_3O_8 " in Thermodynamics of Nuclear Materials, Proceedings of Symposium, Vienna, May 21, 1960, p. 693.

and O_2 from water decomposition, and H_2 from the UO_2 -steam reaction. The percentage of the sample which was H_2 from the UO_2 -steam reaction was determined from the following formula (see ANL-7055, p. 180):

$$\% H_2 \text{ from } UO_2 \text{ reaction} =$$

$$(\% H_2) - 2[(\% O_2) - 0.268(\% N_2)] \quad (9)$$

The results of the analyses of the gas samples from two typical experiments are given in Table V-7 where it is shown that the analysis of the "blank" gas samples indicated that no reaction occurred while the sample was at the $650^\circ C$ position in the furnace.

The atomic ratios of oxygen to uranium were calculated from the results of each of the four methods of analysis for this series of experiments. Good agreement

TABLE V-7. HYDROGEN EVOLUTION FROM THE UO_2 -STEAM REACTION IN THE HIGH-PRESSURE FURNACE

Experiment	Gas Composition			Gas Volume [ml (STP)]		Calculated H_2 from UO_2 -Steam Reaction (%)
	% H_2	% O_2	% N_2	Total	H_2	
UO-1 blank ^a	61.3	31.6	2.8	367	0	0.0
UO-1 run ^b	71.1	24.4	1.1	837.6	191.8	22.9
UO-2 blank ^a	62.2	31.8	1.3	452	0	0.0
UO-2 run ^b	67.6	27.5	1.3	1123.7	150.6	13.4

^a Gas sample taken with UO_2 at $650^\circ C$.

^b Gas sample taken during UO_2 -steam reaction at $1500^\circ C$.

TABLE V-8. OXYGEN-TO-URANIUM RATIOS OF UO_2 SAMPLES BEFORE AND AFTER EXPOSURE TO STEAM AT $1500^\circ C$

Experiment	Time ^a (min)	Observed Atomic Ratio of Oxygen to Uranium				
		By Weight Gain Method	By Gravitric Analysis	By H_2 Evolution	By X-ray Diffraction	
					Major	Minor
Control pellet	0	—	2.008	—	2.01	—
Control powder ^b	0	—	2.010	—	2.01	—
UO-6	15	2.076	2.069	—	—	—
UO-7	15	2.075	2.066	2.060	—	—
UO-3	30	2.106	2.102	2.091	—	—
UO-4	30	2.106	2.106	2.088	—	—
UO-1	70	2.149	2.148	2.121	2.01	2.22
UO-5	70	2.142	2.138	2.126	—	—
UO-2 ^b	120	2.159	2.161	2.110	2.24	2.01
UO-8	120	2.158	2.159	2.146	—	—
UO-9	240	2.170	2.176	2.160	—	—
UO-10	240	2.173	2.177	2.184	—	—

^a Nominal sample time at $1500^\circ C$.

^b Pellet crushed to powder prior to experiment.

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FIG. V-12. Oxygen-to-Uranium Ratio after Exposure of UO_2 to Steam at $1500^\circ C$ and One Atmosphere Pressure.

between the independent measurements is shown (Table V-8). In one experiment (at 120 min) the pressed and sintered UO_2 pellet was crushed to powder before exposure to steam. No difference in the behavior of this sample was noted.

A plot of the final composition (O/U ratio), taken from the weight gain data in Table V-8, as a function of the square root of time is shown in Figure V-12. The reaction rate follows an apparent parabolic law for the first 70 min and then tapers off to a final composition of about $UO_{2.17}$. The oxidized samples were noticeably darkened by oxidation; however, they did not crack or fragment.

c. DISCUSSION

The results of the isothermal experiments confirm the reaction of UO_2 with steam reported in the TREAT experiments. It should be noted at this point that the temperature at which the oxidation occurred in the TREAT experiments is not known. The composition, $UO_{2.19}$, was obtained when the oxide pellets were heated to the vaporization temperature, about $3300^\circ C$; however, this does not mean that the reaction actually occurred at extreme temperatures. The large fission energy which produced the high temperature also produced a high degree of sample fragmentation which

was probably necessary for the reaction to proceed in the short time available during cooling in a water environment during the TREAT experiments. Once fine particles were produced at a high temperature, they then cooled to room temperature in liquid water so that the final oxidation may have occurred at any temperature during the cooling period.

The extent of reaction at 1500°C, after long exposure to steam, is in good agreement with the value calculated in the thermodynamic analysis given earlier in this report. Both the calculations and the experiments indicated that the UO_2 is oxidized to $\text{UO}_{2.17}$ at 1500°C when excess steam is present.

It is of interest to examine the equilibrium UO_{2+x} composition that would be expected under conditions where there is always some hydrogen in contact with the solid oxide. If the steam phase in contact with the solid oxide contains about 10% hydrogen, then the ratio $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ may be set equal to 10. Solving equation 3, the partial pressure of oxygen becomes

$$P_{\text{O}_2} = \left(\frac{10}{K_p} \right)^2. \quad (10)$$

Using Equation 10 and the values from Table V-5 for $\log K_p$ at 1027 and 1427°C, the following values were calculated for $\log P_{\text{O}_2}$: -12.13 at 1027°C and -7.40 at 1427°C. Reference to these values of $\log P_{\text{O}_2}$ in Figure V-11 indicates that the equilibrium x in UO_{2+x} is 0.00 at 1027°C and about 0.02 at 1427°C. It is therefore apparent that the UO_2 -steam reaction will be greatly suppressed if some hydrogen remains in contact with the solid oxide. It is for this reason that UO_2 clad with a reactive metal such as stainless steel or Zircaloy does not appear to react with steam either in furnace experiments or in TREAT experiments. The hydrogen which is produced continuously by metal-steam or metal-water reaction is probably sufficient to prevent significant oxidation of UO_2 . The reaction of UO_2 in the presence of a reactive metal would be expected to become significant only after the metal has been completely oxidized.

4. Studies with Aluminum- U_3O_8 Cermet Fuel (HFIR Fuel) in TREAT (R. O. IVINS, F. J. TESTA)

Studies of the metal-water reactions in TREAT are continuing. In these studies the physical behavior of typical reactor fuel materials and the extent of their reaction with water are determined under conditions directly simulating a nuclear excursion accident in a water-cooled reactor. The objectives of the program are:

- to determine the extent of reaction between the fuel materials and water,
- to determine the fuel temperature and pressure history during the excursion, and
- to determine the physical damage that occurs as a result of the transient.

A series of experiments has been performed with aluminum- U_3O_8 cermet core fuel. The samples were 1 in. by 0.5 in. sections of a High Flux Isotope Reactor (HFIR) fuel plate. The plate was clad with 10 mils of 6061 aluminum over the 30-mil thick aluminum-41.45 w/o U_3O_8 cermet core. Similar studies with aluminum-uranium alloy fuel samples have previously been described (ANL-6725, p. 212). The previous studies were performed with Spert 1-D fuel plate samples and with unclad SL-1 fuel plate material.

The experimental technique consisted of subjecting an autoclave containing the sample (weight ~1.3 g) submerged in 45 cc of water with 60 cc of free volume (helium filled) to a burst of neutrons in TREAT. The reactor power and autoclave temperature and pressure

were recorded on an oscillograph. The reactor period varied from 50 to 152 msec. The extent of metal-water reaction was computed from the amount of hydrogen evolved (measured by mass spectrometric analyses of gas samples taken from each autoclave) on the assumption that the aluminum present reacted as follows:

Experiments were performed under three conditions of water temperature and initial autoclave pressure. Seven experiments were performed with water at 30°C with an overpressure of 20 psia helium. Two experiments were performed with water at 285°C with an overpressure of 1000 psia (964 psia steam and 36 psia helium). These two sets of experimental conditions were identical with those used in the previous studies with aluminum-uranium alloy fuel material. An additional series of three experiments was performed with the cermet fuel in water at 120°C with an overpressure of 600 psia (570 psia helium and 30 psia steam). Experiments under the latter conditions were specifically requested by engineers at Oak Ridge National Laboratory who are engaged in the design of the HFIR reactor.

The results of the 12 experiments with HFIR fuel samples are summarized in Table V-9. The samples retained their plate-like shape at fission energy inputs

TABLE V-9. RESULTS OF EXPERIMENTS WITH HFIR FUEL SPECIMENS SUBJECTED TO TRANSIENT FISSION HEATING IN TREAT

Fission Energy Input (cal/g)	CEN Run No.	TREAT Characteristics		Initial Sample Weight (g)	Extent of Metal-Water Reaction (%)	Appearance of Sample after Transient
		Period (msec)	Int. Power (Mw-sec)			
Initial Conditions: 30°C water with 20 psia He overpressure						
133	198	152	53.2	1.291	0.2	Intact
335	200	148	134	1.296	1.2	Intact, slightly bulged
420	199	109	168	1.288	1.4	Intact, center bulged
425	201	109	170	1.292	2.5	Intact, bulged, badly ruptured
440	213	100	176	1.304	2.2	Intact, bulged, ruptured
645	204	109	258	1.300	74.6	One large particle, gray powder
1062	205	68	425	1.300	28.4	One large particle, several metallic fragments, gray powder
Initial Conditions: 120°C water with 600 psia overpressure (570 psia He and 30 psia H ₂ O)						
350	210H	113	140	1.307	0.3	Intact, slightly bulged
550	211H	61	220	1.296	93.9	One large globule, small amount gray powder
890	212H	64	360	1.304	92.2	One large globule, small amount gray powder
Initial Conditions: 285°C water with 1000 psia overpressure (964 psia H ₂ O and 36 psia He)						
413	206H	106	165	1.303	11.8	Intact, bulged, ruptured
658	207H	104	263	1.305	91.3	One large globule, gray powder

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FIG. V-13. Photographs of Samples of HFIR Fuel Plate subjected to Transient Fission Heating in TREAT in 30°C Water with 20 psia Helium Overpressure. (Energy inputs less than 500 cal/g.)

as high as 440 cal/g, even though 230 cal/g of energy is sufficient to melt the aluminum cladding and the aluminum in the matrix of the fuel. The appearance of the five plates irradiated in 30°C water at energies

between 133 and 440 cal/g is shown in Figure V-13 (an unused plate is also shown for comparison). The appearance of a plate irradiated in 120°C water at 350 cal/g of fission energy input and that of one irradiated

in 285°C water at 413 cal/g are shown in Figure V-14; these specimens also retained the plate-like shape of the original samples.

The irradiated plates shown in Figures V-13 and V-14 show that progressively more severe damage to the fuel plates occurred as the fission energy input was increased. The plate which received 133 cal/g was only slightly darkened, whereas the plates which received between 335 and 440 cal/g were bulged and distorted and contained crater-like holes. The latter appearance suggests that gas had been evolved from the core of the fuel and had bubbled through the molten cladding. Of the fuel samples which received 440 cal/g of energy or less, only one reacted to an extent greater than 2.5%. This sample was irradiated in 285°C water (CEN-206H) and reacted to the extent of 11.8%.

The samples subjected to energies greater than about 500 cal/g lost their resemblance to plates. In Figure

V-15, photographs of the two samples irradiated in 30°C water (20 psia helium) at energies of 645 and 1062 cal/g are shown. The residues consisted of (1) a single large globule containing most of the U_3O_8 , (2) some smaller particles which were oxide-coated metallic aluminum, and (3) a fine powder which was principally alumina (αAl_2O_3). In the experiment with an energy input of 645 cal/g, extensive reaction occurred (74.6% of the aluminum reacted) and there was only a small number of small aluminum particles present. In the experiment with an energy input of 1062 cal/g, the aluminum reacted to the extent of 28.4%, and there were many small aluminum particles present in the residue.

The changes in the samples that occurred in the high energy experiments in heated water were different in character from those that occurred in the corresponding experiments in 30°C water. In Figure V-16, photo-

1/2 in.

CEN Run Number	210H	206H
Water Temperature, °C	120	285
Overpressure, psia	600	1000
Fission Energy Input, cal/g	350	413
Reactor Period, msec	133	106
Extent of Reaction, %	0.3	11.8

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FIG. V-14. Photographs of Samples of HFIR Fuel Plate subjected to Transient Fission Heating in TREAT in Heated Water. (Energy inputs less than 500 cal/g.)

1 in.

CEN Run Number	204
Fission Energy Input, cal/g	645
Reactor Period, msec	109
Extent of Reaction, %	74.6

205
1062
68
28.4

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FIG. V-15. Photographs of Samples of HFIR Fuel Plate subjected to Transient Fission Heating in TREAT in 30°C Water with 20 psia Helium Overpressure. (Energy inputs greater than 500 cal/g.)

CEN 211H

CEN 212H

CEN 207H

1/2 in.

1/2 in.

CEN Run Number	211H
Water Temperature, °C	120
Overpressure, psia	600
Fission Energy Input, cal/g	550
Extent of Reaction, %	61
	93.9

212H
120
600
890
64
92.2

207H
285
1000
658
104
91.3

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FIG. V-16. Photographs of Samples of HFIR Fuel Plate subjected to Transient Heating in TREAT in Heated Water. (Energy inputs greater than 500 cal/g.)

TABLE V-10. QUANTITY OF ALUMINUM- U_3O_8 CERMET FUEL RETAINED AS A SINGLE GLOBULE IN RESIDUE FROM HIGH ENERGY EXPERIMENTS IN TREAT

CEN Run No.	Water Temperature (°C)	Extent of Aluminum-Water Reaction (%)	Calculated Total Weight of Sample Residue ^a (g)	Measured Globule Weight (g)	Percent of Sample in Globule
204	30	74.6	1.92	1.06	55
205	30	28.4	1.54	0.38	25
211H	120	93.9	2.08	1.93	92
212H	120	92.2	2.07	1.68	81
207H	285	91.3	2.06	1.99	96

^a Total Weight = 0.36 g U_3O_8 + 0.94 g Al + (% Reaction/100) 0.84 g O.

age of the total original sample weight (including the calculated quantity of oxygen uptake based on the hydrogen evolved during aluminum-water reaction). The single globule accounted for from 81 to 96% of the entire sample in the experiments in heated water, but accounted for only 25 to 55% of the sample in the experiments in 30°C water. Thus it is clear that sample fragmentation was greatly suppressed in the heated water, high pressure environment.

The physical behavior of the HFIR fuel samples was quite similar to that of the aluminum-uranium alloy fuels previously run in TREAT (ANL-6725, p. 212). The behavior of the two materials is compared in Table V-11. The major difference in the physical behavior of the two materials is the strength which the HFIR material exhibits in retaining its shape at energies higher than that required to completely melt the

TABLE V-11. COMPARISON OF BEHAVIOR OF CERMET (HFIR) AND ALUMINUM-URANIUM ALLOY FUEL SPECIMENS SUBJECTED TO TRANSIENT FISSION HEATING IN TREAT

Fission Energy Input (cal/g)	Maximum Sample Temperature (°C)	Sample Behavior	
		HFIR Fuel	Alloy Fuel ^a
<150 150-230	<660 660	No melting, negligible reaction. Aluminum (cladding and matrix) melting occurs; fuel retains its shape and slight bulges appear; only few tenths of a percent reaction.	No melting, negligible reaction. Melting occurs, fuel begins to lose its shape; only few tenths of a percent reaction.
230-500	660-1400	Aluminum melts, sample bulges badly; holes appear in surface but plate-like shape is retained. Reaction <2.5% in 30°C water, <11.8% in 285°C water.	Samples melt and form large globules; reaction <12% in both 30°C and 285°C water.
>500	>1400	Samples in 30°C water produce one large globule and smaller particles and fine powder; extensive reaction occurs. Samples in 120°C and 285°C water become large void-filled globules almost completely reacted (>90%).	Samples in 30°C water fragment, extensive reaction occurs. Samples in 285°C water become large void-filled globules almost completely reacted.

^a Samples of Spert 1 and SL-1 fuel plates (see ANL-6725, p. 212).

graphs are shown of residues from experiments in 120°C (600 psia) and 285°C (1000 psia) water at energies of 550, 658, and 890 cal/g. The samples in these runs were almost completely reacted and were fused into single large globules with large internal void spaces. Small quantities of very finely divided alumina were suspended in the water and deposited on the walls of the autoclave.

The results of weighings performed on each of the large globules recovered from the high energy experiments are given in Table V-10 and illustrate the difference in the form of the residues between experiments in 30°C water and in heated water. The weight of the single large globule from each high energy experiment is listed in the table and expressed as a percent-

cladding and the aluminum in the matrix (230 cal/g). The aluminum-uranium alloy fuel samples, in contrast, formed large single globules upon melting.

The unusual strength of molten aluminum- U_3O_8 dispersions has been reported by Fleming et al.¹² In these experiments the pressure differential required to produce sag in aluminum- U_3O_8 composites was determined up to 1015°C, which is 355°C higher than the aluminum melting temperature. Considerable strength was apparent at the highest temperature studied. Metallographic studies indicated that the strength may

¹² J. D. Fleming, J. W. Johnson, and S. H. Bomar, Final Report of Project No. B-153 Tork II, Reactions in Al-34 w/o U_3O_8 Dispersions, Georgia Institute of Technology Report (July 1, 1964).

Aluminum-U₃O₈ Cermet (HFIR) Plates

Aluminum-Uranium Alloy Plates

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FIG. V-17. Extent of Reaction of Fuel Samples containing Aluminum as Their Major Constituent in TREAT Metal-Water Experiments.

have been due to the development of a continuous network made up of the U₃O₈ and possibly Al₂O₃. The formation of a ceramic network may have been promoted by the thermite reaction between U₃O₈ and aluminum to form UO₂, Al₂O₃, and uranium-aluminum intermetallic compounds. The tests showed that reacted specimens were considerably stronger than unreacted specimens.

In the TREAT experiments at high energies the physical behavior of the cermet and metallic fuels was

almost identical. In 30°C water, fragmentation of the HFIR samples occurred above a threshold somewhere in the energy range of 440 to 550 cal/g. A similar threshold at about 530 cal/g was found in the studies with the alloy fuels.

The residues of both fuels consisted of various sized particles of partially oxidized metal and powdered alumina (α Al₂O₃). The only difference was that a single larger particle, consisting mainly of uranium oxide, was formed in the runs with the cermet fuel.

In the heated-water experiments at high energy both materials formed single large globules, with relatively small quantities of finely divided material suspended in the water and dispersed on the various internal parts of the autoclave.

The chemical behavior of the two materials was also quite similar. The extent of reaction is plotted as a function of fission energy input for the cermet and metallic fuels in Figure V-17. The similarity in behavior is shown by a comparison of these two graphs. Appreciable reaction did not occur until the fission energy input was high enough to cause melting. At energies below the thresholds discussed above, only moderate reaction occurred with either material; the highest reaction found was 11.8% in a heated-water (285°C) run with a HFIR plate at 413 cal/g. At energies above the threshold, very extensive reactions occurred with both materials. The three HFIR samples in heated water were more than 90% reacted. The two HFIR samples in 30°C water also exhibited high extents of reaction: 74.6 and 28.4% at energies of 645 and 1062 cal/g, respectively. The alloy plates in heated water at energies above the threshold reacted from 75 to 90%. In 30°C-water runs, the extent of metal-water reaction of the alloy plates varied from 10 to 60% as the energy input increased from 530 to 1400 cal/g. The autoclave pressure traces have shown only gradual rises to equilibrium values representing the hydrogen, steam, and helium present at the autoclave temperature several seconds after the transient. This is illustrated in Figure V-18, where pressure-time traces are shown for four HFIR runs at various energies and various initial autoclave temperatures.

The mechanism of the fuel plate-water reactions is evidently very complicated. It is postulated that at low energies where breakup does not occur or the plates do not lose their shape, the aluminum cannot react extensively, i.e., the nature of the reaction is to form a protective oxide film, and cooling rates are sufficient to prevent ignition. At energies sufficient to cause the plate surface temperatures to reach 1200 to 1400°C (estimated to be about 530 cal/g), the fuel samples are fluid enough to break up in 30°C water. In 120°C and 285°C water, even though breakup does not occur, the samples are fluid enough to flow and continuously

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FIG. V-18. Pressure, Temperature, and Reactor Power as a Function of Time for TREAT Metal-Water Runs with HFIR Fuel.

disrupt the protective oxide film. As fresh surface area forms, more extensive reaction occurs. It is likely that energy produced by this surface reaction is sufficient to raise the metal temperature to values where an ignition can occur. About 4% reaction is sufficient to heat an aluminum sample adiabatically from 1200°C to 1750°C, where ignition has been demonstrated to occur in laboratory experiments (see ANL-6648, p. 196). Ignition is followed by nearly complete reaction at an apparent burning temperature of about 2050°C. Although reaction in the burning regime is extensive, the reaction rate is low, requiring about 30 sec for consumption of a pellet 8 mm in diameter (ANL-6800, p. 338).

The quantitative similarity between the results of TREAT experiments with aluminum- U_3O_8 cermet fuels and with aluminum-uranium alloy fuels suggests

that the thermite reaction in the cermet fuel to form Al_2O_3 and aluminum-uranium intermetallic compounds is not an important energy source. Although the concentration of U_3O_8 in the HFIR fuel core is 41%, the overall concentration of U_3O_8 in the clad fuel material is only 27%. It is the latter concentration which is important in estimating the energy release from the thermite reaction for two reasons: (1) laboratory studies with aluminum-rich cermets have shown that this reaction is relatively slow, although the thermal conductivity of aluminum is very high; and (2) the TREAT experiments have shown no tendency for the cladding to separate from the fuel core in low energy transients. Laboratory experiments (see ANL-6800, p. 390) with aluminum- U_3O_8 compacts containing 30% U_3O_8 showed that an energy release occurred which could increase the fuel temperature about 300°C; how-

ever, the self-heating rate was very low (about one minute was required). In these experiments, a cold cermet sample was plunged into a furnace which was at a temperature of 1250°C. The temperature-time curve of the sample was then examined for evidence of rapid self-heating. Several HFIR fuel samples were similarly tested in the laboratory furnace; there was no evidence of self-heating due to the thermite reaction.

These laboratory studies were not pursued further

to determine why self-heating was not detected in HFIR fuel, 27 w/o U_3O_8 , even though a reproducible indication of self-heating was obtained with 30 w/o U_3O_8 compacts and with Argonaut fuel, 39 w/o U_3O_8 (ANL-6800, p. 398). Nevertheless, the demonstrated slowness of the thermite reaction in samples of low U_3O_8 content precludes significant energy releases during the critical few seconds in a TREAT experiment that determine whether or not extensive aluminum-water reaction will occur.

5. Scale-Up Experiments in TREAT on UO_2 -Core Fuel Clusters¹³

(R. C. LIIMATAINEN, F. J. TESTA)

Experiments were continued in TREAT to investigate the safety problems associated with the behavior of UO_2 -core, metal-clad fuel specimens under conditions simulating a power excursion. Specifically, the purpose of the current scale-up transient tests is to obtain information on the chemical and physical changes which take place upon meltdown of a subassembly or a portion of a nuclear reactor core. Particular emphasis is placed on determining the extent of metal-water reaction, the peak pressure produced, and the final particle size distribution of the fragmented fuel cluster. These parameters are then correlated with the energy of the reactor pulse.

The basic experimental technique consists of loading an autoclave with the fuel cluster submerged in water and subjecting the autoclave to a burst of neutrons in TREAT. The fission heat generated in the enriched core of the fuel pins by the neutron burst causes meltdown of the test pins to occur. After the transient, the hydrogen evolved is measured by means of a mass spectrometer, and from this the extent of metal-water reaction is computed. Also, sieve-screen analyses are made on the residue from the fragmented fuel to determine the particle size distribution, from which the mean size is calculated.

Previously, as part of this program, data were obtained using single UO_2 -core pins clad with Zircaloy-2 or type 304 stainless steel (see ANL-6900, p. 254). Also, transient experiments were conducted on 9-pin clusters of unclad uranium metal (see ANL-6925, p. 209). Recent experiments have utilized 9-pin clusters of UO_2 -core fuel clad with either Zircaloy-2 or type 304 stainless steel (see ANL-7055, p. 190). The total weight of UO_2 -core material in a 9-pin cluster is about 760 g. Two of the experiments utilized Zircaloy-clad specimens and two utilized stainless steel-clad fuel

specimens. The metal cladding weighed about 240 g, thus giving a total weight of 1 kg for the entire cluster. The scale-up autoclave was previously described and a drawing of the in-pile assembly given (ANL-6925, p. 209). Figure V-19 shows a photograph of the 9-pin UO_2 -core fuel cluster in its original condition.

Direct fission product, or burnup, analyses performed on each of the ten pellets in two UO_2 -core pins that remained intact during TREAT transient CEN-202S has shown that there is somewhat more internal heat generation at the very ends of the pins than in the central portions. These results are summarized in Table V-12; the flux depression effect is caused by self-shielding. Good agreement between the two completely independent determinations of energy input can be seen.

The data from the four UO_2 scale-up experiments that have been completed to date are shown in Table V-13 and in Figures V-20, V-21, V-22, and V-23. The photographs show the configurations of the clusters after being subjected to the reactor bursts indicated by the oscillograph records. Examination of the fuel pins from run CEN-202S (Figure V-20) indicated that the threshold of destruction had just been exceeded in this experiment. For this test, the energy input was 250 cal/g of UO_2 , an energy which is sufficient to heat the core adiabatically from room temperature to the melting point of UO_2 , and to melt one-half of the UO_2 . It can be seen from Figure V-20 that the rupture and damage of the cladding was confined to the top of the pins. Two conditions are believed to have contributed to this particular phenomenon. Firstly, from Table V-12, it is apparent that the top pellet received somewhat more fission heating than the other pellets. Secondly, there is evidence that, although the lower $\frac{3}{4}$ of the fuel pins remain submerged in water, the upper $\frac{1}{4}$ may have been in a steam environment or a bubbled steam-water mixture for a period of time. Exposure of the cladding to steam instead of water would

¹³ We gratefully acknowledge the cooperation of James Boland and the TREAT personnel of the ANL Idaho Division.

greatly decrease the heat transfer rate from the fuel to the coolant and thus increase the time available for metal-water reaction.

The more energetic transients, with reactor periods of from 74 to 87 msec, resulted in almost complete fragmentation of the fuel pins and extensive formation of

08-8647

FIG. V-19. 9-Pin Fuel Cluster before Meltdown in TREAT. (UO₂-core, type 304 stainless steel-clad fuel pins each 0.42 in. in dia. by 5 $\frac{5}{8}$ in. long.)

TABLE V-12. AXIAL DISTRIBUTION OF FISSION ENERGY IN 10-PELLET, UO₂-CORE FUEL PIN AFTER SCALE-UP EXPERIMENT IN TREAT
TREAT Transient CEN-202S

Pellet Number	Vertical Position	Fission Energy Input (cal/g UO ₂)	
		rod 1 ^a	rod 2 ^b
1	Top	306	352
2		238	268
3		230	273
4		236	258
5	Center	250	258
6		250	300
7		244	278
8		248	265
9	Bottom	253	272
10		300	297

^a Burn-up analysis made by CEN Division on the basis of total gamma radiation from sample.

^b Burn-up analysis made by Idaho Division on the basis of radiochemical determination of ⁹⁵Zr (half-life, 65 days; fission yield, 6.2%).

relatively fine particles. Figure V-24 shows an evaluation of the particle size, expressed as a mean diameter (surface to volume), versus the fission energy input. Also shown in Figure V-24, for comparison, are the results of experiments with single pins of metal-clad UO₂. It is evident that the larger fuel pins in these scale-up experiments also had a larger mean size upon breakup than did the small single pins.

Calculations were performed to study the disposition of the energy released during the transient meltdown experiments. The calculations for the six scale-up experiments performed to date are summarized in Table V-14; they show that the chemical energy release ranges from 2 to 53% of the total energy release. Additional calculations used the observed peak pressure in the autoclave in conjunction with an arbitrary heat loss fraction. The best overall agreement between observed peak autoclave pressure and calculated peak autoclave pressure was obtained using the assumption that 70% of the total energy had been absorbed by the autoclave at the time of peak pressure. The corresponding water temperature and gas composition given in Table V-14 were calculated on the basis of this assumption.

These calculations provide insight into the mechanism of heat transfer to the autoclave and suggest an explanation for the possibility that the upper section of the sample bundle in run CEN-202S was exposed to steam. Using the assumption that 70% of the energy was lost to the autoclave before the peak pressure was reached provides an estimate of the overall heat transfer coefficient, thus:

TABLE V-13. SUMMARY OF UO₂-CORE, METAL-CLAD, 9-PIN SCALE-UP EXPERIMENTS IN TREAT

Conditions:

1. Fuel pins were UO₂, 10% enriched with ²³⁵U, clad with either Zircaloy-2 or type 304 stainless steel. Pin dimensions: 0.42-in. dia. by 5½ in. long; 10 UO₂ pellets per pin, 25 mil-thick cladding, 3-mil gap between core and cladding.
2. Subassemblies consisted of 9-pin clusters on ¾-in. centers in 3 by 3 square array.
3. Fuel subassemblies submerged in distilled water initially at ambient reactor temperature (~25°C).
4. 20 psia helium atmosphere above the water.

	CEN-TREAT Transient Number			
	202S	209S	203S	208S
<i>Reactor Characteristics</i>				
Integrated power (Mw-sec)	202	391	373	382
Period (msec)	117	87	74	87
Peak power (Mw)	508	1190	1225	1145
Fission energy input (cal/g UO ₂)	250	485	463	475
<i>Results</i>				
Peak pressure rise (psig)	54	304	233	110
Cladding	Zr-2	Zr-2	SS-304	SS-304
Extent of reaction of metal cladding with water (%)	4	24	24 ^b	23 ^b
Fuel appearance after transient	Cladding started to melt	Complete fragmentation	Complete fragmentation	Complete fragmentation
Mean particle size of residue, d_{sv} (mils)	420 ^a	132	84	95

^a Original diameter of pins.^b Based on 0.40 liter H₂ per g SS to allow comparison with previous experiments. Corrected values for percent reaction of stainless steel, based on 0.51 liter H₂ per g SS (see Table V-1), can be obtained by multiplying by 0.78.

$$Q = UA\Delta T \quad (12)$$

where Q = heat transfer rate,
 U = overall heat transfer coefficient,
 A = inner area of autoclave, and
 ΔT = temperature difference.

For CEN-202S, the heat transfer coefficient, U , is calculated to be about 200 Btu/(hr) (ft²) (°F), equivalent to 0.027 cal/(sec) (cm²) (°C). Such a high value suggests that the principal heat transfer mechanism is boiling and recondensation on the autoclave walls. Values of $U = 20$ Btu/(hr) (ft²) (°F) are indicative of convective heat transfer, while values of $U = 800$ are not uncommon for condensing steam. The maximum pressure in CEN-202S of 74 psia places a limit of about 6 g of water in the vapor phase at any one time. This quantity is small enough to suggest that the entire bundle would always remain submerged; however, the large quantity of energy (143,900 cal) transferred to the autoclave, mostly by vaporization and condensation, corresponds to the vaporization and condensation of 270 g of water, or 1/3 of the water in the autoclave. It thus appears that the upper section of fuel rods in run CEN-202S could have been uncovered if there was a significant holdup of condensate on the wall of the autoclave and on the structural components above the fuel bundle. A large-scale holdup of condensate would not be expected in an equilibrium boiling situation; however, in a transient boiling process,

the force of steam issuing from the fuel region of the autoclave could easily have delayed return of large quantities of condensate. Thus, it may be concluded that the more severe damage apparent at the upper ends of the fuel rods in run CEN-202S, Figure V-20, was due partly to the exposure of cladding to steam instead of water and partly to a slightly greater fission energy input.

The time at which failure or rupture of the cladding occurs is not certain; the oscillograph records give no positive indication of this event *during* the reactor pulse. The minor rupture which occurred in run CEN-202S probably did not occur until just at the end of the transient, since all of the integrated power was required to achieve the heating and partial melting of the UO₂. Each of the other three oscillograph records shows the beginning of a rapid rise in pressure at about 2.5 sec, measured from the time that significant heating of the UO₂ began. That is, meltdown and reaction started just when the fission heating was over. Two interesting points of contrast are worthy of note in the meltdown of the UO₂-core, metal-clad clusters, relative to the uranium-metal-core (unclad) clusters. The first is in the time of failure. The previously reported (ANL-6925, p. 209) energetic uranium transient, CEN-197S, gave precise indication of meltdown right at the peak of the reactor pulse, whereas each of the UO₂ runs showed no perturbation of the reactor power-time

curve, and significantly, the pressure in the autoclave began to rise only when the transient had just been completed. The second point of contrast is that the maximum pressures in the two uranium-core experiments were attained (see Table V-14) at 1.2 to 1.6 sec, whereas the maximum pressures in the four UO_2 experiments were attained only after 20 to 50 sec from the start of the transient. It is postulated that, during the reactor pulse, almost all of the fission heat generated within the UO_2 stays in the UO_2 ; that is, the adiabatic approximation is considered valid. Only after the transient is over and the now-molten UO_2 has been in direct contact with the cladding material for some finite time (perhaps about $\frac{1}{2}$ sec) does the Zircaloy or stainless steel attain its melting point. Then the integrity of the cladding is, of course, destroyed and fragmentation occurs. At this time the molten UO_2 and cladding contact the water, which increases the rate of hydrogen generation and the vaporization of the water. Hence, the time delay in the pressure rise relative to the reactor power peak in the UO_2 case.

Figure V-25 shows the results of all of the TREAT studies with stainless steel-clad UO_2 fuel. It is evident from this figure that no significant stainless steel-water reaction is observed until the UO_2 has reached its melting point. Only when the UO_2 melts does the stainless steel itself undergo meltdown and concurrent reaction with water. This reconstruction of the events occurring during the transient experiments is consistent with laboratory studies of the stainless steel-steam reaction in the high pressure furnace (see Section V.A.2. of this report). The furnace experiments also showed that stainless steel is relatively unreactive toward steam until the stainless steel melts.

Figure V-26 shows that for the Zircaloy-2-clad fuel a similar situation exists; again, no significant reaction is observed until the threshold of UO_2 melting has been reached. This phenomenon is also illustrated in Figure V-24, which gives a plot of the degree of fragmentation for all of the UO_2 -core fuels studied in TREAT as a function of fission energy input. The figure shows that the threshold for fuel element fragmentation coincides directly with the melting of the UO_2 core.

In Figures V-25 and V-26, the extents of metal-water reactions in the scale-up experiments are compared with earlier results on single, small pins. The extent of reaction with stainless steel is slightly higher for the fuel-pin clusters than for single pins, whereas the extent of reaction with Zircaloy is slightly lower. However, these differences are within the probable limits of reproducibility of the in-pile, transient tests. The comparison indicates that there is no marked change in the extent of metal-water reaction upon

fuel meltdown when a cluster of pins is used instead of a single pin. This, therefore, lends additional confidence in the application of these results to actual reactor cores.

An important factor in the safeguards analysis of reactor meltdown incidents is the peak pressure produced. It would be expected that the peak pressure would be proportional, at least to some degree, to both the total energy released inside the autoclave and also to the hydrogen evolved. The correlation of pressure rise with total energy release is shown in Figure V-27 and includes the two previous scale-up experiments

Cluster after Transient

Oscillograph Record

108-9575

FIG. V-20. TREAT Transient CEN-202S: UO_2 -Core, Zircaloy-2-Clad Fuel Pins.

Cluster after Transient

Particle Size Distribution

Oscillograph Record

108-9577

FIG. V-21. TREAT Transient CEN-209S: UO₂-Core, Zircaloy-2-Clad Fuel Pins.

Cluster after Transient

Particle Size Distribution

Oscillograph Record

108-9578

FIG. V-22. TREAT Transient 203S: UO_2 -Core, Type 304 Stainless Steel-Clad Fuel Pins.

Cluster after Transient

Particle Size Distribution

Oscillograph Record

108-9579

FIG. V-23. TREAT Transient 208S: UO_2 -Core, Type 304 Stainless Steel-Clad Fuel Pins.

with uranium metal. Figure V-27 suggests that as more heat (fission and chemical) is dumped into the water, the maximum pressure attained during the meltdown also goes up.

A detailed evaluation of the overall reaction rate

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FIG. V-24. Degree of Fragmentation of UO_2 -Core Fuel Pins subjected to a Reactor Pulse. (Fuel pins submerged in water.)

108-9581

FIG. V-25. Results of Meltdown Experiments in TREAT with UO_2 -Core, Type 304 Stainless Steel-Clad Fuel Pins submerged in Water. (30°C H_2O , 20 psia.)

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FIG. V-26. Results of Meltdown Experiments in TREAT with UO_2 -Core, Zircaloy-2-Clad Fuel Pins submerged in Water.

108-9582

FIG. V-27. Peak Pressure Rise in TREAT Metal-Water Scale-Up Experiments as a Function of the Total Energy (Chemical + Nuclear) Released Per Gram of Water in the Autoclave.

within the autoclave (which simulates a reactor pressure vessel) will require development of a computer

TABLE V-14. ENERGY CALCULATIONS FOR ALL 9-PIN SCALE-UP EXPERIMENTS IN TREAT
Listed in order of specific energy release, cal/g H₂O.

	CEN-TREAT Transient Number					
	196S	202S	208S	209S	203S	197S
Fuel Pin:						
Core material	U	UO ₂	UO ₂	UO ₂	UO ₂	U
Core weight (g)	490	760	760	760	763	490
Cladding material	none	Zr	SS	Zr	SS	none
Cladding weight (g)	—	246	234	244	232	—
Water Coolant:						
Wt. of H ₂ O (g)	500	750	1250	1250	750	500
Nuclear Energy:						
Energy input (cal/g core)	124	250	475	485	463	302
Fission energy (cal)	60,760	190,000	362,000	368,000	354,000	148,000
Chemical Energy:						
Metal-water reaction (%)	10.7	4.1	23.1	24.2	24	56
H ₂ evolved (STP) (liters)	9.9	4.9	22.2	29.0	22.4	51.5
Heat evolved from reaction (cal)	31,250	15,700	7,600	92,000	7,900	163,500
Total Energy Release (cal)	92,010	205,700	369,600	460,000	361,900	311,500
Chemical contribution to total (%)	34	8	2	20	2	53
Specific energy release (cal/g H ₂ O)	184	275	295	368	483	623
Time after Initiation of Transient at which Maximum Pressure Occurred (sec)	1.6	33	20	50	33	1.2
Water Temperature: ^a						
Calculated water temperature rise (°C)	55	83	89	110	145	187
Calculated final water temperature (°C)	85	113	119	140	175	217
Calculated Partial Pressures at Time of Maximum Pressure: ^a						
H ₂ O (psia)	8	23	28	52	129	318
He (psia)	26	28	29	30	33	36
H ₂ (psia)	31	20	82	113	96	236
Calculated Total Pressure in System (psia)	65	71	139	195	258	590
Observed Maximum Pressure in System (psia)	85	74	130	324	253	590

^a Calculated on the basis that 70% of the total energy had been transferred to the autoclave at the time of peak pressure.

program in which the temperature-time history experienced by the cladding is calculated. This involves calculation of the rate of heat transfer from the UO₂ to the cladding and the rate of heat loss from the cladding to the water by boiling. For Zircaloy-2, the reaction rate can then be found by integrating the parabolic rate law for zirconium over the resulting temperature-time history, as was done for the furnace experiments described in Section V.A.2. of this report. It must also be determined to what extent the energy of the reaction perturbs the temperature-time history of the cladding. For stainless steel, no simple reaction rate law is available; however, it is likely that the experiments described in Section V.A.1. of this report,

combined with studies currently in progress, will result in the formulation of a useful reaction rate law.

Future scale-up experiments will incorporate two major changes: (1) the reactor transient will be a "flat top" rather than a pulse,¹⁴ and (2) the sample will be located above the water rather than submerged. These conditions will simulate certain aspects of a loss-of-coolant accident, whereas previous experiments have simulated power excursions.

¹⁴ In a "flat top" transient, fission heating remains reasonably constant for a period of about 10 sec, whereas in a pulsed transient, the time scale for heating is about 1 sec with a gaussian-shaped power-time heating curve.

6. Short-Period Transient (Kiwi-TNT) Irradiation (R. C. LIIMATAINEN, R. O. IVINS, F. J. TESTA)

The Kiwi-TNT test at the Nuclear Rocket Development Station in Nevada in January 1965 provided a means for obtaining metal-water reaction data during a short period (0.6 msec) transient. Previous transient experiments have been performed in TREAT, with reactor periods ranging from 50 to 500 msec. The Kiwi-TNT transient gave nearly adiabatic heating, thus simulating a very "fast" reactor excursion.

Prior to the Kiwi-TNT excursion, capsules containing typical reactor fuel materials were placed at various distances from the reactor. The preceding report (ANL-7055, p. 183) described the capsules and sum-

HNO_3 , and the total uranium content was found colorimetrically.

An increase in the extent of metal-water reaction with peak uranium temperatures is clearly shown in Figure V-28. Figure V-28 also shows a comparison of the Kiwi-TNT results with two other, quite independent, sets of data on high temperature uranium-water reactions. The two dashed lines show the previous TREAT meltdown data in room temperature and heated water (see ANL-6596, p. 191) and the two solid lines show the corresponding data from condenser discharge correlations with uranium wires.¹⁵ The con-

TABLE V-15. METAL-WATER REACTION DATA FOR URANIUM ALLOY^a FUEL SUBJECTED TO KIW-TNT SHORT PERIOD TRANSIENT

No.	Distance ^b (ft)	Estimated Fission Energy Input (cal/g)	Estimated Peak Adiabatic Core Temperature ^c (°C)	Condition of Fuel after Transient	Metal-Water Reaction (%)	d_{sv} ^d (mils)
1	$\frac{2}{3}$	420	3800 (L + V)	Fragments and fine particles	77	6
2	2	200	3800 (L + V)	Completely melted into fine particles	76	3
3	3	125	2500 (L)	Fragments and fine particles	52	6
4	3.5	100	2200 (L)	Melted into globules and fines	65	21
5	5	63	1133 (L)	Melted into globules and fines	21	19
6	6	50	1133 (S + L)	Partially melted	3.4	98

^a 93.5 w/o U, 5 w/o Zr, 1.5 w/o Nb, 20% enriched, 0.2 in. dia. by 0.5 in. long.

^b Distance between autoclave and reactor vessel.

^c Physical state of sample at that temperature indicated by V(vapor), L(liquid), and/or S(solid).

^d Mean volume-to-surface particle size of fragmented fuel sample.

marized most of the results of the test. However, the data on the extent of uranium-water reaction for the unclad uranium alloy (5 w/o Zr, 1.5 w/o Nb) pins have only recently become available; these are given in Table V-15. The extent of reaction of uranium with water was determined by analysis of the meltdown residues, rather than by direct hydrogen measurement, the method used in all previous in-pile metal-water reaction experiments.

Three of the samples were analyzed by the following method. The unreacted uranium (metal) was dissolved in bromine-ethyl acetate; the uranium oxide residue was then dissolved in nitric acid. The uranium and UO_2 contents were determined by performing a colorimetric uranium analysis on each portion of the sample.

For two of the samples an alternative procedure was used. The sample was first hydrided, whereby the uranium metal was converted to the hydride and the oxide remained as UO_2 . Then the sample was dehydrided by heating, and the hydrogen evolved was measured with a gas chromatograph, thus determining the amount of uranium metal present in the original sample. Following this, the entire sample was dissolved in

denser discharge data indicated that the particle size of the uranium and the water temperature were the principal factors determining the extent of uranium-water reaction. The particle sizes found in the Kiwi-TNT test are shown in Figure V-29 together with earlier electrical and fission heating results. The condenser discharge correlations in both Figures V-28 and V-29 are based on computer analyses.¹⁵

The metal temperatures plotted as the abscissa in Figure V-28 were calculated for the Kiwi data and the condenser discharge data from the energy input to the appropriate samples (fission energy for the Kiwi data and electrical energy for the condenser discharge method) on the basis that adiabatic heating occurred. In both cases, the temperatures refer to an initial value which does not include additional self-heating which might occur as a result of energy released during metal-water reaction. It was thus assumed that in these two experiments, the sample

¹⁵ L. Baker, Nonisothermal Reaction of Uranium with Water by the Condenser Discharge Method, Nucl. Sci. Eng., 25 (2), 116 (June 1966).

108-9424

FIG. V-28. Extent of Uranium-Water Reaction: A Comparison of Experimental Data.

temperature was raised instantaneously to the calculated value by the rapid heating method.

The heating rate in TREAT experiments, by contrast, is relatively low (reactor periods of about 100 msec) so that significant heat is lost during the heating process. It is, therefore, not meaningful to convert fission energy input from TREAT experiments to adiabatic temperature rise. Thus, it was necessary to use an estimated temperature scale for these TREAT runs based primarily on interrelating observations of phase changes (i.e., onset of melting of uranium, complete melting of uranium, evidence of vaporization) coupled with heat transfer (loss) considerations, all as a function of fission energy input.

The shaded area in Figure V-28 represents a zone in which uranium-water reaction is likely to occur under certain temperature conditions. The demarcation of the zone is useful in reactor safeguards analysis for predicting the consequences of a power excursion which leads to overheating of the uranium metal in the core of a water-cooled reactor. A possible explanation for the general agreement of the Kiwi-TNT data (samples initially at ambient temperature) with the results of the condenser discharge and TREAT experiments at higher temperatures is the following. In the Kiwi-TNT test the capsules were in the fireball which enveloped the Kiwi reactor and near surroundings for an appreciable length of time. Also, there was some gamma heating of the capsules. Hence, the water

108-9583

FIG. V-29. A Comparison of the Extent of Uranium-Water Reaction as a Function of Mean Particle Diameter.

in the capsules was undoubtedly heated during the transient to about 100°C, during which time the uranium-water reaction took place. It was shown during the analysis of the condenser discharge data that the water temperature is an important factor because the reaction of small metal particles is largely controlled by gas phase diffusion of water vapor through the hydrogen generated by the reaction. Thus, the reaction rate is seriously impeded when the bulk water temperature and the corresponding water vapor pressure are very low, i.e., 25°C and 0.5 psia. In studies of the zirconium-water reaction (ANL-6548), it was shown that the reaction was unaffected by water temperature over a range from 100°C to 315°C, but was impeded when the water temperature was only 25°C.

In applying the data of Figure V-28 to containment design, it must be realized that the data represent only general guide lines and that the severity of the particular reactor incident will also depend on other factors. For example, if reactor reactivity considerations indicate that a 2500°C maximum temperature could be attained in cold water (reactor shut down), about 25% uranium-water reaction would result. However, if hot water were present (reactor operating), then one would expect the same 2500°C uranium temperature to release hydrogen and chemical energy corresponding to 75% metal-water reaction.

From the plot of particle size versus extent of metal-water reaction (Figure V-29), it is apparent that

again there is a region in which one can expect the mean diameter to fall depending upon the type of excursion and the reactor condition at the start of the excursion. Both the condenser discharge and the Kiwi-TNT experiments with short-period meltdown gave fine particles (d_{sv} from 3 to 10 mils) and as a result considerable uranium-H₂O reaction occurred. However, the TREAT experiments, with relatively longer periods (slower heating), showed quite a contrast in behavior. A minimum d_{sv} value of 17 mils was observed for the residue, a value which was more or less constant over the range of 10 to 50% uranium-H₂O reaction. A possible explanation for this difference is twofold. Firstly, the rapid heating causes more violent fragmentation (i.e., finer particles) and secondly, in the rapid excursion there is less time for conglomeration or coalescence of molten droplets. (Larger globules were observed only in the slower transients.)

To summarize, the Kiwi-TNT data fit into an overall pattern when they are compared to both the earlier in-pile (TREAT) and laboratory (condenser discharge) results. Regions and extents of uranium-water reaction, within the limits of reproducibility of the data from these three methods, have been established which should be of use in related problems of nuclear reactor safety. In particular, the importance of temperature of metal, temperature of water, reactor period, and particle size have been delineated.

7. Calculation of the Extent of Metal-Water Reaction During a Loss-of-Coolant Accident (R. O. IVINS, L. BAKER, JR.)

The calculational study to predict the extent of metal-water reaction that would occur during a loss-of-coolant accident in a water-cooled power reactor has continued. The objective of this study is to demonstrate the application of metal-water reaction data to a reactor accident situation. The calculations described here pertain to a stainless steel-clad, UO₂-core fueled reactor. Calculations for a zirconium-clad reactor core have been presented in previous reports (ANL-6925, p. 215 and ANL-7055, p. 192) and in the open literature.¹⁶

The reactor conceived for the Loss of Fluid Test (LOFT) facility^{17, 18} was used as a model in these

studies. The cladding was assumed to be 15-mil thick stainless steel in the present analysis, whereas 25-mil thick zirconium cladding was used as a basis for the previously reported calculations. The analysis of the bottom inlet pipe break (i.e., below the core) described by J. M. Waage et al of Phillips Petroleum¹⁷ was used as far as possible as the basis for the metal-water reaction calculations in these studies. Their analysis assumes a blowdown, caused by a pipe break that completely uncovers the reactor core. The core temperature then rises owing to decay heating and eventually the core collapses as a result of melting of the cladding.

a. METHOD OF CALCULATION

In order to take into account the nonuniform distribution of decay energy throughout the core, the core was divided into ten sections. This was accomplished by segmenting the core into thirteen radial zones of equal volume. Eight of these zones were of

¹⁶ L. Baker, Jr. and R. O. Ivins, Analyzing the Effects of a Zirconium-Water Reaction, *Nucleonics* **23**(7), 70 (July 1965).

¹⁷ J. M. Waage et al, Preliminary Safety Analysis Report, LOFT Facility, Report IDO-16981, Phillips Petroleum, April 1964.

¹⁸ T. R. Wilson et al, An Engineering Test Program to Investigate a Loss-of-Coolant Accident, Report IDO-17049, Phillips Petroleum Co., October 1964.

TABLE V-16. RESULTS OF SEGMENTATION OF LOFT REACTOR CORE INTO TEN SECTIONS

Ratio of Power in Section to Average Power in Core		No. of Core Segments in Power Section	Percent of Core in Power Section
Range	Average		
2.16-2.40	2.28	4	2.56
1.92-2.16	2.04	12	7.69
1.68-1.92	1.80	8	5.13
1.44-1.68	1.56	16	10.26
1.20-1.44	1.32	22	14.10
0.96-1.20	1.08	16	10.26
0.72-0.96	0.84	18	11.54
0.48-0.72	0.60	18	11.54
0.24-0.48	0.36	26	16.67
0-0.24	0.12	16	10.26

TABLE V-17. CALCULATED EQUILIBRIUM TEMPERATURES OF CORE SECTIONS AFTER BLOWDOWN

Case B: The energy stored in the fuel during full power operation is fully retained by the fuel

Percent of Core in Section	Ratio of Power in Section to Average Power in Core	UO ₂ Average Temperature at 50 Mw Operation (°C)	Equilibrium Temperature of UO ₂ Core and Indicated Cladding (°C)	
			Zirconium	Stainless Steel
2.56	2.28	1495	1289	1249
7.69	2.04	1368	1184	1148
5.13	1.80	1241	1078	1047
10.26	1.56	1113	972	945
14.10	1.32	986	867	844
10.26	1.08	858	761	742
11.54	0.84	731	655	640
11.54	0.60	603	550	538
16.67	0.36	476	444	437
10.26	0.12	349	337	336

low enrichment and five were of high enrichment. Each radial zone was further divided into twelve axial segments, which were also of equal volume. The resulting 156 equal-volume segments (12 cylindrical segments in the center and 144 surrounding doughnut-shape segments) were grouped into ten sections based on their average power ratio. The power sections were designated by division of the maximum peak-to-average power ratio (2.4) into tenths (i.e., 0-0.24, 0.24-0.48, ... 2.16-2.4). The percent of the core in each power section is listed in Table V-16. This segmentation of the core has previously been discussed in detail (ANL-6925, p. 215).

Two limiting assumptions of core temperature distribution after blowdown were made, since it was not apparent from the LOFT analysis¹⁷ how much cooling of the core would be accomplished during blowdown. The two extreme cases considered were:

Case A: The reactor core is cooled during blowdown to a uniform temperature of 544°F (285°C), the coolant operating temperature.

Case B: The energy stored in the fuel during full power operation is fully retained by the fuel while the cladding energy is dissipated, i.e., only the cladding is cooled to the coolant temperature of 544°F (285°C).

The initial temperatures of each section resulting from the Case B assumption are presented in Table V-17. A detailed discussion of the determination of these initial section temperatures was presented in ANL-7055, p. 192.

The method of calculation of the extent of reaction and of chemical and decay energy for the individual core sections was previously developed in detail for the case of zirconium cladding (ANL-6925, p. 216). A similar analysis has been used in the calculations presented here for the case of stainless steel cladding.

The chemical reaction between stainless steel and steam is of a different nature than the zirconium-steam reaction, and thus the calculations required a slightly different approach. Since the reaction rate at temperatures below the melting point of stainless steel, 1370°C, has been shown to be relatively low (ANL-6900, p. 239), the assumption was made that negligible reaction occurred below the melting point in this analysis.

At temperatures above the melting point of stainless steel, the reaction with steam has been shown to be vigorous and rapid (see Section V.A.1. of this report), resulting in a frothed oxide (probably molten). A theoretically based rate law has not as yet been found to describe the reaction, mainly because of the difficulty of ascribing a surface area to the molten froth of cladding and oxide that forms during the reaction. Also, in the course of the loss-of-coolant accident being considered, it is apparent that the amount of available steam would limit the reaction, as has been shown to be the case in the similar analysis with the zirconium cladding. Thus, it was assumed that the stainless steel would react with all of the available steam when the metal reached a temperature of 1400°C (i.e., slightly above its melting point).

It was assumed in this analysis that, for complete reaction of the metal, spinel-type compounds M_3O_4 are formed and that 0.51 liter of hydrogen (STP)/g is evolved. (The stoichiometry and thermodynamics of the stainless steel reaction with water are discussed in Section V.A.1. of this report.) A value of 155 cal/g of steel was used for the heat of reaction, assuming that the molten cladding forms molten oxides.

Some of the other important assumptions made in

the calculations for both the stainless steel and zirconium cladding are the following:

1. The initial average decay heating rate is 0.0633 of the operating power level of 256 kw/liter UO_2 ; thereafter, the decay heating rate follows the time variation given in the LOFT analysis report (see ANL-6925, p. 216, Figure V-36).

2. The decay energy is distributed throughout the core after blowdown in the same manner as the reactor power during steady-state operation.

3. Heating and possible chemical reaction of support structures in the core are neglected. Only fuel and cladding are considered to be in the reactor core.

4. The temperature distribution across individual fuel rods (fuel and cladding) is flat.

5. There are no heat losses from the reactor core before it collapses.

6. A steam flow of 1000 lb/hr represents a convective flow of steam through the core.

7. A steam flow of 100 lb/hr represents a more limited flow, i.e., a limited amount of water available.

The last two assumptions listed above are the same

108-9584

FIG. V-30. Calculated Temperature-Time Curves for Each Power Section for No Stainless Steel-Steam Reaction in Loss-of-Coolant Accident. [Case A. Initial section temperatures 544°F (285°C).]

108-9585

FIG. V-31. Calculated Temperature-Time Curves for Each Power Section for no Stainless Steel-Steam Reaction in Loss-of-Coolant Accident. (Case B. Initial section temperatures are those at operating power.)

as those made in the previous analysis for the zirconium-clad core (ANL-6925, p. 215 and ANL-7055, p. 194). They represent a reasonable estimate of steam availabilities in this loss-of-coolant analysis.

b. CALCULATION OF TEMPERATURE-TIME HISTORY OF INDIVIDUAL CORE SECTIONS

A calculation of the temperature-time history for the ten sections of the core (see Figure V-30) was made assuming that initial section temperatures were all 285°C (Case A) and that no chemical reaction occurred. Melting of the stainless steel cladding is indicated in the figure, but the UO_2 melting is not included. The cladding begins to melt at 275 sec after blowdown, and the cladding in one-half of the core is melted at 820 sec after blowdown. The latter is indicated in Figure V-30 by the melting of the first six power sections, which represent 50% of the core.

A similar temperature-time history of the ten sections for the Case B assumption is shown in Figure V-31. In this case stainless steel cladding begins to

108-9586

FIG. V-32. Calculated Temperature-Time Curves for Each Power Section for Stainless Steel Cladding Reacting with Limited Quantities of Steam in Loss-of-Coolant Accident. [Case A. Initial section temperatures 544°F (285°C).]

TABLE V-18. COMPARISON OF TIMES REQUIRED TO MELT CLADDING FOR VARIOUS STEAM FLOW RATES

Steam Flow	Time at which Melting of Cladding Begins ^a (sec)		Time to Melt One-half of Cladding ^a (sec)	
	Case A	Case B	Case A	Case B
Zirconium Cladding				
Unlimited	240	20	560	230
1000 lb/hr	300	70	680	330
100 lb/hr	390	110	1050	630
No flow (no metal-water reaction)	430	115	1250	790
Stainless Steel Cladding				
All steam flow rates	275	20	820	430

^a Case A: initial section temperatures 544°F (285°C).

Case B: initial section temperatures are those at operating power (see Table V-17).

melt only 20 sec after the blowdown, since the sections are assumed to be hotter initially. One-half of the cladding in the core is melted after only 430 sec.

With the additional energy of the stainless steel-

steam reaction, the temperature of each section rises slightly faster after reaching 1400°C. This is shown in Figure V-32 where the temperature-time histories of five of the sections (Case A) are plotted for (a) no steam flow, (b) 1000 lb/hr steam flow, and (c) 100 lb/hr steam flow. The total reaction of the cladding would supply sufficient energy to raise the core and cladding 197°C. Therefore, a steam flow rate of 1000 lb/hr, equally distributed through the core, accounts for a 22°C temperature rise every 100 sec. The steam flow rate of 100 lb/hr accounts for a 2.2°C temperature rise in 100 sec. With these flow rates, complete reaction takes 894 and 8,940 sec, respectively. The case of unlimited steam flow was not calculated since it would simply be a rise of 197°C occurring instantaneously when each section reached 1400°C. This results from the assumption that the stainless steel-steam reaction rate is only limited by the steam availability.

In Table V-18, the times at which melting of the cladding begins and the times at which 50% of the cladding is melted are listed for both stainless steel and the previously determined zirconium cladding. Since it has been assumed that negligible reaction of stainless steel with steam occurs below its melting point, the times of melting of the stainless steel cladding are identical, regardless of the steam flow rate. This is not true for the zirconium cladding, since the extent of metal-water reaction, and hence the steam flow rate and initial section temperatures, has a marked effect on the meltdown history of the cladding, as shown in Table V-18.

In addition, the heats of reaction of the two cladding metals affect the subsequent temperature-time history of the sections with different magnitude. Complete zirconium-steam reaction results in a temperature rise of 3026°C for both core and cladding, while, as has been pointed out above, the complete stainless steel-steam reaction results in a temperature rise of only 197°C.

c. EXTENT OF CHEMICAL REACTION OF THE CLADDING

The extent of reaction of the total stainless steel cladding, plotted as a function of time after blowdown, is shown in Figure V-33 for the Case A situation. The results for the zirconium cladding previously reported are included in the figure. Curves for both the 1000 and 100 lb/hr steam flow are shown.

With steam flow of 1000 lb/hr, both the zirconium and stainless steel cladding reach appreciable extents of reaction by 2000 sec (73 and 61%, respectively). It should be noted, however, that the core is assumed to remain intact. The major difference in reaction behavior of the two metals is a delay of about 200

sec in the curve for the stainless steel-steam reaction. Similar results are observed for 100 lb/hr steam flow, with the stainless steel-steam reaction being delayed about 300 sec.

The extent of reaction of the total cladding for the Case B situation, also plotted as a function of the time after blowdown, is shown in Figure V-34. Again, curves for both 1000 and 100 lb/hr steam flow rate are shown; the curves resemble those for Case A (Figure V-33) with the exception that reaction occurs much sooner as a result of the higher initial temperatures. The delay in the stainless steel-steam reaction curve is shorter, being about 150 sec for 1000 lb/hr steam flow and about 100 sec for 100 lb/hr steam flow.

In Figure V-35 the extent of reaction of the stainless steel and zirconium cladding is plotted as a function of time for the situation with an unlimited supply of steam. The curves for both cases of initial reaction temperatures are shown. The curves for stainless steel cladding were calculated by assuming that an entire section would completely react when it reached 1400°C. The resulting step-like plot was smoothed by passing a line through the midpoints of the steps. A similar step-like plot was previously calculated for zirconium cladding (ANL-6925, p. 221 and ANL-7055, p. 196) since each section ignites in turn as its temperature reaches a certain level. This step-like plot was also smoothed in the same manner before inclusion in Figure V-35.

108-9400

FIG. V-33. Calculated Percent Reaction-Time Curves for Entire Reactor Core with Limited Quantities of Steam in Loss-of-Coolant Accident. [Case A. Initial section temperatures 544°F (285°C).]

108-9587

FIG. V-34. Calculated Percent Reaction-Time Curves for Entire Reactor Core with Limited Quantities of Steam in Loss-of-Coolant Accident. (Case B. Initial section temperatures are those at operating power.)

108-9588

FIG. V-35. Calculated Percent Reaction Curves for Entire Reactor Core with an Unlimited Quantity of Steam in Loss-of-Coolant Accident.

In each case, the stainless steel-steam reaction curve is slightly delayed beyond the corresponding zirconium-steam reaction curve.

It should be noted that 320 lb of water is necessary for complete reaction of the zirconium cladding, whereas 249 lb of water is necessary for complete

TABLE V-19. TIME REQUIRED FOR COLLAPSE OF CORE AND EXTENT OF STAINLESS STEEL-STEAM REACTION BASED ON THE AVERAGE NUCLEAR DECAY AND CHEMICAL ENERGY CONTENT

Steam Flow	Average Core Energy Sufficient To Melt Cladding Completely (1370°C)				Average Core Energy Sufficient To Begin To Melt Fuel (2800°C)			
	Collapse Time ^a (sec)		Metal Reacted ^a (%)		Collapse Time ^a (sec)		Metal Reacted ^a (%)	
	Case A	Case B	Case A	Case B	Case A	Case B	Case A	Case B
Unlimited	830	350	44	38	2560	1850	80	73
1000 lb/hr	910	400	18	10	2580	1860	65	68
100 lb/hr	918	407	2.0	1.0	2700	1970	20	14
No flow (no metal-water reaction)	920	410	—	—	2750	2010	—	—

^a Case A: initial section temperatures 544°F (285°C).

Case B: initial section temperatures are those at operating power (see Table V-17).

reaction of the stainless steel cladding. Thus, the same percent reaction represents less hydrogen evolution for the stainless steel cladding than for the zirconium cladding.

d. LOSS OF INTEGRITY OF THE REACTOR CORE

These calculations ignore the loss of core integrity as the temperatures become excessive. As a result, they predict eventual complete reaction of the core cladding. However, the extreme temperatures reached make it apparent that the core will be severely damaged and eventually collapse. Since a realistic model of core collapse does not presently exist, some indication of the time when collapse occurs can be obtained by the method used by the LOFT designers.¹⁷ The time when the core collapses onto lower support structures was assumed to be that time when the average of the energy accumulated in the core is sufficient to melt the cladding.

In Table V-19 the times when the average core energy is sufficient to melt the stainless steel cladding for the various cases are tabulated. Since it is not apparent that the melting of the cladding alone will cause core collapse in an oxidizing atmosphere, the times when the average core energy is sufficient to bring the fuel and cladding temperature to 2800°C (UO₂ melts) are also given in the table. In addition, the extent of the total stainless steel-steam reaction at each of these times is included in Table V-19. It should be emphasized that calculation of these times is based on an average energy accumulated throughout

the core, i.e., complete heat transfer, in contrast to the times given in Table V-18 in which no heat transfer between power sections is assumed.

Even though the core collapses, the chemical reaction between cladding and steam will continue until either the temperatures are lowered or the supply of steam is depleted. A complete discussion of the collapse and subsequent chemical reaction that could occur for the zirconium cladding was previously reported (ANL-6925, p. 222 and ANL-7055, p. 197). The arguments are the same for the stainless steel cladding. If the eventual collapse of the core occurs into an empty vessel, the reaction can continue with either steam or air, depending only on the availability of the oxidizing media. If, however, the core collapses into a large pool of water, a quenching reaction could occur which is terminated by cooling of the debris. The extent of reaction occurring in the quenching reaction can be estimated from the condenser discharge experiments (ANL-6648, p. 194).

e. DISCUSSION

The results of the calculations for a zirconium-clad core have been discussed in detail (ANL-6925, p. 225 and ANL-7055, p. 198). Most of the general comments are applicable to the calculations utilizing stainless steel cladding. The discussion will be limited here to a comparison of the stainless steel and zirconium results.

The major points in comparing the reactions of the two cladding materials with steam in the analysis of a loss-of-coolant accident are:

1. The zirconium reaction is much more energetic. Complete adiabatic reaction of the 25-mil zirconium cladding can raise the fuel and cladding temperature 3026°C, whereas reaction of the 15-mil stainless steel cladding can raise the temperature only 197°C.

2. The rates of reaction of both metals become fairly high as the temperatures increase. Vigorous stainless steel reaction is initiated at about 1400°C, while the zirconium reaction accelerates rapidly above 1200°C. The rates of both reactions become so high that it is apparent they will be steam limited. However, the energy liberated by the zirconium-steam reaction raises the temperature more rapidly.

3. The amounts of hydrogen evolved are slightly different. The 25-mil zirconium cladding produces 1.3 times as much hydrogen as the 15-mil stainless steel cladding produces, assuming complete reactions.

4. The collapse may be markedly different in each case. The zirconium reacts either as a solid (below 1852°C) or as a liquid with a solid ZrO₂ as the product (below 2700°C, the melting point of ZrO₂). The stainless steel reacts as a liquid (above 1370°C) to form a mixture of liquid oxides (M₂O₄) with a froth-

ing of the materials. It is difficult to provide a clear-cut collapse model. It is apparent, however, that at temperatures between the melting point of the cladding (Zr, 1852°C; SS, 1370°C) and that of the oxide core, collapse will occur. The amount of steam or air available to the cladding will change its physical properties and strongly affect the collapse mechanism. In the cases where the availability of steam is very limited (100 lb/hr or lower), collapse will more likely occur at temperatures near the melting point of the cladding. However, with an abundant supply of steam the zirconium is converted into ZrO_2 , which is a solid at higher temperatures than the metal. For stainless steel, the effects of the frothing that accompanies the

reaction with steam are difficult to predict in modeling the collapse. In general, however, the temperatures of collapse should be somewhat higher with an abundant supply of steam.

The time required for the core collapse and the subsequent melting of supporting structures can be of considerable length (of the order of an hour). Extensive reaction can occur during this time. It should also be noted that only the cladding was considered to react in these calculations. The control rods and support structures that can be brought to high temperatures during the meltdown can also absorb decay heat following initiation of the accident and can subsequently react with steam.

B. FAST REACTOR SAFETY STUDIES

1. Fuel-Coolant and Cladding-Coolant Interaction Studies (D. SWIFT, J. PAVLIK)

A survey study of the possible physical or chemical interactions between fast reactor materials and sodium coolant has been continued. These experiments consisted of inductively heating small samples (~0.3 cc) of the materials to temperatures in the range of 1500 to 2400°C and dropping the samples into liquid sodium. The experiments were carried out in an argon glovebox; details of the apparatus are described in a previous report (see ANL-6925, p. 226).

The results of a number of experiments with molten zirconium, vanadium, nickel, mild steel, and type 304 stainless steel, and with solid niobium, niobium-1 w/o zirconium, molybdenum, and tantalum have been reported (ANL-7055, p. 199). In none of these experiments was there any evidence of chemical interaction. The materials which were solid when dropped were simply quenched by the sodium, whereas the molten samples all suffered some degree of fragmentation depending upon the initial sample temperature and the particular material used. Type 304 stainless steel proved to be the most vigorously interacting material as judged by observed violence and the degree of fragmentation suffered.

During the present report period, a number of experiments have been carried out to investigate further the fragmentation phenomenon in sodium and to compare it with quenching of molten metals in water and several other liquids.

a. EXPERIMENTS WITH CLADDING MATERIALS IN SODIUM

In the preliminary experiments with stainless steel, the molten spheres were dropped into sodium at

250°C which was contained in a 2-in. dia. cylindrical vessel. One of the spheres dropped at 2100°C was recovered in one piece as a ragged plate-like residue; however, Fastax films of subsequent experiments in which a 2-liter beaker (~5-in. dia.) was used indicated that particle fragmentation occurred at drop temperatures well below 2100°C. A series of experiments was, therefore, conducted in which stainless steel samples were dropped at temperatures ranging from 1425 to 2000°C into sodium at 250°C contained in the 2-liter beaker. The residues from these experiments are shown in Figure V-36. It is evident that partial fragmentation occurs at drop temperatures as low as 1550°C and that the extent of fragmentation increases with temperature.

Another series of experiments with stainless steel samples was performed to determine the effect of the sodium temperature on the extent of fragmentation and the appearance of the residue. In these experiments the stainless steel samples were heated to 2200°C and dropped into sodium at 250, 450, 600, 700, and 820°C, respectively. The residues from the first three experiments were similar in appearance (small shiny particles), and the extent of fragmentation was similar. The residue from the 700°C sodium experiment consisted primarily of shiny particles, but contained some gray powder of considerably lower density. The entire residue from the drop into 820°C sodium was gray powder; microscopic examination of this powder indicated that it consisted of very small metallic particles adhering together in lumps. Chemical analysis of the residue gave no evidence of interaction with sodium, and X-ray diffraction analysis

108-9138B

FIG. V-36. Residues of Type 304 Stainless Steel Dropped into 250°C Sodium.

showed only gamma (fcc) iron. It is apparent that the only effect of higher sodium temperatures is a more thorough dispersion of the stainless steel.

The interactions of several solid refractory cladding materials with 250°C sodium have been reported (ANL-7055, p. 200). Experiments with molten titanium, vanadium, and vanadium-20 w/o titanium have now been performed at drop temperatures of 2050, 2200, and 2100°C, respectively. The residues from these experiments are shown in Figure V-37. All of the samples suffered fragmentation, but to a much lesser degree than the stainless steel. The metallic appearance of the residues indicated that no chemical interaction had occurred.

b. EXPERIMENTS IN OTHER LIQUID METAL QUENCHING MEDIA

Experiments in which stainless steel samples at various temperatures were dropped into liquid potas-

sium and liquid lithium indicate that fragmentation occurs with other liquid metals besides sodium. The residues from these experiments are shown in Figure V-38 and V-39. The fragmentation in lithium was less extensive than in sodium, whereas fragmentation in potassium was slightly more extensive. Thus for these alkali metals the extent of fragmentation increases with decreasing boiling point.

c. EXPERIMENTS WITH FUEL MATERIALS

Experiments have been performed in which samples of uranium metal were heated to temperatures of 1700, 2000, and 2450°C and dropped into 250°C sodium. The residues from these experiments are shown in Figure V-40. As originally recovered, the residues were metallic, indicating no chemical interaction; however a brief exposure to air resulted in an oxid blackening. The samples suffered fragmentation, but the major portion of the uranium formed distended

V, 2200°C Drop

Ti, 2050°C Drop

V-20 w/o Ti, 2100°C Drop

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FIG. V-37. Residues of Several Molten Metals dropped into 250°C Sodium.

sheets or filaments in an irregular network. The residues from the 2000 and 2450°C drops were very similar in appearance, being somewhat more finely divided than the residue from the 1700°C drop.

Experiments with UO_2 dropped into 250°C sodium have been carried out at drop temperatures of 900 and 2100°C. As previously reported (ANL-7055, p. 200), nonmetallic materials cannot be heated with a levitation coil. Therefore, the UO_2 samples were heated by radiative transfer from a tantalum susceptor. The residues from these experiments are shown in Figure V-41. The rapid quench of the sample dropped at 2100°C caused it to crack in numerous places. It was apparent that sodium was taken up into the cracks; although a brief alcohol rinse of the pellet following the quench gave a clean surface, within a few days the surface was covered with sodium oxide coating. No evidence of chemical interaction was observed after either the 900 or 2100°C drop.

d. EXPERIMENTS TO COMPARE MOLTEN METAL QUENCHING IN WATER AND SODIUM

The experiments performed in this study have shown that molten metals suffer some degree of fragmentation when quenched in sodium. Experiments of a similar type, in which molten aluminum, zirconium, nickel, and uranium were dropped into water, showed no such effect, although the aluminum and uranium did undergo chemical reaction with the water under suitable conditions (see, for example, ANL-6800, p. 38). One might hypothesize that the oxide layer formed in water gives the molten drop a rigid shell and thus prevents fragmentation.

1800°C Drop

2000°C Drop

2150°C Drop

2250°C Drop

108-9137A

FIG. V-38. Residues of Type 304 Stainless Steel dropped into 250°C Potassium.

This hypothesis was tested by dropping molten silver (at 1900°C) and gold (at 2600°C), neither of which forms an oxide coating in air or water, into 25°C water. The residues are shown in Figure V-42,

108-9136A

FIG. V-39. Residues of Type 304 Stainless Steel dropped into 275°C Lithium.

108-9009A

FIG. V-40. Residues of Molten Uranium dropped into 250°C Sodium.

108-9011A

FIG. V-41. UO_2 Pellets dropped into 250°C Sodium.

108-9012B

FIG. V-42. Quenched Residues of Gold and Silver.

and it is clear that no fragmentation occurred. However, when molten silver at 1900°C was dropped into 250°C sodium, extensive fragmentation occurred, as seen in the same figure. The results of these experiments suggest that the failure of molten metals to fragment in water is not a result of the formation of oxide films. Instead, the differences observed when very hot molten metals are quenched in sodium and in water must be due to differences in the physical properties of liquid sodium and water.

C. HYPOTHESIS FOR FRAGMENTATION OF QUENCHED MOLTEN METALS

A likely explanation for molten metal fragmentation was developed in which the physical properties of

the molten metal are neglected and primary attention is given to the quenching fluid's boiling characteristics. This hypothesis simply predicts whether or not metal fragmentation will occur, while the extent of fragmentation is assumed to depend on the properties of the molten metal.

The boiling of a liquid is generally classified in three regimes, namely, nucleate, transition, and film boiling, which occur in turn as the difference between the surface temperature and the boiling point is increased. Film boiling is hydrodynamically "quiet," whereas nucleate and transition boiling are attended by considerable turbulence caused by the growth and collapse of bubbles. This is especially true when the bulk liquid is below the saturation temperature, a

Bismuth (M.P. 271°C)

Tin (M.P. 232°C)

Lead (M.P. 327°C)

Zinc (M.P. 420°C)

Aluminum (M.P. 659°C)

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FIG. V-43. Residues of Low-Melting Metals dropped into 0°C Water. (All samples dropped at 825°C.)

condition known as subcooled boiling. It has been assumed by Westwater¹⁹ that nucleate boiling cannot take place on a surface whose temperature is higher than the critical temperature of the liquid. Then, it follows that transition boiling changes to film boiling at some temperature above the critical temperature. The quenching of very hot metals proceeds in the following order: first film boiling, then at a lower temperature the boiling enters the transition regime, then the nucleate regime, and, finally, quenching is completed by convective heat transfer without boiling.

If the melting point of a metal is within the region of violent boiling (transition or nucleate), it is hypothesized that the metal will suffer fragmentation. If, on the other hand, the metal has solidified while in the film boiling regime, then, according to the hypothesis fragmentation should not occur. This criterion does seem to be consistent with the observed behavior of aluminum (m.p. 660°C), uranium (m.p. 1132°C), nickel (m.p. 1425°C), and zirconium (m.p. 1860°C) which fragment in sodium but not in water. For water,

if we assume that the transition to violent boiling occurs near the critical temperature (373°C), then all these metals will already have solidified before reaching the violent boiling temperature region. Sodium, on the other hand, has a boiling point of 882°C and a critical temperature of 2300°C, so that all of these metals are still molten in the region of violent boiling.

f. ADDITIONAL QUENCHING EXPERIMENTS TO TEST THE HYPOTHESIS

If this hypothesis for metal fragmentation is valid for water, then metals which have melting points below the transition temperature of water should fragment in water when dropped in the molten state. Experiments were performed in which tin (m.p. 232°C), bismuth (m.p. 271°C), lead (m.p. 327°C), zinc (m.p. 420°C), and aluminum (m.p. 660°C) were heated to 825°C and dropped into water at 0°C. The residues from these experiments are shown in Figure V-43. The first three metals suffered considerable fragmentation while the last two, which have melting points above 373°C, did not fragment.

It thus appears that the transition temperature for

¹⁹ J. W. Westwater, *Advances in Chemical Engineering*, Vol. 1 Academic Press, New York, 1957, p. 43.

water is rather close to the critical temperature. Experiments with Wood's Metal (m.p. 70°C) and Rose's Metal (m.p. 96°C) also fit the criterion properly, since these samples fragmented in similar experiments. Further experiments with water indicated that subcooled boiling was necessary for fragmentation; if the water temperature was raised to 60°C, tin, bismuth, and lead did not fragment.

These same materials heated to 600°C and quenched in liquid nitrogen did not suffer fragmentation; this is likewise consistent with the fragmentation criterion, since nitrogen has a critical temperature of -147°C, well below the melting points of the metals.

According to the fragmentation criterion presented above, a molten metal should not fragment in a liquid

if its melting point is above the boiling transition temperature (which for water appears to be near the critical temperature). In order to test this with liquid metals, a sample of platinum at 1900°C (m.p. 1710°C) was dropped into liquid mercury (b.p. 357°C, critical point 1450°C). This sample suffered fragmentation, contrary to expectation. It appears, therefore, that for liquid metals the transition temperature may be well above the critical temperature; unfortunately, the present understanding of liquid metal boiling is far less complete than for water.

A detailed understanding of the nucleate, transition, and film boiling regimes with liquid metals is required in order to advance further the current, tentative hypothesis of the mechanism of fragmentation.

2. Transient Heat Transfer Studies: Measurement of Heat Flux from a Heated Metal Sphere Moving through Water and Liquid Sodium (R. O. IVINS,

L. BAKER, JR., N. W. GREEN,²⁰ R. A. JANDRISEVITS,²⁰ R. M. RICE,²⁰ J. JAMES²¹)

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

a. EXPERIMENTAL MEASUREMENTS

The experimental apparatus, which is described in detail in ANL-7055, p. 206, consists of a swinging arm (or pendulum) with a knife blade attached to the arm. A small metal sphere is attached to a thermocouple at the end of the blade. (The attachment is made by welding the wires of the Pt/Pt-10% Rh thermocouple to opposite sides of the sphere.) The metal sphere is heated in an electrical furnace to the desired temperature with the arm in a raised position. The raised arm is then released and, as it swings, the sphere is dragged through a tank of water or liquid sodium appropriately placed below the pivot of the arm. The time required for the ball to pass through the water or sodium is measured with an electronic counter-timer that is initiated and stopped by the impulses from two photocells. The photocells are triggered by the passage of the arm when the sphere enters and leaves the liquid.

Several series of experiments have been performed with a ¼-in. dia. nickel sphere in water. The sphere was initially heated to temperatures ranging from 150 to 1000°C. Experiments were performed with water temperatures of 30°C, 60°C, and 94°C at atmospheric pressure. The distance of travel through the water was varied by changing the water depth in the tank; path lengths of from 12 to 25.5 in. were employed. The average velocity of the ball varied between 12 and 13 ft/sec owing to slight differences in the initial position of the arm. Gravity was the only driving force used to impart motion to the pendulum arm.

The millivolt-time record from the thermocouple output was displayed on a Brown pen recorder and was used to determine the temperature of the sphere, both as it entered and as it left the water; the technique used was previously described (ANL-7055, p. 207). Plots of the amount of decrease in the sphere temperature as it passed through the water *vs* the initial sphere temperature are given in Figures V-44, V-45, and V-46 for the data collected in 30°C, 60°C, and 94°C water, respectively.

In Figure V-44, four sets of data obtained in 30°C water are plotted. Two of the sets of data were obtained with the same water level in the tank and, thus, with constant path length (25.5 in.) and immersion time. The other two sets of data were obtained for path lengths of 19.5 and 12 in. For each path length, the temperature drop increased smoothly with increasing initial sphere temperature. Indication of possible peaks around 1000°C were noted; however, since the maximum initial temperature achieved was only 1030°C the peaks were not clearly delineated. Experiments

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²¹ Co-op student from Savannah State College.

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FIG. V-44. Temperature Drop through 30°C Water as a Function of Initial Sphere Temperature for Swinging-Arm Experiments. (1/4-in. dia. nickel sphere.)

108-9590

FIG. V-45. Temperature Drop through 60°C Water as a Function of Initial Sphere Temperature for Swinging-Arm Experiments. (1/4-in. dia. nickel sphere.)

108-9591

FIG. V-46. Temperature Drop through 94°C Water as a Function of Initial Sphere Temperature for Swinging-Arm Experiments. (3/4-in. dia. nickel sphere.)

utilizing the longer path lengths resulted in greater temperature drops; a maximum temperature drop of 410°C was observed for a sphere initially at 1000°C with a 25.5-in. path length through the water.

In Figure V-45, five sets of data are plotted that were obtained in 60°C water with path lengths of 12.0, 19.5, and 25.5 in. For all three path lengths, a peak in the temperature drop occurred with initial sphere temperatures in the range of 600 to 700°C. The maximum temperature drop recorded was about 260°C.

Three sets of data taken in 94°C water are shown in Figure V-46. Two path lengths were used. In these experiments the high temperature of the water (6°C subcooling) resulted in very small temperature drops (of the order of 20°C). The greatest temperature decrease (85°C) occurred with initial sphere temperatures in the range of 100 to 200°C for both the 19.5 and 25.5 in. path lengths. These temperature drops are very small compared with those obtained in the cooler water (Figures V-44 and V-45) and the scatter of the data is more apparent.

b. CALCULATIONAL STUDIES

In order to evaluate the data taken with the swinging arm apparatus, a computer program was written to solve the differential equations describing the energy flow in a sphere with a constant coefficient of heat transfer at the surface. The program calculates the temperature distribution and average surface heat transfer coefficient from the temperature drop, time of submersion, and physical properties of the sphere.

The program is based on the analytical solution of Carslaw and Jaeger²² to the differential equation of heat conduction in a sphere derived from Fourier's law,

$$-k \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + r^2 \rho C_p \frac{\partial T}{\partial t} = 0 \quad (13)$$

and utilizes the following nomenclature:

- ρ Density
- C_p Heat capacity per unit mass
- k Thermal conductivity
- h Heat transfer coefficient
- K Thermal diffusivity ($= k/\rho C_p$)
- r Radius of shell
- a Radius of sphere
- η Nusselt number/2 ($= ha/k$)
- α_n Coefficients of the Carslaw and Jaeger solution (i.e., Eigenvalues)
- t Time
- T Temperature at time, t
- T_1 Initial sphere temperature
- T_w Water temperature
- n Subscript integer

Equation 13 assumes that the physical properties are constant with respect to temperature. The analytical solution, assuming a constant heat transfer coefficient and the boundary conditions

$$T = T_1 \quad \text{when } t = 0, \quad (14)$$

²² H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press, 1959, p. 237.

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FIG. V-47. Computed Heat Transfer Coefficients from Swinging-Arm Experiments with $\frac{1}{4}$ -in. Dia. Nickel Spheres. (Velocity of sphere through water: 12 ft/sec.)

$$\frac{\partial T}{\partial r} = 0 \quad \text{when } r = 0, \quad (15)$$

and

$$-k \frac{\partial T}{\partial r} = h (T - T_w) \quad \text{when } r = a, \quad (16)$$

has been shown to be

$$\theta = \frac{2\eta}{ar} \sum_{n=1}^{\infty} A_n \sin(\alpha_n r) \exp(-K \alpha_n^2 t) \quad (17)$$

where

$$A_n = \frac{\alpha_n^2 a^2 + (\eta - 1)^2}{\alpha_n^2 [\alpha_n^2 a^2 + \eta(\eta - 1)]} \cdot \sin(\alpha_n a) \quad (18)$$

and where

$$\theta = \frac{T - T_w}{T_1 - T_w}. \quad (19)$$

Values of α_n , where $n = 1, 2, 3 \dots$ can be obtained as the roots of the equation

$$a \alpha_n \cot(a \alpha_n) + \eta - 1 = 0 \quad (20)$$

These equations were programed for the CDC 3600 computer. Temperature-drop values at various initial sphere temperatures (Figures V-44, V-45, and V-46), the corresponding immersion times, the weight and diameter of the sphere, and estimates of the physical

properties in the temperature range of interest were inserted into the computer. The corresponding heat transfer coefficients calculated by the computer are plotted in Figure V-47 as a function of the average surface temperature²³ of the sphere for each of the three water temperatures.

Similarly, the average heat fluxes that were computed for each set of variables are plotted in Figure V-48, also as a function of the average surface temperature. A peak (maximum) flux occurs at 500°C for the 60°C water data and at about 800°C for the 30°C water data. For the 94°C water (6°C subcooling), the heat flux appears to be rising as the average surface temperature is lowered. The classic work of Nukiyama²⁴ suggests a maximum heat flux, i.e., the peak flux associated with the nucleate boiling and transition boiling regimes, at about 150°C for water at its boiling point. The peaks apparent in the 30°C and 60°C water (70°C and 40°C subcooling) data occur at sphere surface temperatures indicative of film boiling. These peaks may be associated with characteristics of two phase flow around the sphere. The Reynolds num-

²³ The average of the measured temperature of the sphere as it enters the water and the computed surface temperature of the sphere as it leaves the water.

²⁴ S. Nukiyama, Maximum and Minimum Values of Heat Transmitted from Metal to Boiling Water under Atmospheric Pressure, *J. Soc. Mech. Eng. Japan* **37**(206), 367 (1934).

108-9423

FIG. V-48. Computed Heat Fluxes from Swinging Arm Experiments with $\frac{1}{4}$ -in. Dia. Nickel Spheres. (Velocity of sphere through water: 12 ft/sec.)

ber for a $\frac{1}{4}$ -in. dia. sphere with a velocity of 12 ft/sec in water at 100°C is 80,000. However, the fluid flow situation has not been characterized for the case of a boiling liquid.

In order to study further the heat transfer and flow characteristics of the system, the following studies will be performed:

1. Data will be obtained for several velocities and sphere diameters.
2. Motion picture studies will be performed.
3. Shorter path lengths will be used in order to lower the temperature drops.
4. Materials of higher thermal conductivity will be employed in order to decrease the temperature gradient in the sphere.

The latter two modifications will yield average heat transfer coefficients that apply over narrower ranges of sphere surface temperature and should improve the correlations of the data. With data obtained for various sphere sizes and velocities a correlation of the data will be attempted similar to that of Motte and Bromley.²⁵ They have developed a correlation for film boiling of subcooled liquids flow-

ing across tubes. A similar correlation may be applicable to the case of a sphere.

The magnitude of the heat fluxes computed approached $4.6 \times 10^6 \text{ Btu}/(\text{ft}^2)(\text{hr})$ [equivalent to $350 \text{ cal}/(\text{cm}^2)(\text{sec})$] in 30°C water (70°C subcooling) at average surface temperatures of 800°C . This is considerably greater than those reported²⁴ for non-subcooled nucleate boiling at atmospheric pressure [$\sim 0.5 \times 10^6 \text{ Btu}/(\text{ft}^2)(\text{hr})$], but is comparable with those fluxes obtained²⁵ in forced convection subcooled boiling with cylinders.

c. STUDIES IN LIQUID SODIUM

Studies of the transient heat transfer from hot spheres to liquid sodium are in the stage of apparatus construction. The swinging arm method in modified form will be used. An arm of 8 in. radius has been constructed. Motion through the sodium is achieved using a printed-circuit d-c motor of the type used to drive computer tape units. Remote operation of the motor has been achieved which allows the experimenter to move the sample sphere from a furnace through the sodium at a preset velocity, backward to a holding position at low velocity, and again into the furnace position. The experiments will be performed

²⁵ E. I. Motte and L. A. Bromley, Film Boiling of Flowing Subcooled Liquids, Ind. Eng. Chem. **49**, 1921 (1957).

in an argon-filled glovebox. A 1/2-in. dia. tantalum sphere has been successfully machined and will be equipped with a W-5% Re/W-26% Re thermocouple which is insulated with vitrified BeO. The thermocouple, encased in a tantalum tube, will be welded to the sphere

near the stagnation point (leading point) and the thermocouple protection tube will emerge from the trailing surface of the sphere. It is expected that other sphere sizes will also be employed in these studies.

3. High-Temperature Physical Properties: Heat Capacity of Liquid UO_2 (L. LEIBOWITZ, L. W. MISHLER)

The heat capacity of UO_2 above its melting point, an important quantity in fast reactor safety calculations, has never been measured. A program has been initiated to carry out these measurements. The general approach will be to encapsulate UO_2 in tungsten and find its heat content either by conventional drop calorimetry or by cooling curve measurements.

Two alternative heating methods have been examined, namely, electron beam and induction heating. It was found that a 1/2-in. dia. by 1-in. long tungsten cylinder could be heated to its melting point using a 15-kw induction generator and a simple 4- or 5-turn induction coil. Exploratory work with an electron beam furnace was, therefore, discontinued, because of

the greater simplicity and lower cost of induction heating equipment.

The next step was to decide whether or not tungsten would be a suitable material for holding the UO_2 . Temperatures as close to the melting point of tungsten as possible and times of about 15 min would be desirable. In this regard the work of Hausner²⁶ was encouraging; he reported successful encapsulation of UO_2 in tungsten up to about 2950°C. Similar tests of compatibility were initiated here. Two pressed and sintered tungsten crucibles (1/2-in. OD and 1 in. long with 1/16-in. thick walls) were half filled with $\text{UO}_{2.0}$

²⁶ H. Hausner, *J. Nucl. Mater.* 15, 179 (1965).

a. Maximum temperature: 2950°C

b. Maximum temperature: 3150°C

pellets of about 95% theoretical density, and electron-beam welded shut. Using an induction generator in an argon atmosphere, one capsule was heated to 2950°C and the other to 3150°C. Heating of the first crucible was ended after about 1 min at 2950°C, when arcing occurred between the capsule and the coil. In the second test, heating was terminated when a liquid was seen on the bottom of the crucible, also after about 1 min at temperature. Both crucibles were sectioned following the tests; these sections are shown in Figure V-49. No gross attack of the tungsten is evident; however, under careful microscopic examination a crack could be seen in the lower corner of the higher temperature capsule. (The crack may have been produced by thermal stresses introduced during initial heating; arcing difficulties caused rapid cooling of the crucible several times.) X-ray diffraction study of the heated uranium dioxide showed no change from the

original $\text{UO}_{2.0}$. Electron microprobe examination is currently being carried out to determine the extent of interpenetration of uranium and tungsten.

Uranium dioxide-filled tungsten capsules are currently being prepared using a wide variety of sources of tungsten. In addition to behavior at high temperatures, ease of fabrication, weldability, and mechanical properties are important considerations in selecting the capsule material. These properties may vary depending on the method of producing the tungsten capsules. As the capsules become available, tests similar to those described above will be performed and a choice made of the most satisfactory container material. Various aspects of high temperature calorimetry are being examined at the same time, and a selection will be made of the most suitable calorimeter, pyrometers, and drop mechanism.

4. Other Fast Reactor Safety Studies (L. BAKER, JR., M. CHASANOV, D. F. FISCHER)

Two additional research programs are being pursued in the area of fast reactor safety. One of these is the determination of the extent of fuel migration and segregation in mixed uranium-plutonium fuels. A significant degree of segregation in an operating reactor might seriously decrease the effectiveness of Doppler broadening as a shutdown mechanism since the time required for fission heat generated in plutonium-rich regions to be transferred to uranium-rich regions would be greater than for heat transfer in unsegregated fuel. This additional heat transfer time would delay increased neutron absorption (and decreased reactivity) in a reactor. In the investigation, the behavior of mixed fuels such as uranium and plutonium oxides, carbides, and nitrides under a thermal gradient will be investigated. Segregation within fuel samples will be determined by chemical and metallographic analyses.

The migration studies are in the apparatus development stage. Several modifications of a gradient furnace have been tested with plutonium-free samples. It is expected that a heating element consisting of a single tungsten foil, resistively heated, will be adequate for

heating one end of a sample pellet to a temperature well above 2000°C, while the other end remains at a much lower temperature. Orders have been placed for a vacuum system suitable for use with the gradient furnace within a plutonium glovebox. A thin sectioning machine for precise slicing of samples has been received and tested. Existing analytical and metallographic facilities will be used.

The other program in the area of fast reactor safety is still in the planning stage. It is an experimental study of the pressures produced when liquid sodium reacts with air in simulated spraying accidents. Of primary interest in this study is the nature of the oxide aerosol produced under various conditions. A pneumatically operated piston device is being designed for the purpose of spraying about 15 g of molten sodium into air-filled enclosures of various sizes and shapes. The total pressure rise and the extent and rate of reaction will be measured using rapid response pressure transducers. The measured pressures will be compared with theoretical maximum pressures computed from thermodynamic data (see ANL-7055, p. 208).

VI

Energy Conversion¹

(C. E. Crouthamel, J. C. Hesson, A. D. Tevebaugh, J. D. Bingle)

This report is a summary of all the work done to date on regenerative electrochemical systems in this laboratory. Concurrently, an American Chemical Society Monograph² on the subject has been prepared, for 1966 publication, which will give a comprehensive review of all the known work on regenerative cells.

There has been, and there still is, considerable confusion surrounding the precise definition of a regenerative electrochemical system. In the strictest sense it is a system into which energy is fed (usually heat) and from which electrochemical energy departs; it is an energy conversion system closed with respect to mass. In the systems studied in this laboratory, an emf cell would function in the low temperature isothermal leg of a Carnot cycle to form a cell product and produce electrical energy. In the high temperature isothermal leg, the cell product would be decomposed into the cell reactants, which would be separated and returned to their respective electrode compartments of the cell. The two isothermal legs would be connected by an adiabatic countercurrent heat exchanger. In actual practice, imperfections in these cyclic operations would not allow the maximum Carnot efficiency to be achieved. The Carnot cycle efficiency limitation represents the price paid for converting random kinetic energy (thermal energy) into directed energy (electrical) and regardless of the method of regeneration, e.g., thermal or electrical, the Carnot cycle efficiency is the maximum theoretical efficiency of the cycle.

Energy conversion systems which have received the most research and development attention in the past ten years are metal vapor turbines, thermionic diodes, magnetohydrodynamic generators, and thermoelectric devices. In comparison to any one of these four systems, regenerative electrochemical systems have received less support by several orders of magnitude. Nevertheless, conservative estimates of the practical cyclic efficiencies for several bimetallic systems and the lithium hydride system have been made (see ANL-6925, p. 243 and Ref. 2), and these efficiencies compare

favorably with values estimated for the other systems. One outstanding difference exists, however, between the regenerative electrochemical converter and all the other systems, namely, the ability of the former to operate at high power densities in the temperature region below 1500°C. This is potentially an important advantage, because a larger number of heat sources are available in this temperature region and also because the problems with materials of construction are markedly reduced.

The regenerative electrochemical converter can be virtually free of mechanical parts and, in comparison to the other systems, the flowing liquids or gases are very low velocity streams. Nevertheless, liquid metal-fused salt static and dynamic corrosion data are needed; information in the literature is both poor and limited. A survey² made in 1965 on corrosion of container materials by the liquid metals, bismuth, lead, and tin, and by fused alkali and alkaline earth fluorides, chlorides, and hydroxides indicates two major problems with this type of data. The first problem is that a great deal of the work was done with impure metals, wet salts, or under poorly controlled experimental conditions so that the results do not represent the actual situation for clean systems and pure liquid salts or liquid metals. The second problem is that the scope of the data is too limited in many of the systems. This is especially true for the temperature variable; very few results above a temperature of about 800°C are known. Also, relatively few dynamic corrosion data obtained under temperature gradients such as would exist in a cyclic electrochemical converter have been published. Probably, the most severe and limiting materials problem in these systems will be due to mass transport of material between the two temperature regions.

However, for the systems under study at Argonne, promising materials have been found which are not subject to corrosion in a dynamic system. The recent development of refractory metal vapor deposition techniques opens the door to relatively cheap fabrication of complex components, e.g., heat exchangers and boilers, which can be lined with metals such as tantalum, niobium, and tungsten.

¹ A summary of this section is given on pages 15 to 18.

² C. Crouthamel and H. Recht, editors, *Regenerative Electrochemical Systems*, American Chemical Society, in press.

A. REGENERATIVE EMF CELLS—PHYSICAL-CHEMICAL LABORATORY STUDIES (C. E. CROUTHAMEL)

The application of regenerative electrochemical systems utilizing liquid metals and fused salts is still handicapped by a lack of basic thermodynamic, chemical, physical, kinetic, and solid state data. However, the information in all these fields is increasing rapidly. A basic program at Argonne has been involved in studies of galvanic cells of two types—the bimetallic concentration cell and the lithium hydride cell.

The hydride cell consists of an anode of liquid lithium metal, an electrolyte of molten lithium halides, and a hydrogen gas cathode. The cell oxidizes lithium metal to lithium ions at the anode and reduces hydrogen gas to hydride ions at the cathode to form the cell product, lithium hydride.

The bimetallic concentration cells have two liquid metal electrodes in contact with a molten salt electrolyte. The cell reaction is the oxidation of the anode metal to produce metal ions in the electrolyte, while at the cathode the metal ions in the electrolyte are reduced to form a cathode alloy. High cell voltages are

obtained by selecting anode and cathode metals which have a strong interaction.

A study of the solubility of intermetallic compounds in fused salts is continuing. The solubility of LiHg (the most stable of the alkali-mercury compounds) was found to be negligible at 518°C in a eutectic mixture of LiCl-LiF. This is in contrast with the relatively high solubilities previously observed for Li_2Te , Li_3Bi , Li_7Sn_2 , and $\text{Li}_{10}\text{Pb}_3$.

In the regenerator portion of the cycle, temperature-pressure-composition relationships in the vapor-liquid equilibria over liquid metals and, in some instances, over fused salts are needed. The literature contains relatively little data for bimetallic systems. A program has been under way to obtain these data on systems of interest by two types of measurements. The first is a total pressure measurement made either by the quasi-static (Rodebush-Dixon) technique or by a boiling point method. In the second type of measurement, the atom composition of the vapor is obtained by transpiration techniques.

1. Lithium Hydride Cell Studies (C. E. JOHNSON, R. R. HENRICH, E. HATHAWAY)

The lithium hydride cell was selected as one of the systems for laboratory investigation after an evaluation of the available data in the literature.³⁻⁵ This system appeared unusually promising if difficulties associated with the cathode, which uses porous metal frits as the hydrogen gas electrode, could be eliminated. The primary difficulties in using a porous metal electrode were the occurrence of a variable catalytic activity at the surface of the frits and the flooding of the frits either by hydrogen gas or fused salt electrolyte. Despite these difficulties, Mine Safety Appliance Corporation⁴ developed a hydride cell, which produced an emf of 0.3 volt with a current density of 200 amp/sq ft (~ 215 ma/cm²) when operating at 570°C.

The cell consisted of a liquid lithium anode, a lithium fluoride-lithium chloride fused salt eutectic mixture

as an electrolyte, and a stainless steel cathode. The cathode was in the form of a screen or a porous micro-metallic gas electrode. The duration of cell operation and other conditions under which the stated voltage and current density were achieved were not published in the literature.

More recent studies on lithium hydride cells have been carried out by Thompson Ramo Wooldridge.⁶⁻⁸ The results of this work, done concurrently with the work here at Argonne, indicated that iron and niobium are the only materials that could be found which possessed the requisite characteristics for use as hydrogen diffusion diaphragms, i.e., the rate of diffusion of hydrogen through both materials was appreciable at 400 to 500°C, and both materials were compatible with the cell environment. Most of the cell experiments at Thompson Ramo Wooldridge were actually carried out with iron diaphragms; however, the results of a

³ T. A. Ciarlariello and R. C. Werner, *Chem. Eng. Progr.* **57**, 42 (1961).

⁴ R. E. Shearer, Study of Energy Conversion Devices, Progress Reports to U.S. Army Signal Research and Development Laboratory, Fort Monmouth, N. J., Report 1, MSAR-59-119, 1959; Report 2, MSAR-60-12, 1960; Report 3, MSAR-60-56, 1960; Report 4, MSAR-60-110, 1960; Report 7, MSAR-61-99, 1961.

⁵ R. C. Werner and R. E. Shearer, U.S. Patent 3,031,518, April 24, 1962.

⁶ S. S. Carlton, Electrode Development Program, ASD-TDR-62-241, TAPCO, Division of Thompson Ramo Wooldridge, Inc., Cleveland, Ohio, 1962.

⁷ J. M. Fuscoe, S. S. Carlton, and D. P. Laverty, Regenerative Fuel Cell System Investigation, WADD-TR-60-442, Thompson Ramo Wooldridge, Inc., Cleveland, Ohio, 1960.

⁸ H. J. Schwartz, S. S. Carlton, and J. M. Fuscoe, Regenerative Fuel Cell System, ASD-TDR-62-18, Thompson Ramo Wooldridge, Inc., Cleveland, Ohio, 1962.

single, 45-min run in which a niobium diaphragm was utilized have been reported.⁶ This run indicated that, at 549°C and 1 atm pressure, current densities of over 1000 amp/sq ft (~ 1076 ma/cm²) of electrode area could be achieved by a lithium hydride cell using a niobium diaphragm. Much effort had to be expended, however, to keep the niobium diaphragm free of surface contamination by oxygen at the operating temperature of the cell.

The primary emphasis of our research has been to provide the fundamental data necessary to solve those problems which would be encountered in attaining a successful regenerative lithium hydride electrochemical system. Areas of investigation have included the following: (1) examination of the rates of permeation of hydrogen through various metal diaphragms and testing of the diaphragms in cells for possible application as the cathode in place of the more conventional porous metal electrode; (2) studies of the electrolyte solvent properties which would produce optimum cell operating conditions; (3) establishment of values for thermodynamic functions such as the free energy, enthalpy, and entropy of the cell product, lithium hydride; and (4) investigation of those conditions under which successful regeneration could be accomplished.

a. ELECTRODES

Certainly a most significant phase in the development of a workable lithium hydride cell has concerned

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FIG. VI-1. Hydrogen Permeation Isobars of Vanadium and Armco Iron.

the gas electrode, or cathode. The immediate region of contact between the reactant, electrolyte, and electrode is important because it is here that electron transfer takes place. The hydrogen gas must transfer electrons from the electrode at the same time as it enters into the electrolyte as an ion. In conventional operation, the gas electrode requires a three-phase site which must be as large as possible in order to achieve a practical rate for the electrode process. Gases, being non-conductors and having no strength, must be supplied through a medium which conducts electricity and yet provides the greatest possible area wherein the gas, conductor, and electrolyte are in mutual contact. In the past, electrically conducting porous media, such as sintered metals, have been employed as gas electrodes. Through careful control of pore size, the electrode area can be made quite large and, with appropriate catalysts, the efficiency of the electrode is adequate.

A problem exists with such electrodes, however, in that porous media inherently tend to absorb liquids by capillary action, causing the gas-electrode-electrolyte interface to retreat within the electrode. When this condition (known as flooding) occurs, the electrode is prone to severe polarization and, as a result, the cell output is decreased considerably.

Since certain metals are readily permeable to hydrogen at the cell temperature, it was recognized that an unusual opportunity existed for circumventing the problems of flooding and the need for catalysts for the gas electrode. It was postulated that the gas electrode could be formed of a solid thin sheet of metal through which the hydrogen could be transmitted by means of interatomic diffusion. Hydrogen would thus be supplied in the atomic state at the metal-fused salt interface.

Hydrogen permeation studies were therefore initiated on selected metals that are compatible with the lithium hydride, lithium metal, and fused salt environment. Materials such as palladium and silver-palladium alloys, which have high hydrogen permeability, were not considered because of their incompatibility with lithium metal; hence, the permeation studies were restricted to iron, iron-molybdenum alloys, vanadium, and niobium.

Data for Armco iron, vanadium, and iron-molybdenum alloys have previously been reported in ANL-6687, p. 196 and ANL-6900, p. 323. Figure VI-1 displays some of the pertinent data obtained for Armco iron and vanadium from these permeation studies. Even though the permeation rate of hydrogen through iron is low,⁹ and for this reason would be capable of supporting only about one-tenth the current densities desired, iron is still somewhat attractive because it is

⁹ R. R. Heinrich, C. E. Johnson, and C. E. Crouthamel, J. Electrochem. Soc. **112**, 1067 (1965).

self-cleaning at cell operating temperatures in a hydrogen atmosphere, i.e., hydrogen reduces the iron oxides. The use of special cathode design to effect a significant increase in current density may still be practical in a cell using an iron diaphragm. Alloys of molybdenum and iron gave results⁹ which were essentially the same as those for pure iron. Vanadium, on the other hand, appears to be an excellent diaphragm material.¹⁰ It has a high hydrogen permeability at moderate temperature ($\sim 500^\circ\text{C}$) and is compatible with the cell environment. If a higher cell operating temperature is desired, this material can sustain a theoretical current density in excess of 1000 ma/cm^2 at 600°C and 1 atm hydrogen pressure. Because vanadium is not self-cleaning at normal cell temperatures, some preparation of the metal is needed before its maximum permeation rate is achieved. This preparation consists of baking the metal in vacuum at a temperature of 850°C to remove as much of the surface oxide contamination as possible. Further, vanadium is one of a group of metals (V, Nb, Ta) which have a negative absorption coefficient with temperature, that is, the metal absorbs greater quantities of hydrogen at lower temperatures than at higher temperatures. If vanadium metal is cooled in hydrogen, the metal lattice will be expanded and the expansion will further increase the permeation rate at the low temperatures.

No permeation data are presented for niobium because of the difficulty in obtaining reproducible results. Such data as were collected, however, correspond reasonably well with the available literature information.¹¹ Studies reported by Thompson Ramo Wooldrige⁶ on a lithium hydride cell utilizing a niobium diaphragm appear to be inconsistent with the literature data. The high current densities (3000 ma/cm^2) mentioned in this report are not supported by any literature data known to us. Rather, it appears that at 500°C for a 0.010-in. thick metal diaphragm, the maximum theoretical current density should be about 300 ma/cm^2 .

Although it does seem that hydrogen-permeable membranes offer distinct advantages, other parameters, such as operation at lower cell temperatures (300 to 350°C) to give higher cell voltages, may be more important. Under these low temperature conditions, the conventional porous electrodes appear to offer the only possible way of achieving high current densities.

Molten lithium exhibits an extremely high surface tension. Our observations indicate that lithium sometimes may coalesce over a $\frac{1}{2}$ -in. hole without entering. It was also observed that lithium frequently will not

wet other metals unless they are thoroughly fluxed. In the presence of a fused salt, the lithium metal will completely wet the metal surface and readily displace the fused salt. The anode is thus conceived as being basically a metal disc of controlled porosity through which the lithium metal is fed. The lithium will preferentially wet and saturate the porous metal disc and by capillary action displace any fused salt that has crept into the anode.

A less sophisticated form of this electrode has been used throughout our experimental program. The lithium metal was retained on a sintered metal fiber sponge (SS-430). The interfacial tension of the liquid lithium on the sponge is such that the metal can be retained in place below the surface of the electrolyte. This situation may change if the density of the electrolyte is very high (such as for the fused salt iodides) thereby producing a greater buoyancy on the light metal.

b. ELECTROLYTE

An electrolyte, to be suitable for use in a lithium hydride cell, should have the following properties: (1) reasonable solubility for lithium hydride, (2) thermodynamic stability with respect to the very electro-positive lithium metal, (3) stability at regeneration temperatures, and preferably a low vapor pressure at this temperature, and (4) low solubility for the anode metal. Halide salts of lithium metal are the only known substances which meet these requirements. Data describing the solid-liquid equilibrium for the lithium hydride-lithium halide systems^{12, 13} were obtained by thermal analyses. A summary of some of the pertinent data is as follows:

System	Minimum Melting Point ($^\circ\text{C}$)	LiH (m/o) in Eutectic Composition
LiH-LiCl	495.6	34.0
LiH-LiBr	453.3	29.7
LiH-LiI	390.8	23.5
LiH-LiF	684	solid solution

The first three systems are simple eutectics with the stated melting points and compositions. The LiH-LiCl and LiH-LiBr systems have been described in detail in ANL-6725, p. 228, and ANL-6800, p. 413, respectively. Temperature-composition data and thermodynamic functions of each component for the LiH-LiI binary are given in Figure VI-2 and Table VI-1. Data for the LiH-LiF system were obtained from the work of Messer and Mellor¹⁴ and are included here for the sake of completeness.

¹² C. E. Johnson, S. E. Wood, and C. E. Crouthamel, *Inorg. Chem.* **3**, 1487 (1964).

¹³ C. E. Johnson, S. E. Wood, and C. E. Crouthamel, *J. Chem. Phys.* **44**, 884 (1966).

¹⁴ C. E. Messer and J. Mellor, *J. Phys. Chem.* **64**, 503 (1960).

¹⁰ R. R. Heinrich, C. E. Johnson, and C. E. Crouthamel, *J. Electrochem. Soc.*, **112**, 1071 (1965).

¹¹ R. W. Rudd, D. W. Vose, and S. Johnson, *J. Phys. Chem.* **66**, 351 (1962).

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FIG. VI-2. LiH-LiI Solid-Liquid Equilibrium—under 1 atm $H_2(g)$.

Analysis of the solid-liquid equilibrium data^{12, 13} for the first three compositions given above has indicated that these systems exhibit unusual behavior. The binary systems all show positive deviations from ideality, which, in the limit of pure lithium hydride, may be explained by assuming that the lithium halides exist predominantly as dimeric species. It also appears that in the limit of the pure lithium halide, the lithium hydride exists as an un-ionized monomer. These interpretations are based upon the observed cryoscopic constants (ν) for these solutions and a theoretical analysis of the solid-liquid equilibria data. These interpretations agree with the concept of the apparent nonionic character of molten lithium hydride, evidenced by its low electrical conductivity¹⁵ (at 685°C, specific conductance = $0.036 \text{ ohm}^{-1} \text{ cm}^{-1}$) near the melting

¹⁵ K. Moers, *Z. Anorg. Allgem. Chem.* **113**, 179 (1920).

TABLE VI-1. THERMODYNAMIC PROPERTIES OF THE SYSTEM LiH-LiI

Composition (m/o LiH)	Equilibrium Temperature (°K)	Excess Free Energy ^a		Excess Chemical Potential ^a	
		$\Delta\mu_{LiI}^M$ (cal/mole)	$\Delta\mu_{LiH}^M$ (cal/mole)	$\Delta\mu_{LiI}^E$ (cal/mole)	$\Delta\mu_{LiH}^E$ (cal/mole)
0.0	741.1	—	—	—	—
5.0	728.2	—61.0	—	13.2	—
10.0	714.7	—125	—	24.7	—
15.0	698.7	—201	—	25.1	—
20.0	678.7	—295	—	5.6	—
23.5	664.0	—365	—1715	—11.8	196
30.0	712.3	—	—1425	—	278
35.0	747.1	—	—1220	—	340
40.0	777.2	—	—1040	—	375
45.0	801.0	—	—900	—	371
50.0	825.1	—	—760	—	378
55.0	845.3	—	—640	—	363
60.0	864.2	—	—532	—	345
65.0	880.0	—	—442	—	312
70.0	894.2	—	—360	—	273
75.0	906.3	—	—293	—	225
80.0	918.1	—	—226	—	181
85.0	929.1	—	—165	—	135
90.0	939.3	—	—108	—	88.3
95.0	949.2	—	—53.7	—	43.1
100.0	959.5	—	—	—	—

^a See Reference 12 for equation defining these symbols.

point, its estimated low dielectric constant,¹⁶ and the covalent character of the lithium-hydrogen bond.¹⁷

In order to increase the Carnot cycle efficiency and cell voltage, the lithium hydride cell should be operated at low temperatures; thus, low melting electrolytes are desirable. It is probable that the most practical electrolyte for use in the lithium hydride cell will be a ternary system composed of two lithium halides and lithium hydride. Two such ternary systems have been investigated. The first, LiH-LiCl-LiF, is attractive because it contains fluoride ion, which is believed to be active in reducing the possibility of metal dispersions in the fused salt. The second LiH-LiCl-LiI is also attractive because of its low eutectic melting point, about 330°C.

The three binary systems which form the boundaries of the ternary LiH-LiCl-LiF system have the following characteristics: the LiH-LiCl binary has a simple eutectic that melts at 495.6°C and contains 34.0 m/o LiH, the LiH-LiF binary consists of a continuous series of solid solutions with a minimum melting point of

¹⁶ A. S. Filler and E. Burstein, *Bull. Am. Phys. Soc.* **5**, 1 (1960).

¹⁷ M. S. Ahmed, *Phil. Mag.* **42**, 997 (1951).

4°C, and the LiCl-LiF system has a simple eutectic that melts at 501°C and contains 30.5 m/o LiF.

The LiH-LiCl-LiF system was investigated by thermal analysis techniques which have been previously described¹² (see also ANL-6596, p. 203). Five composition cross sections were studied over the whole range of compositions from pure lithium chloride to the lithium hydride-lithium fluoride boundary. Five other cross sections were investigated only in a limited concentration range. These data are summarized in Table VI-2 and have been used to plot the isotherms given in Figure VI-3. The diagram of the crystallization surface of this ternary consists mainly of a continuous crystallization field of solid solutions and a small field of pure lithium chloride. The minimum temperature in this ternary system is 459°C.

The LiH-LiCl-LiI system is also being studied by thermal analysis, but at present, the data are incomplete.

c. ELECTROCHEMICAL CELL

Determination of Thermodynamic Data for Lithium Hydride. The only thermodynamic data for lithium hydride available in the literature are enthalpy data derived from calorimetric measurements.^{18, 19} In view of this paucity of systematic thermodynamic data for lithium hydride, studies were undertaken to establish, by means of emf measurements, values for the standard thermodynamic functions (ΔG_f° , ΔH_f° , ΔS_f°) for the formation of solid lithium hydride over as wide a temperature range as possible.

The lithium hydride formation cell may be represented as

Li(ℓ)/LiX(ℓ) saturated with LiH(s)/H₂(g) 1 atm, Fe,

where LiX represents a lithium halide. The half cell reactions, Li(ℓ) $\rightarrow$ Li⁺ + e⁻ and $\frac{1}{2}$ H₂ + e⁻ $\rightarrow$ H⁻, at the anode and cathode, respectively, sum to give the cell reaction Li(ℓ) + $\frac{1}{2}$ H₂(g) $\rightarrow$ LiH(s). For a cell with all three substances in their standard states, namely, pure liquid lithium metal, pure solid lithium hydride, and pure hydrogen gas at one atmosphere pressure, it is readily seen that the Nernst equation,

$$E = E^\circ - RT/nF \ln \left(\frac{a_{\text{LiH}}}{a_{\text{Li}} a_{\text{H}_2}^{1/2}} \right), \quad (1)$$

reduces to $E = E^\circ$.

The essential parts of the standard lithium hydride cell assembly are illustrated in Figure VI-4. The cell,

¹⁸ S. R. Gunn and L. G. Green, J. Am. Chem. Soc. **80**, 4782 (1958).

¹⁹ C. E. Messer, L. G. Fasolino, and C. E. Thalmayer, J. Am. Chem. Soc. **77**, 4524 (1955).

TABLE VI-2. THERMAL ANALYSIS DATA OF LiH-LiCl-LiF TERNARY SYSTEM

LiCl (m/o)	Crystallization Temperature (°C) of Ternary System Composed of Indicated Binary Mixture Plus LiCl				
	10 m/o LiH-90 m/o LiF	30 m/o LiH-70 m/o LiF	50 m/o LiH-50 m/o LiF	70 m/o LiH-30 m/o LiF	90 m/o LiH-10 m/o LiF
0	833.2	778.5	704.6	692.0	684.0
5	816.5	763.5	696.0	676.5	672.0
10	799.5	747.0	685.0	661.5	660.0
15	779.0	730.0	672.5	646.5	648.0
20	759.0	711.5	657.5	630.5	634.5
25	737.5	691.5	640.0	614.0	621.0
30	715.0	670.5	620.0	597.0	606.5
35	690.5	648.0	598.5	579.5	592.0
40	665.0	624.0	575.0	562.0	577.0
45	637.5	597.5	548.5	543.0	561.5
50	608.0	559.5	521.0	523.5	546.0
55	577.5	538.0	492.0	503.0	529.5
60	543.0	503.5	462.5	481.5	512.5
65	510.5	475.5	480.0	485.0	474.0
70	497.5	498.5	502.5	505.0	510.0
75	519.0	519.5	520.5	524.0	529.0
80	539.5	539.0	539.5	542.0	546.5
85	558.0	556.5	557.5	559.5	563.5
90	576.0	574.0	574.5	577.0	579.0
95	592.0	590.5	591.0	592.5	593.5
100	607.0	607.0	607.0	607.0	607.0

LiH (m/o)	Crystallization Temperature (°C) of Ternary System Composed of Indicated Binary Mixture Plus LiH				
	70 m/o LiCl-30 m/o LiF	75 m/o LiCl-25 m/o LiF	77.5 m/o LiCl-22.5 m/o LiF	80 m/o LiCl-20 m/o LiF	85 m/o LiCl-15 m/o LiF
0	501.0	519.0	529.0	538.0	557.0
5	497.5	505.5	515.5	525.5	543.5
10	495.0	489.5	500.5	511.0	528.5
15	493.0	470.0	485.0	495.5	513.5
20	490.5	461.0	466.5	468.0	497.0
25	501.0	485.0	475.5	464.5	480.0
30	518.0	507.0	500.5	493.0	494.0
35	534.5	527.5	521.5	516.0	517.5
40	550.5	545.5	540.5	536.0	537.5
45	565.5	562.0	557.5	554.0	555.0
50	580.0	577.0	573.0	570.0	571.5

contained in a furnace well below an inert atmosphere box (not shown), is isolated from the box by a cover through which the stainless steel support tubes extend. Both the lithium anode and the hydrogen cathode are insulated by beryllia tubing. The lithium metal is contained on the sintered metal fiber sponge, as described previously. The cathode consists of a stainless steel bubbler tube to which an Armeo iron bubbler cap had been welded. Pure hydrogen gas (purified by diffusion through a silver-palladium alloy) is passed over the iron

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Fig. VI-3. Diagram of the Crystallization Surface of the Ternary System LiH-LiCl-LiF.

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Fig. VI-4. LiH Cell Assembly.

surface for the catalytic reduction of hydrogen to hydride ions. Emf's are taken at a pressure of one atmosphere of hydrogen.

Reagent grade lithium chloride, lithium bromide, and lithium iodide were purified by standard techniques^{20, 21}

²⁰ H. A. Laitinen, W. S. Ferguson, and R. A. Osteryoung, *J. Electrochem. Soc.* **104**, 516 (1957).

²¹ D. L. Maricle and D. N. Hume, *J. Electrochem. Soc.* **107**, 354 (1960).

TABLE VI-3. EMF-TEMPERATURE DATA FOR LITHIUM HYDRIDE CELL

59.8 m/o LiI- 40.2 m/o LiH		59.8 m/o LiBr- 40.2 m/o LiH		55.1 m/o LiCl- 44.9 m/o LiH		40.0 m/o LiCl- 60.0 m/o LiH	
Emf (volt)	Temp (°K)	Emf (volt)	Temp (°K)	Emf (volt)	Temp (°K)	Emf (volt)	Temp (°K)
0.3934	673.2	0.3440	733.7	0.3076	777.2	0.2845	803.2
0.3915	674.2	0.3412	738.7	0.3033	782.2	0.2822	810.2
0.3864	683.2	0.3368	744.2	0.2993	788.2	0.2764	813.2
0.3822	687.2	0.3324	749.7	0.2951	792.2	0.2747	819.7
0.3797	693.2	0.3275	754.2	0.2908	798.2	0.2690	823.2
0.3739	698.2	0.3253	758.2	0.2870	803.2	0.2690	828.2
0.3698	704.2	0.3247	762.2	0.2828	808.7	0.2605	838.2
0.3628	708.2	0.3197	764.2	0.2828	813.2	0.2629	843.2
0.3598	716.2	0.3183	767.7			0.2520	844.2
0.3522	722.2	0.3183	769.7			0.2517	847.7
0.3520	723.7	0.3178	773.2			0.2510	852.2
0.3440	734.2	0.3120	778.2				
0.3387	742.7						
0.3325	747.2						
0.3318	756.2						
0.3228	766.2						

before use. Lithium hydride was made by a technique described by Messer.²²

Emf data for cells of differing lithium halide-lithium hydride compositions are summarized in Table VI

²² C. E. Messer, A Survey Report on Lithium Hydride, USAEC-NYO-9470, October 1960.

comparison of the individual cell data with the composite set showed no apparent inconsistencies, and the data were treated as a whole. The uncertainty in the data obtained with the chloride cells is somewhat greater than that obtained with the bromide and iodide cells. This is because of higher cell operating temperatures for the chloride cells which result in significant corrections of the chloride emf data. The emf data obtained for the bromide and iodide cells were combined and fitted to an equation linear with respect to temperature, and the data for the chloride cells were fitted to a second linear equation. For the temperature range considered, a linear function seemed to fit all the data best. The intercept and slope of the final linear equation were obtained by using an average of the values in the above two equations, weighted according to the number of experimental points in each set of data. The resultant equation

$$E^{\circ} = 0.9081 - 7.699 \times 10^{-4}T \quad (2)$$

was obtained for the temperature range from 673 to 853°K. The standard deviation is ± 2 mv. Calculations were made of ΔG_f° , ΔH_f° , and ΔS_f° at 800°K, and also at 298°K by integration of the best available heat capacity data over the temperature range 800–298°K; these data are given in Table VI-4. Values from the literature^{18, 19, 23} are included in Table VI-4 for comparison.

Studies have also been made of the reactions taking place at the cathode. The equilibrium potential obtained for any experiment was the same for any metal used, namely, pure iron, vanadium, or niobium. The rate of achieving this equilibrium potential for vanadium and niobium, however, was very low. The hydrogen electrode in a lithium hydride cell assumes the potential defined by the overall equilibrium between molecular hydrogen gas and hydride ions in the cell electrolyte. Since this equilibrium is not readily established in the absence of an active surface, the electrode must serve in this capacity as well. The establishment of an equilibrium population of atomic hydrogen on the metal surface of the electrode is achieved only after the bulk metal is saturated with hydrogen. Hydrogen solubility in niobium and vanadium is about 4000 to 7000 times greater than in iron.

The following mechanisms and relative rates agree with the experimental results and delineate the important postulates which establish the equilibrium potential at the hydrogen-hydride electrode:

Rate 1 is the activated adsorption of hydrogen on the metal surface. Rate 2 combines the formation of the gas-metal solid solution and the diffusion of atoms into the metal as a composite rate. The diffusion of hydrogen through the metal lattice is the rate-controlling step under equilibrium conditions. However, the low rate at which hydrogen saturates the metal also controls the rate at which the cell equilibrium potential is established.

The reaction rate, R_3 , was assumed to be very high in comparison with rates R_1 and R_2 . Atomic hydrogen on the electrode surface is rapidly stripped off as the hydride ion by an electron exchange.

The rate of diffusion of atomic hydrogen from the metal surface into the bulk metal lattice was considered the lowest rate. This was consistent with the fact that, in the operation of a metal diaphragm under a hydrogen gas pressure differential of one atmosphere, the permeation rate is inversely proportional to the diaphragm thickness. Vanadium and niobium, compared to iron, have extremely high hydrogen solubility. Thus it is not surprising that an equilibrium population of atomic hydrogen could not be maintained on the fresh vanadium or niobium electrode surfaces until the bulk metal was saturated. Evidence of this condition was the low initial cell potentials for the vanadium and niobium electrodes compared to the virtually immediate attainment of equilibrium potentials for iron electrodes. With a vanadium electrode, equilibrium was attained in hours or days, depending on the cell temperature. Once equilibrium had been attained, on the other hand, the potential of a lithium hydride cell with a vanadium cathode

TABLE VI-4. CALCULATED VALUES^a AND LITERATURE VALUES FOR THE ENTHALPY, FREE ENERGY, AND ENTROPY OF LITHIUM HYDRIDE

	This Work, 800°K	This Work, 298°K	Literature, 298°K
$\Delta H_f^{\circ}(\text{cal mole}^{-1})$	-20,940	-21,790 $\pm$ 290	-21,340 ¹⁹ -21,670 ¹⁸
$\Delta G_f^{\circ}(\text{cal mole}^{-1})$	-6,740	-16,160 $\pm$ 50	-16,450 ^{19, 23} -16,800 ^{18, 23}
$\Delta S_f^{\circ}(\text{cal deg}^{-1} \text{ mole}^{-1})$	-17.7	-18.9 $\pm$ 0.4	-16.3 ²³

$$^a \Delta H_f^{\circ} = nF[T \left(\frac{\partial E^{\circ}}{\partial T} \right)_p - E^{\circ}], \quad \Delta G_f^{\circ} = -nFE^{\circ}, \quad \Delta S_f^{\circ} = nF \left(\frac{\partial E^{\circ}}{\partial T} \right)_p \text{ where } E_{800^{\circ}\text{K}}^{\circ} = 0.2922 \text{ volt}, \left(\frac{\partial E^{\circ}}{\partial T} \right)_p = -7.699 \times 10^{-4} T \text{ volt deg}^{-1}.$$

²³ K. K. Kelley and E. G. King, Entropies of the Elements and Inorganic Compounds, Bulletin 592, Bureau of Mines, 1961.

dropped only slowly even when the hydrogen gas atmosphere was removed from the cell, in contrast with the very rapid potential drop when iron cathodes were used.

Voltammetric and chronopotentiometric studies²⁴ using an iron microelectrode in a lithium chloride-potassium chloride electrolyte have confirmed the rapid rate of R_3 (the stripping of atomic hydrogen from the electrode surface as hydride ion) in the above sequence. These studies also indicated that not all metals would be suitable for use as electrodes in a lithium hydride galvanic cell system. For example, it was demonstrated that the overall process at iron electrodes is much faster than that at tungsten electrodes.

d. CELL REGENERATION

Certainly one of the more attractive features of the lithium hydride cell system is the apparent ease of regeneration. Literature data²² indicate that at 900°C (1173°K), lithium hydride readily dissociates to give an equilibrium hydrogen gas pressure of one atmosphere. The relatively low regeneration temperature and the ease of separation of the hydrogen from the lithium make for convenient cyclic operation in a thermally regenerative cell system. At 900°C, hydrogen diffuses rapidly through iron to give virtually perfect gas phase separation of hydrogen.

The purpose of the regenerator is to dissociate the cell product, lithium hydride, into the reactants, lithium and hydrogen, which may then be returned to their respective electrode compartments for completion of the cycle. The establishment of regeneration conditions requires a knowledge of the characteristics of the reactions and processes concerned with this phase of the lithium hydride cell. In the present work, the gaining of information on the conditions for regeneration was approached by a circuitous route. It was convenient to extend the work on the emf studies of the hydrogen-hydride systems in solutions saturated with lithium hydride to unsaturated solutions. Once the standard emf of the reaction $\text{Li}(\ell) + \frac{1}{2} \text{H}_2(\text{g}) \rightarrow \text{LiH}(\text{s})$ had been determined as a function of temperature, the activity of lithium hydride could be obtained in unsaturated electrolytes of similar cells.

Computed thermodynamic data for lithium hydride, obtained from emf-temperature-composition studies of the lithium hydride cell, are given in Table VI-5. Using the relation $\Delta G = -nFE$, the free energy of formation of lithium hydride was calculated from the cell emf, E . The partial molal free energy, $\tilde{G}$, of lithium hydride in solution is then $\tilde{G} = \Delta G - \Delta G^\circ$, where ΔG° refers to pure solid lithium hydride. The entropy of formation,

ΔS , is obtained from $\Delta S = nF(\partial E/\partial T)_p$ and the partial molal entropy is then, $\tilde{S} = \Delta S - \Delta S^\circ$. The activity of lithium hydride in solution, a , is calculated from $\tilde{G} = RT \ln a$. Other tabulated quantities are the corresponding enthalpies, ΔH and $\tilde{H}$.

With the activity of lithium hydride, determined from the cell emf, one can use these data with the Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{a_{\text{LiH}}}{a_{\text{Li}} P_{\text{H}_2}^{1/2}} \right) \quad (3)$$

to calculate the hydrogen equilibrium pressure at each temperature and composition. With the restrictions that $a_{\text{Li}} = 1$ because we are using pure lithium metal anodes and $E = 0$ because we are calculating the hydrogen equilibrium pressures, the equation reduces to the form

$$2 \left(\frac{-E^\circ}{1.984 \times 10^{-4} T} + \log a_{\text{LiH}} \right) = \log P_{\text{H}_2} \quad (4)$$

Assuming the cell emf to be a linear function of temperature, the equation relating cell emf with temperature, $E^\circ = 0.9081 - 7.699 \times 10^{-4} T$, was extrapolated to 900°C in order to make an estimate of the hydrogen equilibrium pressure at temperatures near those used for regeneration. The data are shown graphically in Figure VI-5 where the logarithm of the hydrogen pressure is plotted as a function of the reciprocal of the absolute temperature. For a solution containing 0.302 mole fraction lithium hydride (N_{LiH}), a dissociation pressure of 129 mm was calculated for a temperature of 900°C.

The validity of this experimental approach seems confirmed by the fact that these data check well with the direct measurements made on several lithium hydride-lithium chloride compositions by the group at Thompson Ramo Wooldridge.⁷ One cannot overlook, however, the disadvantage of the apparently low pressure obtained at nominal regeneration conditions.

Although no design work has been carried out to define a particular regeneration system, some possibilities in equipment design are noteworthy. For regeneration of the lithium hydride system, separation of hydrogen gas from the liquid metal-electrolyte mixture and separation of lithium metal from the electrolyte are required. Both separations have been examined in some detail by the group at Thompson Ramo Wooldridge²⁵ using a compact gas-liquid-liquid separator, a cylinder in which the liquid-gas mixture is introduced tangentially at a high velocity. Beneath the cylindrical section is a conical chamber. The gas is removed from the base of the

²⁴ J. A. Plambeck, J. P. Elder, and H. A. Laitinen, *J. Electrochem. Soc.* **113**, 67C (March 1966) Abstract.

²⁵ D. R. Snoke, Zero Gravity Separator Development for Regenerative Fuel Cell, ASD-TDR-62-240, TAPCO Division of Thompson Ramo Wooldridge, Inc., Cleveland, Ohio, 1962.

TABLE VI-5. COMPUTED THERMODYNAMIC DATA FOR LiH IN LiH-LiCl SYSTEM

	Saturated	Atom fraction LiH (N_{LiH})					
		0.3019	0.2019	0.1020	0.0503	0.0252	0.0104
$(\partial E/\partial T)_P \times 10^4$	-7.699	-5.817	-5.891	-5.416	-5.523	-3.902	-3.230
ΔS (cal/deg)	-17.7	-13.4	-13.6	-12.5	-12.7	-9.0	-7.4
$\bar{S}$ (cal)	0	4.3	4.1	5.2	5.0	8.7	10.3
ΔH (cal/mole)	-16,060	-14,110	-14,860	-15,420	-16,550	-15,500	-16,370
$\bar{H}$ (cal)	0	1,950	1,200	640	490	560	210
600°C (873°K)							
E (volt)	0.2358	0.2632	0.2904	0.3437	0.3873	0.4379	0.5176
ΔG (cal)	-5,437	-6,069	-6,696	-7,925	-8,931	-10,097	-11,935
$\bar{G}$ (cal)	0	-632	-1,259	-2,488	-3,494	-4,660	-6,498
a	1.0	0.6947	0.4840	0.2384	0.1335	0.0682	0.0242
700°C (973°K)							
E (volt)	0.1588	0.2050	0.2314	0.2895	0.3321	0.3989	0.4853
ΔG (cal)	-3,662	-4,727	-5,336	-6,676	-7,658	-9,198	-11,190
$\bar{G}$ (cal)	0	-1,065	-1,674	-3,014	-3,996	-5,536	-7,528
a	1.0	0.5765	0.4207	0.2104	0.1266	0.0571	0.0204
800°C (1073°K)							
E (volt)	0.0819	0.1469	0.1725	0.2353	0.2768	0.3599	0.4530
ΔG (cal)	-1,888	-3,378	-3,978	-5,426	-6,383	-8,299	-10,446
$\bar{G}$ (cal)	0	-1,499	-2,090	-3,538	-4,495	-6,411	-8,558
a	1.0	0.4951	0.3753	0.1903	0.1215	0.0495	0.0181
900°C (1173°K)							
E (volt)	0.0048	0.0887	0.1136	0.1812	0.2216	0.3209	0.4207
ΔG (cal)	-111	-2,045	-2,619	-4,178	-5,110	-7,400	-9,700
$\bar{G}$ (cal)	0	-1,934	-2,508	-4,067	-4,999	-7,289	-9,589
a	1.0	0.4362	0.3410	0.1747	0.1172	0.0439	0.0164

cone, the heavier liquid is removed from its side, and the lighter liquid from its apex.

Exploiting the high permeability of hydrogen gas through certain metals at regeneration temperatures helps simplify the regenerator. In its design, a metal diaphragm can be used to separate the hydrogen gas component from the other gaseous components in the system. There will thus be no problem in dealing with finite vapor pressure that is caused by the electrolyte and is sure to be present in the regenerator.

To date, the only practical cell studies are the early ones by the groups at Mine Safety Appliance Corp. and Thompson Ramo Wooldridge, and the study of a single cell which was done at this laboratory.

In the study at this laboratory, a lithium hydride cell with a vanadium diaphragm was operated for 540 hr at 525°C, giving current densities that exceeded 130 ma/cm² at one-half open circuit voltage (0.3 volt). (This cell was previously described in ANL-6900, p. 325.) Even though this current density is only about one-half the theoretical current density (for a 0.01-in. thick vanadium diaphragm at 500°C), it was achieved without any high temperature pretreatment of the metal diaphragm. No mechanical problems arose during

108-8520

FIG. VI-5. Equilibrium Hydrogen Pressure in LiH-LiCl Mixtures.

the cell run. The slope of a plot of cell emf measured against the logarithm of the hydrogen pressure corresponded to the expected Nernst slope of one, indicating the reversibility of the H_2 , H^+ couple at the vanadium electrode.

The electrolyte constituents or the cathode construction, for the most part, determine design parameters. Because lithium metal has a unique characteristic (high interfacial tension), an anode design incorporating either a sintered metal or controlled-porosity disc will be most suitable. For LiH-LiCl-LiF (minimum m.p. at 456°C) as the electrolyte, a permeable membrane for the cathode would be a possible choice since the cell operating temperature would be $>500^\circ\text{C}$.

The most distinct advantage of the permeable membrane is its ready solution to the assorted problems that have long been present in work with porous metal-gas electrodes. However, as the permeability studies described earlier indicate, the choice of metal for this application is limited to iron and vanadium. Iron has a low hydrogen permeation rate, and vanadium requires pretreatment before it is suitable for use. It should be emphasized that in utilizing a permeable membrane, the temperature of cell operation must be above about 500°C . Only at this temperature and above can the hydrogen permeation rates through the cathode metal support reasonable current densities.

The design of a LiH regenerative cell must provide an adequate hydrogen pressure at the cathode. The quantity of hydrogen diffusing through a metal diaphragm is proportional to the difference in the square roots of the hydrogen pressures on each side. The quantity diffusing through a 0.010-in. thick vanadium diaphragm at 500°C is $0.50 (\sqrt{P_a} - \sqrt{P_b})$, where P_a and P_b are the hydrogen pressures (in atmospheres) on the two sides of the diaphragm. The voltage loss is

$$\Delta E = -\frac{RT}{nF} \ln \frac{\sqrt{P_a}}{\sqrt{P_b} - I/A}, \quad (5)$$

where I is the cell current density in amp/cm² of diaphragm area, and A is related to the theoretical current density (in amp/cm²) for a permeable diaphragm and is equal to 0.50 for $T = 773^\circ\text{K}$. With this equation, it can be shown that cell voltage losses may be as great as 0.1 volt for operating a cell at one-half atmosphere hydrogen pressure and 100 ma/cm² current density. To obtain a high output voltage in the cell, it is necessary to operate the cathode at a pressure as close to one atmosphere as possible; hence, with a hydrogen pressure of about 100 mm from the regenerator, pumps may be needed to increase the hydrogen pressure to one atmosphere or higher. Such P-V work could be a real drain on the cell efficiency, with roughly 50 % of the cell voltage conceivably being used for pumping.

The use of a low-melting electrolyte (for example, the LiH-LiCl-LiI system with a ternary eutectic melting point of 330°C) would offer a number of advantages because the cell could then operate at much lower temperatures. Cell voltages would be significantly higher. This electrolyte is at or near saturation with respect to the lithium hydride component; at saturation, the cell voltage is 0.45 volt. Regeneration pressures could be significantly increased by sending to the regenerator a mixture very rich in lithium hydride (90-95 m/o LiH). Such a mixture could be obtained by precipitating lithium hydride as a pure component from this electrolyte near cell operating temperatures.

Operation of the cell at a lower temperature may necessitate some modification in the construction of the cathode. Data indicate that by reducing the diaphragm thickness to 0.002 in., a theoretical current density of about 300 ma/cm² can be expected at 375°C . Experiments are presently under way to demonstrate the feasibility of this approach.

2. Intermetallic Systems (M. S. FOSTER, G. H. McCLLOUD)

a. SODIUM-BISMUTH CELL STUDIES

Studies of the thermodynamic properties of sodium-bismuth alloys have been made using cells of Type 1:

and of Type 2:

In preliminary studies of cells of Type 2, it was observed that the nonelectrochemical (or irreversible) transfer of sodium from the anode, through the elec-

trolyte, and into the cathode was sufficiently large to cause a steadily decreasing cell potential as the concentration of sodium in the cathode alloy increased. Therefore, a cell of Type 2 could only be operated at a single temperature, thereby necessitating the use of an extrapolated initial cell potential in the calculation of thermodynamic properties. In order to obtain data at more than one temperature per experiment, cells of Type 1 have been operated.

Solid electrolyte for cells of Type 1 was obtained from Harshaw Chemical Company, Cleveland, Ohio, in the form of cups made from single crystals of NaCl. The

cup dimensions were approximately 2.4-cm OD and 4.5 cm high, with 0.32-cm thick wall and bottom. The internal resistance of this electrolyte, when immersed in alloy to a depth equal to a height of 1 cm of metal inside the cup, was calculated from the conductance data of von Antropoff and Mueller²⁶ for solid NaCl. These calculated resistances ranged from 194,200 ohms at 673°K to 482 ohms at 973°K; therefore, it was necessary to use voltage-measuring instruments with high input impedances. A potentiometric recorder with an off-balance input impedance of $>4 \times 10^6$ ohms, an electrometer amplifier with $\sim 10^{14}$ ohms input impedance, and a five-dial potentiometric electrometer with 10^{13} ohms input impedance were used as voltage-measuring devices.

In the cell, the pure liquid sodium anode was contained in the electrolyte cup, and the cup was partially immersed (about 1 cm) in the cathode alloy. The cathode alloy was contained in a tantalum crucible. Electrode leads were made of tantalum. In order to assure temperature uniformity, the tantalum crucible was contained in a thick-walled copper cup. A chromel-alumel thermocouple was used to monitor the temperature of the copper cup, which was the same as that of the alloy.

The results of emf measurements of various cells of Type 1 are shown in Figure VI-6. The cathode composition varied from 0.10 to 0.50 atom fraction sodium (X_{Na}) in bismuth. The scatter of data is indicated in Figure VI-6 by the standard deviation (σ) of the points from the least-squares curves. The discontinuities in the slope of the lines for $X_{\text{Na}} = 0.30$ and 0.40 (indicated by triangular datum points) are taken to indicate the transition from a single liquid phase system at higher temperatures to a two-phase, liquid plus NaBi(s), system at lower temperatures. Hansen and Anderko²⁷ list a value of 598°K for the transition at $X_{\text{Na}} = 0.30$ (compared with the value of 609°K in Figure VI-6) and 683°K at $X_{\text{Na}} = 0.40$ (compared with 692°K from Figure VI-6). Since both alloys become saturated with the same solid on cooling, they are expected to have identical cell potentials at lower temperatures.

The internal resistance (lead resistance was neglected) of three cells of Type 1 with $X_{\text{Na}} = 0.20, 0.30$, and 1.0, respectively, was measured at various temperatures. Currents ranging from 10^{-10} to 1.5×10^{-2} ampere were drawn (depending on temperature), and the internal resistance was calculated assuming that the internal ohmic loss accounted for the entire reduction in cell potential. (The purpose of the cell with $X_{\text{Na}} = 1.0$ was to check for a possible thermocell potential gener-

108-9292

FIG. VI-6. Potential-Temperature-Composition Characteristics of the Cell: Na(l)/NaCl(s)/Na in Bi(l). (X_{Na} = atom fraction Na.)

ated by a temperature gradient in the cell. None was found—the variation of cell potential from zero was <0.004 volt for temperatures between 519 and 974°K.)

The internal resistances of cells with solid NaCl electrolytes are shown in Figure VI-7. Owing to possible differences in the electrolyte area between the electrodes (as a result of differences in the depth of immersion of the cup in the cathode alloy), some scatter in the ordinate values is to be expected. Also shown for comparison in Figure VI-7 is the resistance curve of a cell of arbitrary thickness calculated from the conductivity values²⁸ given for single crystal NaCl (an arbitrary ordinate shift was used to lower the curve calculated from literature data). The point of maximum curvature in the lower (experimental) curve is emphasized by using two straight lines in connecting the data points. This abrupt change of slope has previously been explained on the basis that two mechanisms for conductivity exist which depend on ionic and defect mobility.²⁸ Owing to the presence in the electrolyte of metallic sodium atoms

²⁶ A. von Antropoff and J. Fr. Mueller, *Z. Anorg. Allgem. Chem.* **204**, 305 (1932) as given in AEC-tr-2906.

²⁷ M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, p. 322.

²⁸ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals*, Clarendon Press, Oxford, 1940, p. 38.

108-9322

FIG. VI-7. Internal Resistance of Cells with Solid NaCl Electrolyte.

which have diffused into the crystal lattice, it is convenient in this case to consider the cell conductivity as due to mobility of Na^+ ions and electrons in the lattice. More will be said concerning this phenomenon later.

The rate of irreversible transfer of sodium was studied using a Type 2 cell. The initial cathode composition of this cell was $X_{\text{Na}} = 0.30$ and the electrolyte composition was 53 m/o NaI-32 m/o NaCl-15 m/o NaF. The cell was operated for a period of 143 hr at 817°K. The entire cell was placed inside a massive copper holder so that any temperature gradients in the cell would be minimized. This was done in an attempt to restrict irreversible transfer of sodium to that caused by concentration diffusion alone by repressing thermal convective mixing in the electrolyte. The results are shown in Figure VI-8, where the emf of the cell is plotted as a function of time. From the data shown in Figure VI-8, the initial open circuit potential was estimated to be 0.6084 volt at 817°K. The rate of irreversible transfer is indicated by the falling cell potential (4.02×10^{-4} volt/hr). From a knowledge of the electrolyte area and with the assumption that the dependence on X_{Na} of the cell potential is the same as in cells of Type 1, the rate of irreversible transfer in this cell is estimated to be 0.002 g/(hr) (cm^2) or 0.6 ma/ cm^2 under open-circuit conditions. This indicates the low rate of irreversible transfer

which may be attained for the cell in the absence of thermal convection. When current is drawn from the cell, this rate would be reduced accordingly (see ANL-6925, p. 245).

We note that at a temperature of 817°K and for $X_{\text{Na}} = 0.30$, a cell of Type 1 exhibits a potential of 0.5861 volt (Figure VI-6), while for the same conditions a cell of Type 2 showed a potential of 0.6084 volt (Figure VI-8). A possible explanation for this difference is similar to arguments put forth by Wagner²⁹ and by Karpachev and Pal'gnev³⁰ concerning electrolytes with both ionic and electronic conduction.

The difference in cell voltages may be understood by considering the cell shown in Figure VI-9. The anode is composed of pure liquid sodium metal, the electrolyte consists of a sodium halide (NaX) or a mixture of sodium salts thermodynamically stable with respect to the pure sodium metal anode, and the liquid cathode is composed of an alloy of sodium and bismuth. Electrons flow in the external circuit in the direction indicated, from anode to cathode. The only reactions taking place

²⁹ C. Wagner, Proceedings of the Seventh Meeting of the International Committee on Electrochemical Thermodynamics and Kinetics, 361 (1957).

³⁰ S. V. Karpachev and S. F. Pal'gnev, Trans. Inst. Electrochem. No. 1, pp. 63, 73, 79, 82, Consultants Bureau, 1961.

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FIG. VI-8. Emf of the Cell: $\text{Na}(\ell)/53 \text{ m/o NaI-32 m/o NaCl-15 m/o NaF/Na}$ in Bi. ($X_{\text{Na}} = 0.30$, initially) vs Time of Run (Temperature: 817°K).

at the electrode-electrolyte interfaces are indicated to be as follows:

1) Sodium atoms (Na^0) are ionized at the anode-electrolyte interface and sodium ions (Na^+) are discharged at the cathode-electrolyte interface. The electrons are carried from the anode through the external circuit to the cathode. The Na^+ diffuse into the electrolyte. For each faraday of current passing through the external circuit, t_+^a is defined as the number of equivalents of Na^0 ionizing at the anode in the same time. Similarly, t_+^c is defined for the discharge of Na^+ at the cathode.

2) Neutral sodium atoms (Na^0) are transferred from the anode of pure liquid sodium into the electrolyte. During the passage of one faraday of current through the external circuit, t_0^a is defined as the number of equivalents of Na^0 dissolving in this time. Similarly, t_0^c is defined as the number of equivalents of Na^0 transferred from the electrolyte into the cathode in the same time.

3) Since some electronic conductivity exists in the electrolyte, the process of dissolution and discharge of electrons in the electrolyte takes place at the cathode-

108-9314

FIG. VI-9. Cell with Ionic and Electronic Conductivity. (The " t " quantities are given in terms of equivalents undergoing change during the time required to pass one faraday of current through the external circuit.)

electrolyte and anode-electrolyte interfaces. The negative current and the positive (Na^+) current in the electrolyte must move in opposite directions. For each faraday of current which passes through the external

circuit, t is defined as the number of equivalents of electrons taking part in these reactions (t^c , that at the cathode, and t^a , that at the anode).

Because both processes (1) and (2) may cause a loss of cell potential by the formation of concentration gradients in the cathode, it is postulated that the quantity of cathode alloy be sufficiently large and the alloy be sufficiently well stirred so that at no time do concentration gradients exist in the cathode alloy.

Certain conservation relationships may be set forth. The sum of the positive and negative currents through any plane intersecting the cell is constant, i.e.,

$$t_+^a + t^a = t_+^c + t^c = 1 \quad (6)$$

per faraday of current passed through the external circuit. If steady state conditions apply, then the sum of the Na^+ and Na^0 in the electrolyte must be constant, i.e.,

$$t_+^a + t_0^a = t_+^c + t_0^c. \quad (7)$$

We note that t_0^c is not necessarily equal to t_0^a , since the ionization of Na^0 can take place at some time after the dissolution of Na^0 in the electrolyte.

The amount of Na^0 "lost" by ionization in the electrolyte (which must also be gained in the electrolyte under steady-state conditions) must be equal to the "excess" Na^+ leaving the solution over that coming in as ions, i.e., $(t_+^c - t_+^a)$. But by Equations 6 and 7:

$$t_+^c - t_+^a = t_0^a - t_0^c = t^a - t^c. \quad (8)$$

If we allow one faraday of current to flow in a reversible manner in the external circuit, the Gibbs free energy change for the total reaction can be calculated. This is done in four steps.

Firstly, we consider that part of the reaction which occurs as $(1 - t^c)$ equivalents of sodium are transferred to the cathode electrochemically. Assuming that the chemical potential of Na^+ , μ_{Na^+} , is constant throughout the electrolyte, the change of Gibbs free energy for this part of the total reaction may be written:

$$\Delta G_1 = (1 - t^c) (\mu_{\text{Na}(\text{Bi})} - \mu_{\text{Na}(t)}) \quad (9)$$

where $\mu_{\text{Na}(\text{Bi})}$ is the chemical potential of Na in the cathode and $\mu_{\text{Na}(t)}$ is that of Na in the anode.

Secondly, we consider that part of the reaction which occurs as $(t^c - t^a)$ equivalents of Na^0 are formed in solution in the electrolyte. Note that this Na^0 is formed at various chemical potentials in the electrolyte (a concentration gradient of Na^0 in the electrolyte exists). Therefore, we write:

$$\Delta G_2 = (t^c - t^a) (\bar{\mu}_{\text{Na}^0(\text{NaX})} - \mu_{\text{Na}(t)}) \quad (10)$$

where $\bar{\mu}_{\text{Na}^0(\text{NaX})}$ is an "average" chemical potential of

Na^0 in the electrolyte, or

$$\begin{aligned} \Delta G_2 &= \int_{t^a}^{t^c} (\mu_{\text{Na}^0(\text{NaX})} - \mu_{\text{Na}(t)}) dt \\ &= -\mu_{\text{Na}(t)}(t^c - t^a) + \int_{t^a}^{t^c} \mu_{\text{Na}^0(\text{NaX})} dt. \end{aligned} \quad (11)$$

Integrating by parts:

$$\begin{aligned} \Delta G_2 &= -\mu_{\text{Na}(t)}(t^c - t^a) + \mu_{\text{Na}^0(\text{NaX})}^c t^c \\ &\quad - \mu_{\text{Na}^0(\text{NaX})}^a t^a - \int_{t^a}^{t^c} t d\mu_{\text{Na}^0(\text{NaX})}. \end{aligned} \quad (12)$$

Using the mean value theorem:

$$\begin{aligned} \Delta G_2 &= -\mu_{\text{Na}(t)}(t^c - t^a) + \mu_{\text{Na}^0(\text{NaX})}^c t^c \\ &\quad - \mu_{\text{Na}^0(\text{NaX})}^a t^a - \bar{t}(\mu_{\text{Na}^0(\text{NaX})}^c - \mu_{\text{Na}^0(\text{NaX})}^a). \end{aligned} \quad (13)$$

If we assume that equilibrium exists between the sodium in the electrolyte layer contiguous to an electrode and the sodium in the electrode, then

$$\mu_{\text{Na}^0(\text{NaX})}^c = \mu_{\text{Na}(\text{Bi})} \quad (14)$$

$$\mu_{\text{Na}^0(\text{NaX})}^a = \mu_{\text{Na}^0(t)} \quad (15)$$

Rewriting:

$$\Delta G_2 = (t^c - \bar{t})(\mu_{\text{Na}(\text{Bi})} - \mu_{\text{Na}(t)}). \quad (16)$$

Thirdly, we consider that part of the reaction which occurs when t_0^c equivalents of Na^0 are transferred from the electrolyte into the cathode alloy. But we have postulated that

$$\mu_{\text{Na}^0(\text{NaX})}^c = \mu_{\text{Na}(\text{Bi})}. \quad (14)$$

Therefore:

$$\Delta G_3 = 0. \quad (17)$$

Finally, since the electrons in the system are flowing reversibly, no Gibbs free energy change is indicated for the t^a equivalents of electrons which flow through the cell, i.e.,

$$\Delta G_4 = 0. \quad (18)$$

Combining, for the overall cell reaction:

$$\begin{aligned} \Delta G &= \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 \\ &= (1 - \bar{t})(\mu_{\text{Na}(\text{Bi})} - \mu_{\text{Na}(t)}). \end{aligned} \quad (19)$$

From this, we see that the potential of the cell with both electronic and ionic conductivity is

$$E = (1 - \bar{t}) E_o \quad (20)$$

where E is the observed open-circuit potential, $\bar{t}$ is "average transport number of the electrons in the electrolyte", and E_o , the "true thermodynamic open-circuit potential".

As current is drawn from a cell such as is represented by Figure VI-9, the positive ion current becomes larger. As this occurs, we note that an increased electronic current lowers the concentration gradient of Na^0 in the electrolyte, and thus the true irreversible transfer (t_0^e equivalents per faraday of current passing through the external circuit) will also decrease. On drawing higher and higher currents, the true irreversible transfer will drop to zero (one can imagine all the sodium metal in t_0^e ionizing in solution). However, at this point, the apparent irreversible transfer [$(t_0^e - t^e)$ equivalents per faraday of current passing through the external circuit] will become negative if t^e is greater than zero.

From Equation 20, we conclude that it is not possible to measure directly the true thermodynamic open-circuit potential in a cell which has appreciable electronic conductivity. Electronic conductivity in alkali metal halides arises both from defect mobility at high temperatures and from metal solubility. Bredig³¹ has interpreted the change in conductivity with changing metal concentration in molten electrolytes by stating that even at an infinite dilution of the metal, electrons are able to contribute to current conduction. Therefore, before using the data from Type 1 or Type 2 cells as the true thermodynamic open-circuit potential, one must take certain precautions, viz., the apparent electronic conductivity should be determined.

b. EVALUATION OF BIMETALLIC CELLS

The possible utility of a bimetallic cell system may be evaluated using electromotive force measurements. These have been reported³² (see also ANL-6875, p. 151) for cells of the type

for compositions of the cathode metal from pure bismuth to bismuth saturated with $\text{Li}_3\text{Bi}(\text{s})$ and for temperatures between 775 and 1100°K. A secondary reference electrode which consisted of bismuth saturated with $\text{Li}_3\text{Bi}(\text{s})$ was developed for use in place of a pure lithium anode. Its potential was independently measured against the lithium electrode. The standard free energy of formation of $\text{Li}_3\text{Bi}(\text{s})$ was derived as a function of temperature.

One may conclude from the emf-temperature-composition characteristics of these cells that the open circuit voltage is good (perhaps 0.7 to 0.9 volt). However, the temperature coefficient of the cell potential is low and leads to the conclusion that the activity (and thus the partial pressure) of lithium will be too low for thermal

³¹ M. Bredig, *Molten Salt Chemistry*, M. Blander, Ed., Interscience, New York, N. Y., 1964, p. 384.

³² M. S. Foster, S. E. Wood, and C. E. Crouthamel, *Inorg. Chem.* **3**, 1428 (1964).

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FIG. VI-10. Potential-Temperature-Composition Characteristics of the Cell: $\text{Li}(\ell)/\text{LiCl-LiF}(\ell)/\text{Li in Sn}(\ell)$. (X_{Li} = atom fraction Li.)

regeneration at reasonably attainable temperatures. Further, at temperatures sufficiently high to produce an appreciable partial pressure of lithium over the alloy, the bismuth partial pressure will be sufficiently large to require fractionation of the vapor. Finally, if one attempts to reduce the total pressure in the cell to allow thermal regeneration at a lower temperature, problems are likely to be encountered since the vapor-liquid loop intersects the solid-liquid curve of the phase diagram (see Section VI.A.3. of this report). This is expected to introduce a solid-vapor region which must be traversed in fractionation and which may lead to blockage of the fractionation column. A more detailed discussion of this problem appears in *Regenerative Electrochemical Systems*.²

The emf-temperature-composition characteristics for cells of the type

for compositions of the alloy from pure tin to tin saturated with $\text{Li}_5\text{Sn}_2(\text{s})$ and for temperatures between 775 and 1120°K are shown in Figure VI-10. These data reflect minor corrections of those previously reported (ANL-6800, p. 412). The liquid bismuth reference elec-

trode saturated with $\text{Li}_3\text{Bi(s)}$ has been used extensively in these measurements. Previous results were high owing to a slow rate of equilibration. This phenomenon may lead to a concentration polarization in an operating cell unless sufficient agitation of the liquid cathode alloy is provided.

One may conclude from Figure VI-10 that the open circuit voltage is fair (0.4 to 0.7 volt). The temperature coefficient of the cell potential is again low, thereby indicating that the activity of lithium will be too low to permit regeneration by distillation at readily attained temperatures. If, however, sufficiently high temperatures could be achieved, the partial pressure of tin (unlike that of bismuth) would be expected to remain negligible, owing to its very high boiling point (2993°K). Further, the problems introduced with lowered total pressure are expected to be slightly less difficult, owing to the fact that the melting point of the highest melting compound (Li_7Sn_2 at 1056°K) is lower than that of Li_3Bi (1418°K).

The potentials of cells of the type

for compositions of the alloy from pure bismuth to bismuth saturated with NaBi and for temperatures between 520 and 1040°K presented above may be used to show that the partial pressure of sodium above these alloys will be marginal at practical regeneration temperatures (1073–1173°K). If the total pressure is lowered, the same problems associated with the intersection of the liquid-vapor loop and solid-liquid line are again likely to occur. Electrothermal regeneration, which is considered later in this report, is partially favorable, but the temperature coefficient is not very large.

A review of the thermodynamic properties of lead-rich Na-Pb alloys has been given by Hultgren and associates.³³ The activity of sodium in these alloys is fairly high, thereby indicating the possibility of thermal regeneration, but precluding open circuit potentials much above 0.5 volt. The solid compounds in this system melt below 673°K, allowing operation of the system under reduced pressure and fractionation (if necessary).

Other systems which deserve consideration are the K-Bi and Rb-Bi systems. Both systems have compounds at M_3Bi and MBi_3 .³⁴ The melting points of these compounds are: K_3Bi , 944°K; KBi_3 , 838°K; Rb_3Bi , 915°K; and RbBi_3 , 878°K. In these systems, operating difficulties are expected to include the lack of a low-melting electrolyte of the common ion cation—multiple anion

mixture that is thermodynamically stable in the cell environment. The common ion cation electrolyte prevents possible displacement reactions at the electrodes which might polarize the cell. A low temperature for cell operation is desired for two reasons: (1) to keep the vapor pressures of potassium and rubidium within reasonable limits and (2) to lower the solubility of the alkali metal in the electrolyte and thereby prevent excessively high electronic conductivity. High electronic conductivity in the heavy alkali metal-fused salt systems may lead to very low open circuit potentials, which are already expected to be reduced because of the relatively low interaction energies (melting points) of the compounds. It is also to be noted that the presence of two high melting compounds does not allow much freedom of cathode composition if one is to maintain an all-liquid cathode.

The thermal regeneration procedure discussed heretofore involves the distillation of the anode metal from the cathode alloy in the regenerator. It is possible, of course, to regenerate the system by distilling the cathode metal from the alloy to be regenerated. While this method would, in principle, allow for the possibility of obtaining essentially pure cathode metal for cell use, it would be necessary to distill all, or almost all, of the cathode metal from the alloy. This would represent a very high energy input compared with the energy expected to be required in the distillation of reasonably pure anode metal from the cathode alloy whose composition need not be greatly changed during the course of the distillation. Since the distilled metal will condense at a temperature lower than that of the regenerator, the total energy degraded in the distillation of the anode metal from the alloy will be much less than if the cathode metal were distilled. Therefore, the only systems considered for thermal regeneration have been those in which the anode metal is the more volatile component.

c. REGENERATION OF BIMETALLIC CELLS

We consider the bimetallic cell to be a concentration cell without transference. The cell is represented by

where A is the element used as the liquid anode, n is the charge of the A ions in the electrolyte (which will presumably also be liquid in the cell), and $A(B)$ is the cathode alloy of A and a more noble element, B . The only restriction on the choice of the anion or anion mixture represented by X^- is that thermodynamic stability must exist in the cell environment. The choice of the liquid state for electrodes and electrolytes has been justified previously on the basis of less voltage polarization in the cell during its operation as a power-producing

³³ R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys*, John Wiley and Sons, New York, N. Y., 1963, p. 540.

³⁴ G. Gnutzmann and W. Klemm, *Z. Anorg. Allgem. Chem.* **309**, 181 (1961).

device. The cell reaction may be written

The thermodynamic open-circuit voltage of this cell at its operating temperature, T_1 , is:

$$E_{1, \text{ o.c. }} = \frac{-\Delta\mu_A}{nF} = \frac{-RT_1}{nF} \ln X_A - \frac{1}{nF} \Delta\mu_A^E \quad (21)$$

where F is the value of the faraday, $\Delta\mu_A$ is the chemical potential of A in the alloy used as the cathode, R is the gas constant, X_A the atom fraction of A in the alloy, $\Delta\mu_A^E$ is the excess chemical potential of A in the alloy, and the standard state of A is the pure liquid in the cell environment at the cell temperature. The value of n is one, since only alkali metals will be considered for use as the anode element, A . There are many examples of binary mixtures of an alkali metal and more noble metals which are very nonideal solutions; $\Delta\mu_A^E$ is negative and large in magnitude for these alloys.

In regenerating the system, it would be ideal if at a temperature, T_2 , which could be readily attained in the regenerator, the cell potential (Equation 21) would decrease to zero. In principle, one could then obtain pure liquid A at T_2 with no loss of free energy. This might be done by, for example, distilling $A(g)$ from the alloy to form a gas phase at T_2 and at a pressure of p_2^0 , the vapor pressure of $A(\ell)$ at T_2 (assuming ideal behavior of the gas phase). Therefore, the gas could be reversibly condensed at T_2 to the liquid form which could then be returned (through the appropriate heat exchangers) to the cell at T_1 .

Alternatively, one might regenerate by operating the cell in reverse at T_2 . This method we call electrothermal regeneration. Without a consideration of the voltage or current efficiencies in this idealized case, electrothermal regeneration would enable a separation of $A(\ell)$ at T_2 without the problem of reversibly condensing the gas with no loss of free energy.

Let us now consider the reasonable requirements that the cell potential at T_1 be ~ 0.5 volt and drop to zero at a readily attained regeneration temperature, T_2 (for example, 1123°K). Then, over the temperature range of T_1 to T_2 , some average temperature coefficient of cell potential may be calculated:

$$\left(\frac{\partial E}{\partial T}\right)_{X_A, p} = \frac{\int_{T_1}^{T_2} \left(\frac{\partial E}{\partial T}\right)_{X_A, p} dT}{T_2 - T_1} \quad (22)$$

From this value, we can calculate the average partial molar entropy of A in the alloy

$$\overline{\Delta S_A} = F \left(\frac{\partial E}{\partial T}\right)_{X_A, p} \quad (23)$$

and the average excess partial molar entropy of A in the

alloy

$$\overline{\Delta S_A^E} = \overline{\Delta S_A} - R \ln X_A. \quad (24)$$

If X_A is chosen such that $0.1 \leq X_A \leq 0.4$, then $-4.6 \leq R \ln X_A \leq -1.8$. Therefore, if T_1 is 798°K,

$$\overline{\Delta S_A} = -35.5 \text{ eu} \quad (25)$$

and

$$-33.7 \leq \overline{\Delta S_A^E} \leq -30.9 \text{ eu} \quad (26)$$

or if T_1 is reduced to a lower value of 648°K, we find

$$\overline{\Delta S_A} = -24.2 \text{ eu} \quad (27)$$

and

$$-22.4 \leq \overline{\Delta S_A^E} \leq -19.6 \text{ eu} \quad (28)$$

No values of $\overline{\Delta S_A^E}$ such as those in Equations 26 and 28 have been observed in the systems studied thus far. The large, negative values of $\overline{\Delta S_A^E}$ desired indicate the high degree of association which must take place in the cathode alloy for the ideal system postulated. This suggests that future exploratory experiments may be more fruitful with systems which react more strongly than those studied in the past.

Practical regeneration of the bimetallic cell will involve regenerating A at less than unit activity at T_2 because of an insufficiently low temperature coefficient of the cell potential. This means that gaseous A will be formed in the regenerator at a pressure, p_2 , which is less than the vapor pressure, p_2^0 , of $A(\ell)$ at T_2 , but hopefully greater than the vapor pressure of $A(\ell)$ at T_1 , in order that A may be transferred from the regenerator to the cell with minimum difficulty.

The method of regeneration most commonly considered in the past has been thermal or distillative regeneration. One disadvantage of this method is the low vapor pressure of the alloy at T_2 (though one may use less strongly interacting systems to increase this pressure). Another disadvantage is that the vapor phase formed in equilibrium with the $A(B)$ liquid alloy at T_2 is not pure A (one may use a reflux column to separate A from B , but this will lower the efficiency). A final disadvantage to be discussed here is the effect of solid-vapor regions which are anticipated in the complete phase diagrams of several systems (see Section VI.A.3 of this report). This disadvantage may be countered (to some extent, at least) by increasing the pressure in the system in order to raise the vapor-condensed phase loop.

Electrothermal regeneration has not often been considered in the past. One advantage of electrothermal regeneration is that at T_2 , gaseous A may be regenerated at a pressure which is greater than that of the alloy (but

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FIG. VI-11. Electrothermally Regenerated Cell System. (Not shown are mass flow, heat exchanger, or heat source.)

at the cost of some of the electrical energy produced in the cell). A second advantage is that the vapor formed in the electrolyte cell will be relatively pure, excluding possible contamination by electrolyte. A final advantage is that the problems introduced by the vapor-solid regions of the total phase diagram are bypassed.

Principles of Electrothermal Regeneration. Referring to Figure VI-11, let us define the following terms:

- R_L = electrical resistance of useful work load (ohms)
- I_1 = external electron current from cell (amperes)
- $E_{1,o.c.}$ = open circuit potential of cell at T_1 (volts)
- $E_{p,1}$ = polarization potential of cell at T_1 (volts)
- E_1 = output potential of cell at $T_1 = E_{1,o.c.} - E_{p,1}$ (volts)
- $E_1 I_1$ = power output of cell (watts)
- η_L = useful work load conversion efficiency
- $\eta_L (I_1)^2 R_L$ = useful power output (watts)
- $(I_1)^2 R_L$ = power from cell expended in doing useful work (watts)
- $I_1 E_1 - (I_1)^2 R_L$ = power available to converter (for regenerator cell) (watts)
- η_c = converter (for regenerator cell) conversion efficiency
- $\eta_c [I_1 E_1 - (I_1)^2 R_L]$ = power output of converter to regenerator cell (watts)
- I_2 = electron current flow to regenerator cell (amperes)
- $|E_2|$ = absolute value of potential (volts) required to operate the regenerator cell. E_2 is itself negative, indicating a non-spontaneous process.
- $|E_{2,o.c.}|$ = absolute value of open-circuit potential (volts) required to operate the regenerator cell. $E_{2,o.c.}$ also has a negative value

because the process is not spontaneous.

$E_{p,2}$ = polarization potential (volts) of regenerator cell = $|E_2| - |E_{2,o.c.}| \geq 0$.

$I_2 |E_2|$ = power consumed in regenerator cell (watts)

N_A = number of moles of A transferred from anode to cathode in operating cell at T_1 during time t .

N_B = number of moles of A transferred from anode [alloy of $A(B)$] to cathode in regenerator cell during time t .

e_1 = current efficiency of operating cell at $T_1 = I_1 t / N_A F$

e_2 = current efficiency of the regenerator cell at $T_2 = N_B F / I_2 t$

ζ_1 = voltage efficiency of the operating cell = $E_1 / E_{1,o.c.}$

ζ_2 = voltage efficiency of the regenerator cell = $|E_{2,o.c.}| / |E_2|$

If the system is operating in a regenerative cycle, then $N_A = N_B$. Therefore:

$$e_1 e_2 = \frac{I_1}{I_2} \quad (29)$$

Since the power consumed in the regenerator cell must be (neglecting other losses) equal to the power output of the converter to the regenerator cell:

$$\eta_c [I_1 E_1 - (I_1)^2 R_L] = I_2 |E_2|. \quad (30)$$

Multiplying Equation 30 through by $|E_{2,o.c.}| / I_2 |E_2| E_{1,o.c.}$ and using Equation 29, we obtain

$$\eta_c e_1 e_2 \zeta_1 \zeta_2 - \eta_c e_1 e_2 \zeta_2 \frac{I_1 R_L}{E_{1,o.c.}} = \frac{|E_{2,o.c.}|}{E_{1,o.c.}} \quad (31)$$

This equality must be satisfied if the cell system is operating in a continuous regeneration mode.

In accord with the ideas developed previously, we write the regenerator cell reaction as:

If the vapor pressure of $A(\ell)$ at T_2 is p_2^0 , then:

$$|E_{2,o.c.}| = E_{1,o.c.} + \int_{T_1}^{T_2} \left(\frac{\partial E}{\partial T} \right)_{x_A, p} dT - \frac{RT_2}{F} \ln \left(\frac{p_2^0}{p_2} \right) \quad (32)$$

which may be rewritten as:

$$\frac{|E_{2,o.c.}|}{E_{1,o.c.}} = \frac{E_{cell, o.c., T_2}}{E_{1,o.c.}} - \frac{RT_2}{FE_{1,o.c.}} \ln \left(\frac{p_2^0}{p_2} \right) \quad (33)$$

where $E_{\text{cell, o.c.}, T_2}$ is the open-circuit cell potential (volts) of the cell when operated at T_2 .

Combining Equations 31 and 33:

$$\eta_{\text{ce}} e_1 e_2 \xi_1 \xi_2 - \eta_{\text{ce}} e_1 e_2 \xi_2 \frac{I_1 R_L}{E_{1, \text{o.c.}}} = \frac{E_{\text{cell, o.c.}, T_2}}{E_{1, \text{o.c.}}} - \frac{RT_2}{FE_{1, \text{o.c.}}} \ln \left(\frac{p_2^0}{p_2} \right) \quad (34)$$

An Example of Electrothermal Regeneration. For the bimetallic cell reaction:

with $T_1 = 550^\circ\text{C}$ and $X_A =$ atom fraction sodium in bismuth = 0.4, it has been shown in laboratory studies of a cell with a solid NaCl electrolyte that $E_{1, \text{o.c.}} \simeq 0.515$ volt. By extrapolating data (from the temperature region below 780°C) to $T_2 = 850^\circ\text{C}$, one obtains

$$E_{\text{cell, o.c.}, T_2} = 0.455 \text{ volt.}$$

Since the vapor pressure of pure sodium is 435 mm Hg at 850°C and 12 mm Hg at 550°C , the pressure, p_2 , of sodium formed in the regenerator cell at 850°C will be taken to be the lower value, 12 mm Hg. Using these data and Equation 34, one obtains:

$$\eta_{\text{ce}} e_1 e_2 \xi_1 \xi_2 - \eta_{\text{ce}} e_1 e_2 \xi_2 \frac{I_1 R_L}{0.515} = 0.223 \quad (35)$$

Equation 35 shows that the voltage drop across the useful work load in the external circuit of the cell must be adjusted so as to satisfy this equation.

d. THERMODYNAMICS OF THE LITHIUM-TELLURIUM SYSTEM

The thermodynamic properties of the binary lithium-tellurium system have been studied using electromotive force measurements of a concentration cell without transference. The reference electrode (anode) for the cell consisted of a two-phase mixture of $\text{Li}_3\text{Bi}(\text{s})$ and a bismuth-rich liquid alloy of lithium and bismuth. The second electrode (cathode) was an alloy of lithium and tellurium contained in a porous BeO crucible. The electrolyte was the eutectic 30 m/o LiF-70 m/o LiCl.

Lithium from the reference electrode was added coulometrically to the tellurium at a constant current. The concentration of lithium in the tellurium was calculated directly from the number of coulombs used.

The behavior of the observed cell potential vs. concentration of lithium in tellurium is shown in Figure VI-12. The discontinuity at 0.39 atom fraction lithium taken to indicate the point at which the alloy became saturated with solid Li_2Te .

The observed cell potentials were converted by means of the reference potential at 798°K (which was previ-

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FIG. VI-12. Voltage-Composition Behavior of the Cell: Li (in Bi(ℓ)) saturated with solid Li_3Bi /LiCl-LiF/Li in Te at 798°K .

TABLE VI-6. CALCULATED EXCESS CHEMICAL POTENTIAL OF Li IN Te AT 798°K

Cumulative Total Coulombs Added	Calculated Overall Concentration Li in Te (atom fraction)	Observed Cell Potential (volts)	$-\Delta\mu_{\text{Li}}^E$ (cal/mole)
660	0.056	1.0912	36860
1260	0.10	1.0573	37025
1860	0.14	1.0392	37150
2460	0.18	1.0244	37181
3060	0.22	1.0175	37300
3660	0.25	1.0075	37289
4460	0.29	0.9965	37263
5260	0.32	0.9854	37190
6060	0.35	0.9756	37112
6860	0.38	0.9686	37075
7860	0.41	0.9666	— ^a
8860	0.44	0.9644	— ^a
9860	0.47	0.9646	— ^a
12060	0.52	0.9644	— ^a

^a Two-phase region existed at this overall composition.

ously determined³⁵) to those for the cell:

The standard states are taken to be $\text{Li}(\ell)$ and $\text{Te}(\ell)$ in the cell environment (saturated with electrolyte). From this, the excess chemical potential of lithium in tellurium at the cell temperature (798°K) has been calculated. The results are shown in Table VI-6. The average excess chemical potential, $\Delta\mu_{\text{Li}}^E$, is $-37,145 \pm 135$ cal/mole. A least squares fit of the data to a quadratic function of X_{Li} , the atom fraction Li in Te, resulted in the equa-

³⁵ M. S. Foster, S. E. Wood, and C. E. Crouthamel, *Inorg. Chem.* **3**, 1428 (1964).

tion:

$$\Delta\mu_{\text{Li}}^{\text{E}} = -36568 - 5736 X_{\text{Li}} + 11676 X_{\text{Li}}^2, \text{ cal/mole} \quad (36)$$

which has a standard deviation of 29 cal/mole.

The cell reaction may be written as:

for an overall electrode composition of $X_{\text{Li}} \geq 0.39$. For this reaction we may write

$$\Delta G = -FE = \frac{1}{2} \Delta G_f^\circ - \frac{1}{2} RT \ln X_{\text{Te}} - \frac{1}{2} \Delta\mu_{\text{Te}}^{\text{E}} \quad (37)$$

where X_{Te} is the atom fraction Te in the Li-Te liquid saturated with $\text{Li}_2\text{Te}(\text{s})$, $\Delta\mu_{\text{Te}}^{\text{E}}$ is the excess chemical potential of tellurium in the same liquid, ΔG_f° is the standard free energy of formation of $\text{Li}_2\text{Te}(\text{s})$ from the elements, F is the value of the faraday, and R is the gas constant. The value of $\Delta\mu_{\text{Te}}^{\text{E}}$ was calculated from the Gibbs-Duhem relationship. A constant value of $\Delta\mu_{\text{Li}}^{\text{E}}$ gave $\Delta\mu_{\text{Te}}^{\text{E}} = 0$, whereas the use of Equation 36 yielded $\Delta\mu_{\text{Te}}^{\text{E}} = -50$ cal/mole. Using either value, the standard free energy of formation of $\text{Li}_2\text{Te}(\text{s})$ at 798°K was calculated to be -77.9 kcal/mole with a standard deviation estimated at 0.4 kcal/mole.

3. Liquid-Vapor Equilibrium Studies on the Sodium-Bismuth System (A. K. FISCHER, S. JOHNSON)

To design the regeneration cycle of a sodium-bismuth cell which is to be regenerated by a distillation process, it is necessary to know some details of the pertinent liquid-vapor equilibria. Under certain conditions, solid-vapor equilibria may also occur and would have disruptive consequences for an operating cell. Therefore, the conditions of operation which give rise to these undesirable solid-vapor equilibria must be known in order to avoid them. Data which bear on these problems have been obtained and will be discussed after the relevant phase diagram considerations have been outlined. A full discussion may be found in *Regenerative Electrochemical Systems*.²

For a two-component system, such as the sodium-bismuth system, the phase relations may be represented on a three-dimensional diagram with pressure, temperature, and composition being the three Cartesian coordinates. At a constant pressure, a two-dimensional temperature-composition diagram is obtained by passing a plane through the three-dimensional diagram at the selected pressure value. Most of our attention is focused on such temperature-composition diagrams.

e. SOLUBILITY OF INTERMETALLIC COMPOUNDS IN FUSED SALTS

Previous studies of the solubilities of intermetallic compounds in molten LiCl-LiF have shown that a greater solubility exists for Li_2Te than for Li_3Bi (see ANL-6900, p. 313). Qualitatively, solution color indicated that the solubilities of Li_7Sn_2 or $\text{Li}_{10}\text{Pb}_3$ were probably less than that of Li_3Bi . This suggests that as one approaches the transition metal series, the trend is to lesser solubilities of intermetallic compounds in fused salts. Indeed, one might predict this on the basis that, as one approaches the transition metal series, the bond formed is less ionic in character. The latter is indicated by the lower melting points of the most stable intermetallic compounds (compared with the melting points of the elements).

To test this hypothesis, the solubility of LiHg (m.p. 595°C) in molten LiCl-LiF at 518°C was determined. LiHg was prepared from the elements and activated by neutron bombardment for use in this study. By gamma-counting the radioactive ^{203}Hg in a sample of LiCl-LiF which had been equilibrated at temperature with the activated LiHg, the solubility of LiHg in LiCl-LiF eutectic at 518°C was estimated to be 8.6×10^{-5} m/o. This is much less than the solubility of Li_2Te , which is estimated to be ~ 3 m/o at the same temperature.

All bimetallic systems which are candidates for a regenerative cell show the feature of compound formation. This characteristic is taken as a necessary condition indicating that the cell voltage will be better than just that of a concentration cell. A generalized phase diagram showing this feature, as well as the liquid-vapor loop ($L + V$), is presented in Figure VI-13, where A is the anode component, C is the cathode component, and AC is the compound. The $L + V$ loop, taken to be of the simple ascendant type, shows the boiling point of A to be lower than that of C , a relationship which would be true of all useful bimetallic systems involving an alkali metal, except, in some cases, lithium.

In general, the height of the $L + V$ loop relative to the $AC + L$ regions is a function of pressure, whereas the liquid-solid regions are essentially insensitive to pressure changes. At successively lower pressures, the $L + V$ loop will approach closer and closer to the $AC + L$ hump, and at some specific pressure the loop and the hump will be tangent to each other. If an even lower pressure is considered, the two areas will, in

effect, overlap and the phase diagram will appear as in Figure VI-14. The important feature of this diagram is that a new area has appeared, labelled $V + AC$, which represents equilibria between vapor and solid AC . This means that if a regenerative cell is operated at a pressure corresponding to a temperature-composition phase diagram such as is shown in Figure VI-14, the deposition of solid from the vapor phase is possible in a certain temperature region in the regenerator. Such deposition of solid would threaten to plug the regenerator. To avoid this problem, it is necessary to select a cell operating pressure high enough so that the phase diagram describing the system shows the loop and the hump separated. A suitably high operating pressure may be achieved by selecting a sufficiently high condensation temperature in the regenerator for a given composition of A -enriched distillate. It has been the object of the research reported herein to determine the minimum pressure necessary to effect the separation of the two regions of the sodium-bismuth phase diagram and to obtain information on the composition of the vapor phase in equilibrium with a given liquid phase.

a. EXPERIMENTAL METHODS AND DATA

Two types of measurements have been made: total pressure determinations and vapor composition determinations. The total pressure measurements have been made by either the quasi-static (Rodebush-Dixon)³⁶ technique or by a boiling-point method. These measurements have been performed on selected liquid compositions over a range of temperatures. The vapor composition measurements have been made by the transpiration (carrier gas) technique; selected liquid compositions have been studied at a fixed temperature of 900°C.

The quasi-static technique is unfamiliar to most chemists and the adaptation of the original Rodebush-Dixon method which we have used deserves description.

The apparatus embodying our adaptation of the Rodebush-Dixon technique is schematically drawn in Figure VI-15. To the floor flange of an inert-atmosphere glovebox (1), there is bolted a furnace well (2). Inside the well is placed the sample chamber (3) which has two tubes welded into its roof. These tubes extend up into the cool zone of the well. Into one tube is inserted a thermocouple well (4) which dips just below the surface of the liquid sample. Into the other tube, a 0.25-in. OD tube (5) is inserted with the open lower end just above the roof level of the sample chamber. This tube is connected with the pressure control and measuring system outside the box by means of a vacuum coupling to a tube which leads through the glovebox wall. The well is also connected to the pressure control and measuring system

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FIG. VI-13. General Temperature-Composition Diagram for a Two-Component System which Shows Compound Formation.

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FIG. VI-14. General Temperature-Composition Diagram for a Two-Component System at a Pressure Low Enough to Give Rise to a Vapor Plus Solid Region.

through the side-arm on the well. The pressure control and measuring system contains a vacuum pump (6), valves (7 through 13), and the pressure measuring device (14). The last is a Texas Instruments fused quartz precision pressure gauge. The quartz spiral in

³⁶ W. H. Rodebush and A. L. Dixon, *Phys. Rev.* **26**, 851 (1925).

FIG. VI-16. Total Vapor Pressure over Various Sodium-Bismuth Alloys.

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behavior of a sample of Na_3Bi was examined. Sodium volatilized preferentially, leaving increasingly bismuth-rich residues. In the temperature region from 275 to 300°C, for a system of 75 a/o sodium, the sodium activity coefficients were in the neighborhood of 10^{-2} . The free energy of formation of Na_3Bi at 690°K (417°C) was derived from the mass spectrographic peak heights and refers to the reaction:

A transpiration result not included in Table VI-7 is that for the vapor composition over a melt of 75 a/o sodium at 900°C; the vapor is 98.7 ± 0.3 a/o sodium. It will be seen, this is a region in which the total pressure is very sensitive to slight changes in composition of the melt. This makes it difficult to obtain consistent pressure data, but the difficulty does not apply to the

TABLE VI-7. RESULTS FROM TRANSPIRATION EXPERIMENTS FOR TWO SODIUM-BISMUTH MELTS AT 900°C

	20 a/o Na-80 a/o Bi	40 a/o Na-60 a/o Bi
p_{Na} (mm)	0.82	4.7
p_{Na_2} (mm)	2.3×10^{-4}	8.0×10^{-3}
p_{Bi} (mm)	0.24	0.14
p_{Bi_2} (mm)	0.17	5.6×10^{-2}
$P (= \sum p_i)$ (mm)	1.2	4.9
γ_{Na}	5.7×10^{-3}	1.7×10^{-2}
γ_{Bi}	0.67	0.52

vapor composition, which is relatively insensitive to slight changes in the liquid composition at this point.

b. DISCUSSION

A noteworthy feature of the total pressure plots for the 75 and 80 a/o sodium systems is the break in the

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FIG. VI-17. Schematic Temperature-Composition Phase Diagram Sequence for the Sodium-Bismuth System at Decreasing Pressures. (Pressures decreasing from a to d.)

lines (see Figure VI-16). This feature may be explained in terms of the different temperature-composition phase diagrams which come into play as the pressure is lowered. An appropriate sequence of possible schematic diagrams is shown in Figure VI-17. Part a of Figure VI-17 shows a phase diagram at a pressure just high enough to separate the $V + L$ and $L + \text{Na}_3\text{Bi}$ regions; the regions are almost tangent at point t . If we are measuring the boiling point of a liquid of 75 a/o sodium, we are at point l on Figure VI-17a. If the pres-

sure is lowered and we measure a boiling point for the same liquid, we are at point l on Figure VI-17b. At this point, the pressure is low enough so that the regions of the phase diagram have overlapped to form the region $V + \text{Na}_3\text{Bi}$ (a solid-vapor coexistence region), but the system being measured is still outside of this region. Eventually, the pressure can be lowered enough so that the boiling point of liquid l equals the melting point of Na_3Bi ; the diagram shown in Figure VI-17c corresponds to this pressure. [Up to this point, we have been discussing the total vapor pressure plot of the two-component, two-phase system, 75 a/o Na-25 a/o Bi. If $\log P$ (P is total pressure) is plotted against $1/T$ for this system, a straight line is obtained which corresponds to the part of the 75 a/o sodium line above the break in Figure VI-16.] If the pressure is reduced still more, a phase diagram like Figure VI-17d comes into play and now a liquid of 75 a/o sodium-25 a/o bismuth can no longer exist even though the overall system composition is still the same. Instead, we have a three-phase system of vapor, liquid l , and solid Na_3Bi which is represented by g , the upper isotherm in Figure VI-17d. Boiling point measurements at pressures lower than those which correspond to the diagram shown in Figure VI-17c are actually measuring the vapor pressure over solid Na_3Bi . This situation is reflected in that portion of the 75 a/o sodium line below the break in Figure VI-16.

Comparison of the 75 and 80 a/o sodium pressure plots, shown in Figure VI-16, below the breaks reveals that, at a given temperature, the total pressures are markedly different, despite the fact that solid Na_3Bi is a phase common to both cases. The explanation can be given in terms of Figure VI-17. We may consider two cases, in one of which the overall composition is to the right of point t in Figure VI-17a, and in one of which the overall composition is to the left of t . In other words, the compositions are poorer and richer in sodium than is the composition corresponding to the point of tangency between the $V + L$ loop and the $L + \text{Na}_3\text{Bi}$ region. As the pressure is lowered and overlap of the regions occurs, the point corresponding to the sodium-poorer composition on the $V + L$ liquidus follows down on the liquidus until the point touches the $L + \text{Na}_3\text{Bi}$ region. At this time, solid Na_3Bi appears and the system is represented by the upper isotherm, g , of Figure VI-17b. For the case in which the overall composition is to the left of t (sodium-richer), a lowering of pressure also eventually results in the appearance of solid Na_3Bi , but in this case, the three-phase equilibrium is represented by the lower isotherm, h , Figure VI-17b. Since a temperature-composition diagram is, in its qualitative features, the pressure-composition diagram turned upside down, we can see

that the pressure-composition (constant temperature) diagram corresponding to Figure VI-17b is Figure VI-18. From the latter diagram, it is apparent that the incongruently vaporizing compound, Na_3Bi , can participate in two different three-phase equilibria at two different pressures at the same temperature. This explains the results for the 75 and 80 a/o sodium systems. From the difference between the two curves, one concludes that the point of tangency, t , occurs between 75 and 80 a/o sodium.

Another noteworthy feature of the 75 and 80 a/o sodium pressure plots in Figure VI-16 is that the direction of the break is opposite in the two cases. Below pressures corresponding to the break, as the pressure drops, the liquid composition shifts in the bismuth-enriching direction for those systems represented by the upper isotherm in Figure VI-17; the 75 a/o sodium system is an example. Since bismuth is the less volatile component, the pressure for a given temperature in the $\log P$ vs $1/T$ plot is depressed; a more endothermic vaporization process results. These expectations are borne out by the observed data as shown in Figure VI-16. On the other hand, for a system described by the lower isotherm, such as the 80 a/o sodium system, the liquid composition is shifting in the sodium-enriching direction as the pressure drops. Since the more volatile component is gaining in concentration, the pressure for a given temperature in the $\log P$ vs $1/T$ plot will tend to decrease less with decreasing temperature. Such a tendency corresponds to a less endothermic process and is reflected in the direction of the break for this plot in Figure VI-16.

A final feature which may be noted in Figure VI-16 is that the temperature at which the break occurs is the temperature at which contact is made between the point corresponding to the initial system composition on the liquidus of the $L + V$ loop and the $L + \text{Na}_3\text{Bi}$ solubility curve. This fact enables us to trace out the $L + \text{Na}_3\text{Bi}$ solubility curve if enough measurements on enough systems are made. The idea is basically that of thermal analysis, but is based on liquid-vapor equilibria, rather than solely on condensed phase equilibria. From the limited number of measurements we have made, it has become apparent that the phase diagram in Hansen and Anderko²⁷ for the sodium-bismuth system is in error. This diagram, based on work done in the early decades of this century, shows the melting point of Na_3Bi to be 775°C. The 75 a/o sodium curve in Figure VI-16 indicates that the melting point of Na_3Bi is 842°C. A cooling curve was subsequently obtained which showed the melting point to be at least 838°C. The agreement between the thermal analysis and the break in the vapor pressure curve is excellent,

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FIG. VI-18. Pressure-Composition Diagram Corresponding to Fig. VI-17b.

considering the uncertainty in locating the point at which two lines intersect obliquely.

The total vapor pressure and the transpiration data were combined in order to construct a pressure-composition diagram for 900°C, shown in Figure VI-19. The temperature of 900°C was chosen early in the program as a conceivable regeneration temperature. Figure VI-19 shows that the total pressure drops very rapidly in the composition region corresponding to 75 a/o sodium and thus reflects the influence of compound (Na_3Bi) formation. For a likely composition of material to be returned to the cathode, e.g., 75 a/o bismuth, the vapor composition is seen to be about 10 a/o bismuth. This rather high bismuth content would appear in the anode if the vapor is condensed directly. If purer sodium is to be returned to the anode, some rectification would be necessary.

Another consequence of Figure VI-19 for the regenerative cell may be seen by considering the shape of the temperature-composition curve. This shape would be obtained approximately by inverting Figure VI-19, and is drawn as the $V + L$ loop of Figure VI-17a. Contact between the $V + L$ loop and the $L + \text{Na}_3\text{Bi}$ region occurs on the sodium-rich side of the $L + \text{Na}_3\text{Bi}$ region. From the break of the 80 a/o sodium curve in Figure VI-16 we see that a pressure of at least 240 mm will be needed to separate the two areas of the diagram. This means that the ends of the $V + L$ loop, i.e., the boiling points of pure sodium and pure bismuth at 240 mm, would have to be at 770°C and at about

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FIG. VI-19. Pressure-Composition Diagram for the Sodium-Bismuth System at 900°C.

1350°C, respectively. For likely cathode compositions, the regeneration temperature would be about 1200 to 1300°C. At the present time, it is probably possible to supply such a regeneration temperature. However, techniques and materials are not available to construct a regenerator which would resist the corrosive action of bismuth at such a high temperature. For this reason, it is felt that full development of a sodium-bismuth regenerative cell must await development of the necessary high-temperature technology.

c. OTHER CANDIDATE SYSTEMS FOR A BI-METALLIC REGENERATIVE CELL

Earlier in the discussion it was noted that compound formation is a necessary feature of a bimetallic system if the cell voltage is to be better than that of a concentration cell. There are two other requirements: (1) the system pressure must be chosen to avoid overlap of the compound-formation region of the phase diagram with the liquid-vapor loop and (2) the boiling

TABLE VI-8. POSSIBLE REGENERATIVE CELL SYSTEMS

System	Highest Melting Compound and its m.p. (°C)	Temp. (°C) at which vap. press. = 1 mm		Temp. (°C) at which vap. press. = 10 mm	
		Low-b.p. component	High-b.p. component	Low-b.p. component	High-b.p. component
K-Tl	KTl, 335	325	825	425	1000
Na-Pb	Na ₂ Pb, 400	450	1000	550	~1200
Na-Tl	NaTl, 305	450	825	550	1000

points of the two components should be well separated to facilitate regeneration by distillation. Together, these requirements constitute a test to screen candidate systems.

This test has been applied by listing all metals and metalloids which melt below 600°C. The list included Bi, Cd, Cs, Ga, Hg, In, K, Ti, Na, Pb, Rb, Se, Sn, Te, Tl, and Zn. By consulting Hansen and Anderko³⁷ the pairs which form compounds melting below 600°C were selected. From these pairs, those were picked for which the low boiling point component, at a pressure between 1 and 10 mm, had a boiling point above the melting point of the highest melting point compound.

Amalgam systems were rejected for the following reasons: Mercury is the noble member of the pair in each case so that it would be the cathode metal and would also be the major component of the cathode mixture. Since mercury is also the low boiling point member of the pair, the major component would have to be distilled in regeneration. This is an inefficient operation compared with distilling the minor component.

The systems Bi-Te, Ti-Zn, Se-Tl, and Te-Tl were rejected because of their corrosive nature. The systems Na-Cd, Ti-Tl, and Pb-Tl were rejected because the boiling points of the components are too close to permit easy separation by distillation.

The three remaining systems, K-Tl, Na-Pb, and Na-Tl, are compared in Table VI-8. The sodium-containing systems have an advantage over the K-Tl system in respect to the electrolyte that would be needed; a mixture of sodium halides can provide an electrolyte with a lower melting point than a mixture of potassium halides. Of the two sodium-containing systems, Na-Pb and Na-Tl, the Na-Pb system has an advantage in the somewhat greater spread between the boiling points of its components. It is suggested, therefore, that on the basis of the above considerations the preferred order of study of new systems should be Na-Pb, Na-Tl, and K-Tl.

³⁷ M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

B. REGENERATIVE EMF CELLS—ENGINEERING STUDIES (J. C. HESSON)

Engineering studies have continued with the purpose of investigating the feasibility of developing a practical thermally regenerative emf cell, ultimately capable of being coupled to a reactor, isotope unit, or other heat source. Bimetallic cells are being studied, and experimental work has been conducted on sodium-bismuth and sodium-lead bimetallic systems.

A summary of the engineering thermodynamic and efficiency studies of bimetallic cell systems (sodium-bismuth, sodium-tin, sodium-lead, and lithium-tin) and the lithium hydride cell system has been accepted for publication.²

1. Physical Properties of Electrolytes and Bimetallic Mixtures

(H. SHIMOTAKE, J. TRALMER)

The densities, viscosities, and surface tensions of electrolytes and bimetallic mixtures are needed in order to compute or estimate volumes, liquid levels, flow rates, and surface effects for the engineering design of bimetallic cell and regenerator apparatus. Although many physical properties are available in the literature for pure salts and metals, very little information is available for mixtures of various salts and for alloys or mixtures of metals for temperatures at which regenerative cells are expected to operate. In many cases, the actual properties of mixtures differ greatly from the computed values based on additive volumes of the components. These determinations were initiated during the preceding reporting period (ANL-7055, p. 225) and have been continued during this period.

Determinations of liquid densities were made by measuring the depth of a known weight of the material in a calibrated crucible. Viscosity determinations of the molten electrolyte were made by measuring the

time required for the liquid contained between upper and lower measuring electrode levels in a calibrated cup to flow out through a capillary tube in the bottom of the cup. Surface tension determinations were made by measuring the force required to detach a calibrated annulus ring from the surface of the liquid.

The physical properties of the molten salt eutectic 17.7 w/o NaCl-6.1 w/o NaF-76.2 w/o NaI (31.6 m/o NaCl-15.2 m/o NaF-53.2 m/o NaI) were measured at temperatures up to 800°C. This salt mixture, which has a melting point of about 535°C, is used as an electrolyte for bimetallic cells having sodium anodes. The density, viscosity, and surface tension were found to vary as follows with temperature:

$$\text{density, g/cc} = 3.05 - 0.0009 T \text{ (540 to } 800^\circ\text{C)}$$

$$\text{viscosity, centipoises} = 3.40 - 0.003 T \text{ (560 to } 800^\circ\text{C)}$$

$$\text{surface tension, dynes/cm} = 136 - 0.06 T \text{ (550 to } 750^\circ\text{C)}$$

where T is the temperature in °C.

The densities of sodium-bismuth alloys containing 0, 10.4, 20, 30, 40, and 50 a/o sodium were measured at temperatures from near the alloy freezing points to 800°C. The densities were found to vary from about 10.1 to 5.3 g/cc, as shown in Figure VI-20.

The densities of sodium-lead alloys containing 0, 10, 20, 30, 41, and 50 a/o sodium were measured at temperatures from near the alloy freezing point to 700 or 800°C. The densities were found to vary from about 10.7 to 5.6 g/cc, as shown in Figure VI-21.

The surface tension values of sodium-bismuth alloys containing 30, 40, 45, and 50 a/o sodium were measured at temperatures from about 400 to 700°C. Over this range of composition and temperature, the surface tension showed little variation (242 to 260 dynes/cm). The results are compared in Figure VI-22 with values given in the literature for the pure components.

The measured densities of the sodium-bismuth and

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FIG. VI-20. Densities of Sodium-Bismuth Alloys.

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FIG. VI-21. Densities of Sodium-Lead Alloys.

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FIG. VI-22. Surface Tensions of Sodium-Bismuth Alloys.

sodium-lead alloys (Figures VI-20 and VI-21) are considerably greater than densities computed by additive volumes of the pure metals. On the other hand, the measured densities of the NaCl-NaF-NaI eutectic are very nearly the values computed by additive volumes.

2. Experimental Bimetallic Cells (J. HESSON, G. ROGERS)

a. SODIUM-BISMUTH CELL

The closed sodium-bismuth cell apparatus with 3-in. dia. electrode sections, which was described previously in ANL-7055, p. 226, is still in operation. The cell apparatus does not include a thermally operated regenerator, but is periodically recharged by reversing the current. As of December 9, 1965, it has been in operation for 1 year at 535 to 650°C with no evidence of deterioration of the cell components.

b. SODIUM-LEAD CELL

A sodium-lead bimetallic cell apparatus with attached thermal regenerator has been assembled and operated. In this cell, sodium contained in the cathode metal is distilled in the thermal regenerator and returned to the anode. The cell proper is constructed with a frozen electrolyte-silicone rubber insulator-seal, similar to that of the sodium-bismuth cell now in operation as a battery (see above). The regenerator is constructed of stainless steel and is similar to the regenerator used to demonstrate the feasibility of regenerating sodium from lead (see ANL-7055, p. 227). The cell has 3-in. dia. anode and cathode sections, and the regenerator has

a 1-in. dia. evaporation surface. This cell system was charged with 240.1 g of electrolyte (6.1 w/o NaF-17.7 w/o NaCl-76.2 w/o NaI) and 532.7 g of a 70 a/o lead-30 a/o sodium alloy before being placed in operation.

Nine runs have been made in which the regenerator was used to distill sodium for operating the cell. The runs varied in length from 2 to 7 hr for a total operating time of 36½ hr. The cell was operated at temperatures ranging from 543 to 600°C; the regenerator was operated at temperatures ranging from 825 to 875°C and at pressures from 5.7 to 9 mm Hg. The cathode metal (sodium-lead) was circulated to and from the regenerator thermally.

At 875°C and 8 mm Hg pressure the regenerator furnished sufficient sodium to operate the cell continuously at 7.5 amperes; at 850°C and 7 mm Hg pressure, 5 amperes; and at 825°C and 6 mm Hg pressure, 2.5 amperes.

Cell open-circuit voltages as high as 0.41 volt at 575°C were noted during the runs, thereby indicating that the regenerator had reduced the amount of sodium in the cell cathode from the original value of 30 a/o to about 18 a/o.

Typical cell-voltage versus cell-current performance at a cell temperature of 575°C (regenerator at 875°C and 8 mm Hg pressure) was as follows:

Cell voltage (volt)	Cell Current (amp)
0.39	0
0.355	1
0.28	2.5
0.165	5
0.055	7.5

The limiting factor in this system at present seems to be the sodium-evaporating capacity of the regenerator, which is dependent upon the evaporating surface area

and temperature. The regenerator evaporator surface area is only 0.78 sq in., while the cell electrode cross-sectional area is 7.0 sq in. The effective anode area of the cell is, to a large extent, determined by the quantity of sodium in the anode. The cell resistance is in turn determined by the electrolyte temperature and thickness and by the anode and cathode effective areas. The cell voltage-current characteristics shown above can be improved by reducing the electrolyte thickness and by furnishing more sodium to the cell by means of a regenerator with larger capacity. Future studies will be concerned with determining a ratio of evaporator surface area to cell electrode cross-sectional area that will give optimum performance of the entire cell system.

3. Non-Faradaic Sodium Transfer (J. HESSON, H. SHIMOTAKE, J. ALLEN)

Studies of irreversible or non-faradaic transfer of sodium, i.e., without corresponding production of cell current, in bimetallic cells have been continued. Previously (see ANL-6925, p. 245), the non-faradaic transfer was defined as

$$q_1 = \frac{Q - AIt}{t} \quad (40)$$

where

q_1 = non-faradaic transfer, g/hr

Q = total amount of sodium transferred from anode to cathode during run, g

A = $(3600)(23)/96,500 = 0.857$ g/(amp)(hr)

I = average cell current, amp

t = time of run, hr.

Experimental data for a sodium-bismuth cell showed that the non-faradaic transfer increased as the cell temperature was increased and decreased as the cell current was increased. Figures VI-23 and VI-24 summarize the data obtained with a cell that was larger than that used in work reported in ANL-6925. In the present work, the NaI-NaCl-NaF eutectic was used as electrolyte. It will be noted that the cell electrolyte conductance and the irreversible sodium transfer rate increase with temperature in a similar manner.

A theoretical differential equation was developed for irreversible transfer in bimetallic cells with parallel electrodes of equal areas, where there are no convection currents in the electrolyte. The equation is, for $Z = 1$,

$$q = - \left\{ \left[\frac{FD\rho}{M} X + \frac{k_e}{F_1} \frac{k_i}{k_i + k_e} R_g T \right] \frac{d \ln(\gamma X)}{dl} - \frac{k_e}{k_i + k_e} I \right\} \quad (41)$$

Symbols for the above and following equations are

defined as follows:

A = area of each electrode, cm^2

a = activity of dissolved sodium atoms in the fused salt electrolyte = γX , dimensionless

B = a constant

D = coefficient of diffusivity of sodium atoms in electrolyte—very dilute solution ($X \rightarrow 0$), cm^2/sec

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FIG. VI-23. Irreversible Sodium Transfer Rate and Conductance in an Open-Circuit Sodium-Bismuth Cell as a Function of Temperature. (Electrolyte: NaI-NaCl-NaF eutectic.)

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FIG. VI-24. Irreversible Sodium Transfer as a Function of Cell Current in a Sodium-Bismuth Cell at 590°C. (Cell Dimensions: Anode Diameter: 2.3 cm; Cathode Diameter: 2.2 cm; Electrolyte: NaI-NaCl-NaF eutectic.)

F = Faraday's constant, 96,500 coulombs/equiv.
 F_1 = Faraday's constant, 23,060 cal/(equiv.) (volt)

I = cell current, amp/cm²

I_0 = value of I when $q = 0$

k_e = electronic conductivity of electrolyte, 1/(ohm)(cm)

k_i = metal anode ion conductivity of electrolyte, 1/(ohm)(cm)

$K_e = k_e/X$, 1/(ohm)(cm)

L = distance of cathode from anode, cm

ℓ = distance from anode, cm

M_a = molecular weight of anode metal, g/mole

M = molecular weight of electrolyte, g/mole

$q = q_1 F / 3600 M_a A$ = anode metal irreversible transfer in equivalent amperes per sq cm, where $Z = 1$ for the anode metal.

q_0 = value of q at $I = 0$ (cell open circuit)

R = cell electrolyte resistivity = $1/(k_i + k_e)$, ohm cm

R_g = gas constant, 1.987 cal/(°K)(mole)

T = temperature, °K

X = mole fraction anode metal atoms dissolved in electrolyte, dimensionless

X_A = value of X at anode, ($\ell = 0$), dimensionless

X_C = value of X at cathode ($\ell = L$), dimensionless

Z = electrochemical value of anode metal ($Z = 1$ for alkali metals)

γ = activity coefficient of anode metal dissolved in electrolyte

ρ = density of electrolyte, g/cc.

Subscripts A and C refer to anode and cathode, respectively.

If it is assumed that γ , M , ρ , k_i , and D are independent of X and that K_e is constant, Eq. 41 can be solved. The reasoning that forms the basis for accepting these assumptions follows.

The solubility of sodium in NaI-NaCl-NaF eutectic has been determined (ANL-6925, p. 239) and is:

Temp (°C)	Sodium Solubility (mole fraction)
550	0.0031
600	0.0048
650	0.0068
700	0.0094

If we assume that X_A is equal to the solubility of sodium in the electrolytes, that $a = \gamma X = 1$ for the sodium anode, and that $\ln \gamma = (1 - X)^2 B$ we find that

$$\ln \gamma_{X \rightarrow 0} = \frac{1}{(1 - X_A)^2} \ln \gamma_A \quad (42)$$

$$= \frac{1}{(1 - X_A)^2} \ln \left(\frac{1}{X_A} \right)$$

Thus, because of the low value of the solubility of

sodium in the NaI-NaCl-NaF eutectic at 550°C (which is near the normal cell operating temperature), γ is nearly constant; also, M , ρ , k_i , and D are essentially independent of X . From Bredig,³⁸ the assumption that $K_e = k_e/X$ is constant appears reasonable. The equations were derived for no convection currents in the electrolyte; however, convection currents may exist. This would result in a decrease in the effective distance L .

The solution of the differential equation for the boundary conditions, $X = X_A$ at $\ell = 0$ and $X = X_C$ at $\ell = L$, although not explicit in q or I , is

$$q + I = \left[\frac{k_i R_g T}{F_1 L} + \frac{FD\rho}{LM} \frac{k_i}{K_e} \frac{I}{q + I} \right] \ln \frac{qk_i + (q + I)K_e X_A}{qk_i + (q + I)K_e X_C} + \frac{FD\rho}{LM} (X_A - X_C). \quad (43)$$

For the conditions $q = q_0$ at $I = 0$, and $I = I_0$ at $q = 0$,

$$q_0 = \frac{k_i R_g T}{F_1 L} \left[\ln \frac{k_i + K_e X_A}{k_i + K_e X_C} \right] + \frac{FD\rho}{LM} (X_A - X_C) \quad (44)$$

$$I_0 = \left[\frac{k_i R_g T}{F_1 L} + \frac{FD\rho}{LM} \frac{k_i}{K_e} \right] \ln \frac{X_A}{X_C} + \frac{FD\rho}{LM} (X_A - X_C) \quad (45)$$

Since D , X_A , and k_i increase with temperature, the equations indicate that q_0 and I_0 should increase with temperature. This has been observed for q_0 . The equations indicate that q should decrease with cell current increase, which has also been observed.

These theoretical studies have indicated that the cell voltage loss (thermodynamic potential, E_o , minus terminal voltage, E) due to cell current flow and irreversible transfer is

$$E_o - E = -\Delta E = \frac{1}{k_i} \left[qL + IL - FD \frac{\rho}{M} (X_A - X_C) \right] \text{ volts} \quad (46)$$

and at open circuit ($I = 0$, $q = q_0$), cell voltage loss is

$$\begin{aligned} E_o - E_{oc} &= -\Delta E_{oc} \\ &= \frac{1}{k_i} \left[q_0 L - FD \frac{\rho}{M} (X_A - X_C) \right] \\ &= \frac{R_g T}{F_1} \ln \frac{k_i + K_e X_A}{k_i + K_e X_C} \text{ volts} \end{aligned} \quad (47)$$

where E_{oc} is open circuit voltage. The cell thermo-

dynamic voltage is

$$E_o = \frac{R_g T}{F_1} \ln \frac{\gamma_A X_A}{\gamma_C X_C} \quad (48)$$

where $\gamma_A X_A$ is the activity of the sodium in the electrolyte at the anode, assumed to be equal to the activity of the sodium in the anode, while $\gamma_C X_C$ is the activity of the sodium in the electrolyte at the cathode (γ_A is assumed equal to γ_C), assumed to be equal to the activity of the sodium in the cathode.

The open circuit voltage, E_{oc} , is then

$$\begin{aligned} E_{oc} &= E_o + \Delta E_{oc} \\ &= \frac{R_g T}{F_1} \left[\ln \frac{X_A}{X_C} - \ln \frac{k_i + K_e X_A}{k_i + K_e X_C} \right] \end{aligned} \quad (49)$$

An expression for q is

$$\begin{aligned} q &= FD \frac{\rho}{M} \frac{X_A - X_C}{L} + (E_o - E_{oc}) \frac{k_i}{L} \\ &\quad - \left(1 - \frac{k_i}{L} R_c \right) I \end{aligned} \quad (50)$$

where R_c is the cell resistance for a square centimeter

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FIG. VI-25. Solution of Equation 41 for $K_e K_A / k_i = 0.4$, $K_e / k_i = 100$, $K_e X_A = 0.4$.

³⁸ M. A. Bredig, Mixtures of Metals with Molten Salts, M. Blander, Ed., *Molten Salt Chemistry*, Interscience, New York, 1964, p. 383.

of electrode area in ohm cm^2 and is equal to $(E_{oc} - E)/I$. Here R_c varies somewhat with I .

Equation 43 was solved using the values listed below for the variables:

$$\begin{aligned} D &= 1 \times 10^{-4} \text{ cm}^2/\text{sec} \\ k_i &= 1 \text{ ohm}^{-1} \text{ cm}^{-1} \\ K_e &= 100, 200, \text{ and } 400 \text{ ohm}^{-1} \text{ cm}^{-1} \\ M &= 105 \text{ g/mole} \\ X_A &= 0.004 \\ X_A/X_C &= 10^4, 10^3, 10^2, \text{ and } 10 \\ T &= 585^\circ\text{C} (858^\circ\text{K}) \\ \rho &= 2.5 \text{ g/cc.} \end{aligned}$$

It was found that the two terms in the equation involving $FD\rho/LM$ are small and contribute very little. The fact that the expression $(FD\rho/LM)(X_A - X_C)$ is relatively small indicates that the irreversible transfer

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FIG. VI-26. Solution of Equation 41 for $K_e X_A / k_i = 0.8$, $D = 1 \times 10^{-4}$ sq cm/sec, $M = 105$, $T = 858^\circ\text{K}$ (585°C), $\rho = 2.5$ g/cc., $k_i = 1$, $K_e = 200$, $X_A = 0.004$, $X_A/X_C = 10^4, 10^3, 10^2, 10$.

108-9470

FIG. VI-27. Solution of Equation 41 for $K_e X_A / k_i = 1.6$, $K_e / k_i = 400$, $K_e X_A = 1.6$.

is largely caused by electronic conduction in the electrolyte rather than by direct diffusion of sodium atoms.

The solution of the equation can be expressed as a correlation of Lq/k_i as a function of LI/k_i for the various values of X_A/X_C and K_e . The results for the cases of $K_e X_A / k_i = 0.4, 0.8$, and 1.6 are shown in Figures VI-25, VI-26, and VI-27, respectively.

The graphic solutions for the theoretical equations for non-faradaic sodium transfer, shown in Figures VI-25 to VI-27, explain the phenomenon, noticed in the experimental work, that the non-faradaic sodium transfer decreases with increased cell discharge current. Normally, one might expect that the non-faradaic transfer would be independent of cell current.

The experimental values of irreversible transfer are being correlated with those predicted by the theoretical equations using estimated values of the ionic and electronic conductivities of the electrolyte.

4. Corrosion Studies (H. SHIMOTAKE, J. ALLEN, M. SILVERMAN)

Thermally regenerative bimetallic emf cell systems are regenerated by transferring alloy from the cell cathode to the regenerator (where the anode metal is

distilled) and returning the cathode metal (depleted in anode metal) to the cathode and the anode metal to the anode. The operating temperature of the cells of

interest (Na-Bi, Na-Pb, Na-Sn, Li-Sn) would be about 550°C while that of the regenerator would be about 800°C or higher for the sodium-lead or sodium-tin systems and above 1000°C for the sodium-bismuth or lithium-tin systems. Normally, the fused salt electrolyte would remain in the cell at about 550°C; however, the cathode metal alloy would be circulated between the regenerator at high temperature and the cell at the lower temperature. This could lead to dynamic corrosion owing to flow between regions having these temperature differences; material might be dissolved in the high-temperature regions and precipitated in the low-temperature regions. For these reasons, studies have been directed towards the corrosion of materials of construction by liquid cathode metals at temperatures near 1000°C. Both static and dynamic tests are being conducted. Preliminary work was previously reported (ANL-6925, p. 246 and ANL-7055, pp. 228-229).

A literature survey of corrosion by heavy liquid

metals (bismuth, tin, and lead) and by fused salts (fluorides, chlorides, and hydroxides) has been made and has been accepted for publication.²

a. STATIC CORROSION TESTS

For static tests, the materials under study were usually cut from sheet stock in the form of coupons, $\frac{1}{2}$ by 1 by $\frac{1}{8}$ in. In a test, the liquid cathode metal and the coupon were contained in a crucible fabricated from molybdenum-30 w/o tungsten, an alloy which is considered to be nearly inert to attack by bismuth and tin. The loaded crucible was placed in a stainless steel bomb located in a resistance-heated furnace and was held at the test temperatures for predetermined periods of time. Following the tests, the specimens were examined using a metallographic microscope and, where indicated, an electron microprobe. The test results, including some of those previously reported, are presented in Table VI-9.

Common materials including low-carbon steel, pure

TABLE VI-9. STATIC CORROSION OF REFRACTORY METALS, STEELS, AND ALUMINA BY BISMUTH AND TIN

Test Material	Bismuth			Tin		
	Temp. (°C)	Time (hr)	Results	Temp. (°C)	Time (hr)	Results
Molybdenum	1000	97	No corrosion.	1000	26	Penetration, <15 μ depth.
Niobium	1000	64	Dissolution, 30 μ thickness. Intergranular, <50 μ .	1000	24	Slight dissolution. Intermetallic layer with dendrites, <20 μ thickness.
Tantalum	1000	95	No apparent attack.	1000	96	Penetration, <20 μ depth.
Tungsten	1000	24	No apparent attack.	1000	96	Penetration, <5 μ .
Mo-30 w/o W	1000	97	No corrosion. ^a	1000	67	No corrosion.
	~1000	>1100	No visible attack. Intermetallic layer, ~100 μ thickness.	~1000	>850	No visible deterioration. Intermetallic layer, ~100 μ thickness.
Mo-50 w/o Re	1000	91	No apparent attack. Intermetallic layer, <12 μ . ^a	1000	63.5	No apparent attack. ^a
Nb-1 w/o Zr	1000	167	Severe intergranular attack, <250 μ depth. Specimen became brittle.	1000	160	Intergranular attack, <100 μ depth.
Nb-10 w/o W-2.5 w/o Zr	1000	71.5	Slight dissolution and pittings.	1000	87.5	Slight dissolution and pittings.
Armco Iron	850	24	Slight attack. ^b	—	—	In view of high solubility of Fe, no test was made.
	1000	50	Complete dissolution. ^b			
1040 Steel	1000	22	Intermetallic layer, <80 μ thick. Cr preferentially segregated.	—	—	In view of high solubility of Fe, no test was made.
Type 304 Stainless Steel	850	97	Intergranular, <100 μ depth. No attacks found in vapor phase.	—	—	In view of high solubility of Ni, no test was made.
Type 316 Stainless Steel	700	97	Slight dissolution. Decarburization, <5 μ depth including vapor phase.	—	—	In view of high solubility of Ni, no test was made.
High Purity Alumina	600	99	No attack. No wetting.	600	77.5	No attack. No wetting.
	850	52	Partly wetted and greyed.	850	29	Slightly wetted.
	1000	72	Partly wetted and greyed, not electrically conducting	1000	74	Completely wetted. Slightly conducting.

^a Test previously reported in ANL-7055, p. 228.

^b Test previously reported in ANL-6925, p. 246.

TABLE IV-10. DYNAMIC CORROSION OF STEEL AND STAINLESS STEEL BY BISMUTH, BISMUTH-SODIUM ALLOYS, AND LEAD

Loop Number	Test Material	Liquid Metal	Max. Hot-Leg Temp. (°C)	Min. Cold-Leg Temp. (°C)	Time (hr)	Results
2	1020 Steel	Bismuth	550	450	1000	Dissolution, up to 250 μ depth.
3	1020 Steel	Bismuth	800	700	24	Slight dissolution. Plugs formed, stopping circulation.
4	1020 Steel	Bismuth	850	450	430	Leak developed. ^a Dissolution of up to 60% of the loop metal at the hot leg.
5	1020 Steel	Bismuth	850	450	279	Leak developed. ^a Dissolution of up to 50% of the loop metal at the hot leg. Slight intergranular penetration.
6	1020 Steel	20 a/o Na-Bi	850	450	125	Leak developed. ^a Dissolution of up to 50% of the loop metal at the hot leg.
9	1020 Steel	30 a/o Na-Bi	650	550	1506 ^b	Slight mass transfer. Dissolution of up to 10% of the loop metal at the hot leg.
7	316 Stainless Steel	Bismuth	850	450	300	Leak developed. ^{a,c} Extensive mass transfer. Intergranular penetration.
8	316 Stainless Steel	25 a/o Na-Bi ^d	650	550	4426 ^b	Extensive mass transfer. Dissolution of up to 65% of the loop metal at the hot leg.
11	316 Stainless Steel	Lead	850	650	706	A plug formed in the cold leg section.

^a The leak developed at the entrance section of the hot leg.

^b The experiment was terminated at the indicated time.

^c The loop plugged, but on dissection a small leak was found.

^d The loop was started using 30 a/o Na-Bi as the liquid metal. After 24 hr bismuth was added until the composition of the liquid metal was 25 a/o Na-Bi.

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FIG. VI-28. Dynamic Corrosion of Steel and Stainless Steel by Liquid Bismuth and Sodium-Bismuth Alloy. (850°C hot leg temperature, 450°C cold leg temperature.)

iron, and stainless steels showed some degree of resistance in liquid bismuth at temperatures slightly above 800°C. These materials, however, were not tested in liquid tin because of their high solubility in tin. The refractory metals, except for niobium and its alloys, showed promising results in both bismuth and tin.

Alumina was tested for possible use as an electrical insulating material and appeared to be a satisfactory material for this purpose.

b. DYNAMIC CORROSION TESTS

Dynamic corrosion tests are being conducted by means of loops fabricated of proposed construction materials; molten metals are circulated in these loops by thermal convection. Previous results of this investigation were reported in ANL-6925, p. 246 and ANL-7055, p. 229. A detailed description of the thermal convection loops is given in the former report.

The loops are constructed of $\frac{1}{4}$ -in. pipe (0.54-in. OD and 0.364-in. ID) in the form of parallelograms about 10 in. high and 6 in. wide. Electric heaters are

used to maintain the four legs or sections of the loop at different predetermined temperatures.

The flow rates of liquid metal in the loop are determined by heat balance around the hot leg and also by heat-pulse application, in which a gas torch is applied to a small area of the cold leg for a short period after which the induced high-temperature liquid slug is sensed by a thermocouple inserted in the hot leg. Both methods show good agreement.

At the end of each experiment, the loop is dissected radially and the internal cross-sectional areas of the pipes which have been exposed to the liquid metal are determined by means of enlarged photographs and a planimeter. Minimum thickness of the pipe walls is also measured.

The results of all dynamic corrosion tests conducted to date using steel and stainless steel loops are summarized in Table VI-10. The results for Loops 4 to 9 are plotted in Figures VI-28 and VI-29. The same general pattern of variation in internal cross-sectional areas was observed for all cases.

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FIG. VI-29. Dynamic Corrosion of Steel and Stainless Steel by Sodium-Bismuth Alloys. (650°C hot leg temperature, 550°C cold leg temperature.)

Results for Loops 3, 4, 5, 6, and 7 clearly indicated that neither stainless steel nor low-carbon steel is suitable for use with bismuth at temperatures above 800°C; however, they may be suitable for use in the low-temperature operating section of a bismuth cell.

Loops 8 and 9 were, therefore, run with hot-leg temperatures of 650°C and cold-leg temperatures of 550°C. The operation of these loops was terminated after 4426 and 1506 hr, respectively, although no leaks were found in either. The results are included in Figure VI-29. Dissolution of loop metal at the hot leg due to dynamic corrosion reached ~60% for Loop 8, a type 316 stainless steel loop, after 4426 hr of operation. However, the dissolution for Loop 9, a low-carbon steel loop, was less than 10% after 1506 hr. This result supports the view that low-carbon steel could be used for circulation of bismuth-sodium alloys at temperatures below 650°C.

Loop 11, made of 1/4-in. type 316 stainless steel

pipe, was charged with lead and operated with a hot-leg temperature of 800°C and a cold-leg temperature of 650°C for 706 hr, at which time a plug formed in the cold-leg section. It was clearly noted that the flow rate, even at start-up, was very high. This is in contrast to the bismuth loops (Loops 1 through 9), in which the circulation rate of liquid metal during the start-up period was always low and sluggish. This difference may be attributed to differences in the fundamental fluid characteristics of the two liquid metals.

Loop 10, which was fabricated of molybdenum-30 w/o tungsten, has recently been charged with liquid bismuth and put in operation. Because of the known manufacturing difficulties with this material, considerable care was taken in its fabrication. This loop has been operated with a hot-leg temperature of 1050°C and a cold-leg temperature of 900°C for 340 hr as of December 10, 1965, without indication of failure.

VII

Nuclear Constants¹

(D. C. Stupedia, A. D. Tevebaugh, J. D. Bingle)

The fast neutron program is directed toward the study of neutron cross sections useful in calculations of the breeding gain of fast reactors, and toward the use of the data to test theories of nuclear reactions. The nuclei being studied include fissile and fertile species, and reac-

tor structural and control materials; the types of reactions studied are radiative capture, ratios of capture to fission, and neutron inelastic scattering. In the present program, several of the above types of reactions are under investigation; current progress is reported below.

A. RADIATIVE CAPTURE (D. C. STUPEGIA, C. R. KEEDY, M. SCHMIDT, A. MADSON)

One of the nuclear reactions which absorbs neutrons unproductively in a reactor is radiative capture. The cross sections for radiative capture as a function of neutron energy are needed in order to make proper use of materials proposed for structural and control use in reactors. In addition, the study of neutron capture allows one to test theories of nuclear reactions, and to derive information on the spacings and widths of nuclear energy levels.

The neutron energy range of interest in fast reactors lies between about 0.1 keV and several MeV. In the present program, radiative capture has been studied between 4 keV and 3 MeV, covering most of the fast reactor region.

The basic experimental technique used in the capture work is the activation method. In this method, the nucleus to be studied is exposed to a monoenergetic neutron beam, and the radioactive species produced thereby are counted with either a beta counter or a gamma-ray analyzer. The counting rate of the activation product is then converted to a capture cross section by suitable calibrations which yield the absolute neutron flux and the absolute disintegration rate of the capture product. The monoenergetic neutron beam is produced by the reaction ${}^7\text{Li}(p,n){}^7\text{Be}$ and $\text{T}(p,n){}^3\text{He}$, when lithium and tritium targets are bombarded by protons from the Van de Graaff accelerator. The neutron flux is measured

with a fission chamber, which counts fissions in a thin deposit of uranium.

In the previous report (ANL-7055, pp. 230-231), final data were given for fast neutron capture in rhenium. In addition, relative capture cross sections of ${}^{141}\text{Pr}$ were presented as a function of neutron energy between 0.2 and 2.5 MeV. Absolute cross sections have now been calculated for ${}^{141}\text{Pr}$, and these are shown in Figure VII-1, where our data are compared with the values of Gibbons et al.,² Johnsrud et al.,³ and Konks et al.⁴

Other recently determined data are given in Figures VII-2, VII-3, and VII-4. The cross sections for the production of the 3.7-hr state of ${}^{176}\text{Lu}$ from the major natural isotope, ${}^{175}\text{Lu}$, are compared in Figure VII-2 with the data of Gibbons et al.² Good agreement can be seen. Data for ${}^{139}\text{La}$ is presented in Figure VII-3 along with the data of other investigators.³⁻⁵ Again, good agreement is evident. Figure VII-4 shows the cross sections for ${}^{176}\text{Yb}$, for which no other data are available for comparison.

² J. H. Gibbons, R. L. Macklin, P. D. Miller, and J. H. Neiler, *Phys. Rev.* **122**, 182 (1961).

³ A. E. Johnsrud, M. G. Silbert, and H. H. Barshall, *Phys. Rev.* **116**, 927 (1959).

⁴ V. A. Konks, Yu. P. Popov, and F. L. Shapiro, *Zhur. Eksp. Teor. Fiz.* **46**, 80 (1964).

⁵ R. L. Macklin, J. H. Gibbons, and T. Inada, *Phys. Rev.* **129**, 2695 (1963).

¹ A summary of this section is given on page 18.

108-9275

FIG. VII-1. Radiative Capture Cross Section of Praseodymium-141.

108-9290

FIG. VII-2. Radiative Capture Cross Section of Lutetium-175.

108-9300

FIG. VII-3. Radiative Capture Cross Section of Lanthanum-139.

108-9304

FIG. VII-4. Radiative Capture Cross Section of Ytterbium-176.

B. CAPTURE-TO-FISSION RATIOS IN EBR-II (D. C. STUPEGIA, A. MADSON)

To calculate accurately the breeding gain of a fast reactor, one needs to know the capture and fission cross sections of the primary nuclear fuels and of the various species produced from them through neutron capture. Because of a lack of sufficient quantities of the isotopes of interest or a lack of suitable experimental techniques it is not expected that the required monoenergetic capture and fission data will soon be available. In the meanwhile an alternative experimental program has been undertaken, wherein the ratio of the capture to

fission cross section is being measured as a function of position in the fast neutron spectrum of EBR-II.

Samples of ^{233}U , ^{235}U , ^{238}U , ^{239}Pu , and ^{240}Pu have been placed into EBR-II subassemblies for irradiation in the core and blankets of the reactor (see ANL-6925, p. 251). The samples are presently nearing the completion of their irradiation in the reactor. It is expected that these samples will be returned to ANL during the next six months for analysis to determine the number of captures and the number of fissions which have occurred.

C. NEUTRON INELASTIC SCATTERING (D. C. STUPEGIA, D. LISTER,⁶ A. B. SMITH⁶)

In the study of nuclear reactors, it is necessary to know the cross sections for reactions which degrade the neutron energy spectrum of the reactor. The main mechanism for this degradation is neutron inelastic scattering ($n, n'\gamma$) in which the neutron, after a collision with the target nucleus, leaves the nucleus in an excited state with its own kinetic energy decreased by an amount equal to the energy of the excited state. The excited nucleus then returns to its ground state by emitting one or more gamma rays.

Inelastic scattering cross sections are being studied by measuring the number of gamma rays emitted from the excited state of the target nuclei. The measurements are being made as a function of incident neutron energy and as a function of angle of emission of the gamma rays with respect to the incident neutron direction.

The neutron source is a lithium target bombarded with protons from the 3-MeV Van de Graaff accelerator of the Reactor Physics Division; the gamma-ray detector is a NaI crystal. The most difficult experimental problem in this work has been the high background in the NaI crystal. The high background is caused by the interaction of neutrons with the crystal and by the detection of gamma rays other than those

from the inelastic scattering reaction. This problem has been, to a large part, overcome by using the pulsed proton beam of the Van de Graaff accelerator together with a time-of-flight system which allows the NaI crystal detector to record counts only during that time interval in which the gamma rays from the ($n, n'\gamma$) reaction are expected to arrive at the detector.

Work has recently been completed on the inelastic scattering cross sections for the production of four states of niobium-93 (see ANL-7055, pp. 232-233) as a function of neutron energies up to 1.3 MeV, and the angular distribution of gamma rays from two of these states. The results of this work are being prepared for publication.

A major problem in studying gamma rays from nuclear reactions, in addition to the background problem mentioned above, is the analysis of complex gamma-ray spectra. Development work now is nearing completion at ANL to produce a new type of gamma-ray detector, the lithium drifted germanium crystal. This detector, at a sacrifice in counting efficiency as compared with the presently used NaI crystals, will give a large increase in energy resolution. This development will allow gamma rays to be studied to a much higher degree of accuracy by substantially reducing interference from other gamma rays.

⁶ Reactor Physics Division.

VIII

Analytical Research and Development¹

(R. P. Larsen, R. J. Meyer)

A program for the development of analytical methods for the determination of burnup of fast reactor fuels and for the measurement of fast fission yields is being carried out by the Analytical Group. Although the

primary objective of this program is the development of burnup methods for EBR-II fuels, the methods will also be applicable to other fast reactors.

A. TOTAL RARE EARTHS FOR MONITORING BURNUP (R. J. MEYER, R. D. OLDHAM)

A total rare earth analysis for determining burnup is being investigated. This method has several advantages over methods based on a single nuclide: (1) more material is available for a determination since the combined fission yield of the rare earths is approximately 50%; (2) existing information on fission yields indicates that the combined fission yield of the rare earth nuclides is independent of the fissioning nuclide and the fission neutron energy.

To be applicable to the determination of burnup, a total rare earth analysis should be capable of determining as little as 0.1% burnup with an accuracy of $\pm 1\%$. At 0.1% burnup, approximately 300 μg of rare earths will be formed in every gram of fissionable material. Because of shielding problems it would be desirable to perform the analysis on 100 μg or less.

None of the methods of total rare earth analysis in the literature meet this accuracy requirement at the 100- μg level. The colorimetric methods^{2, 3} are sensitive enough but the molar absorbance indices for the individual rare earths vary significantly and a combined method would not, therefore, be sufficiently accurate. Furthermore, the chromogenic reagents react with a number of other fission products, uranium and plutonium. To separate these interferences would require

the development of a complex separation procedure. The volumetric methods^{4, 5} appear more promising, although those which have been reported do not provide the required accuracy at the 50- to 500- μg level.

The total rare earth titration with ethylenediaminetetraacetic acid reported by Fritz *et al.*⁴ has been modified to meet the accuracy-sensitivity requirement by incorporating photometric end-point detection, a technique in which the absorbance of the solution is measured after each addition of titrant. The titration is performed at a pH of 5.5 to 6.5 using arsenazo I as the indicator; the absorbance measurements are made at 560 $\text{m}\mu$. When there is no further decrease in absorbance with addition of titrant, the endpoint is determined from a plot of absorbance versus quantity of titrant. Because the total volume of titrant is unusually small, about 0.4 ml of 0.001 *N* EDTA at the 50- μg level, the titrant is added with a weight burette of the type described by Seils *et al.*⁶

The results obtained thus far have been very encouraging. At the 500- μg level the relative standard deviation is $\pm 0.5\%$ with no bias. At the 50- μg level, the relative standard deviation is $\pm 1.3\%$ with a $+2\%$ bias.

¹ A summary of this section is given on page 18.

² J. S. Fritz, M. J. Richard, and W. J. Lane, *Anal. Chem.* **30**, 1776 (1958).

³ C. V. Banks, J. A. Thompson, and J. W. O'Loughlin, *Anal. Chem.* **30**, 1792 (1958).

⁴ J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, *Anal. Chem.* **30**, 1111 (1958).

⁵ R. W. Rinehardt, *Anal. Chem.* **26**, 1820 (1954).

⁶ C. A. Seils, R. J. Meyer, and R. P. Larsen, *Anal. Chem.* **35**, 1673 (1963).

The initial results obtained at the 50- μ g level were erratic and always high. This behavior has been attributed to contamination by some interference, such as iron, which is also titrated with EDTA. Attempts to eliminate the contamination by purification of reagents and by improvement of technique have been only partially successful thus far, since a slight positive but reproducible bias remains. Standardization of the

EDTA by photometric titration of a lanthanum standard will permit correction of this bias.

Of the various other elements which may be present in an irradiated fuel, only a few interfere in the rare earth-EDTA titration. Separating these interferences from the rare earths prior to the titration should not be difficult. An investigation into this part of the problem is now under way.

B. DETERMINATION OF THE FAST FISSION YIELD OF PRASEODYMIUM-141 BY NEUTRON ACTIVATION (R. J. MEYER, R. D. OLDHAM, D. SANTELLI)

Praseodymium-141 (stable) is a potentially useful burnup monitor for fast reactor fuels. However, its fast fission yield has not been measured. Of the various analytical techniques which have been used to determine the fission yields of individual nuclides, none is applicable to the determination of praseodymium-141. The difficulty of separating the rare earths from each other precludes spectrophotometric analysis; the fact that praseodymium is monoisotopic precludes mass spectrometric-isotope dilution analysis; and uncertainties in the decay scheme of cerium-141 (31 days) precludes an indirect radiochemical analysis.

Neutron activation affords a means for determining praseodymium with high sensitivity and some degree of specificity. However, the precision of the method would have to be improved from the customarily accepted $\pm 10\%$ to $\pm 1\%$ to achieve the desired accuracy ($\pm 1\%$) for a fission yield determination.

The customarily achieved precision of $\pm 10\%$ in neutron activation analysis is attributable to poor flux monitoring. Because the flux variation with position within most irradiation facilities is often as much as 25% per centimeter, samples and standards within the same capsule do not see the same flux. When successive irradiations of samples and standards in identical containers are carried out, the containers cannot be reproducibly positioned.

The flux monitor technique has been modified in such a way that the problem of integrated flux dependency has been eliminated. A known amount of an element, *A*, (the flux monitor) is dissolved in a solution of the element being determined, *B*. The solution is then irradiated, the gamma activity of element *A* is separated from the activity of element *B*, both element *A* and element *B* are gamma counted, and the activity ratio obtained for the "unknown" mixture is compared to the same ratio obtained with an irradiated solution containing known amounts of both *A* and *B*.

When this technique is used, superior precision is obtained for two reasons: 1) both element *A* and element *B* are subjected to exactly the same flux, and 2) the irradiation times are exactly the same. When both of these requirements are satisfied, and if the irradiation is short compared to the half-lives of the nuclides formed, the ratio of their induced activities, *R*, can be expressed as follows:

$$R = \frac{\lambda_A N_A^0 \sigma_A}{\lambda_B N_B^0 \sigma_B} \quad (1)$$

where λ is the radioactive decay constant, N^0 is the number of atoms initially present, and σ is the neutron capture cross section.

For irradiations of a sample and a standard where the neutron energy spectrum does not vary or where the ratio of σ_A to σ_B is independent of the neutron energy spectrum, equation (1) can be written

$$R = K \frac{N_A^0}{N_B^0} \quad (2)$$

where *K* is a constant. Variation in the ratio of σ_A to σ_B between irradiations of sample and standard is most likely to occur when one, or both, of the elements in question have large resonance capture cross sections in or near the thermal neutron region.

A number of factors must be considered in choosing the element to be used as an internal standard. The more important are:

- 1) The monitor should have no resonance capture peaks in or near the thermal region of the neutron energy spectrum.
- 2) The amount of activity induced in the monitor must be equal to or greater than that induced in the element being analyzed.
- 3) The monitor must be easily separated from the element being determined.

The separation of the constituent of interest and the

monitor could be achieved by chemical means, by scintillation spectrometry, or by differences in half-lives of the elements.

The technique is now being investigated in the neutron activation analysis of praseodymium using sodium as an internal standard. The neutron reactions are:

After the irradiation the sodium is separated from praseodymium by precipitating praseodymium hydroxide on lanthanum hydroxide with sodium hydroxide as the precipitant. This procedure has been tested using sodium-24 and praseodymium-142 tracers and was found to give complete separation and quantitative recovery of both the sodium-24 and praseodymium-142 activities.

To obtain some information concerning precision, the method was tested on a solution containing 200 μg

of praseodymium and 100 μg of sodium per ml. Six 1-ml aliquots of this solution were irradiated separately in CP-5 for 1 min and were then put through the separation procedure. The sodium and praseodymium fractions were individually gross gamma counted and the cpm Pr/cpm Na ratios were calculated. The relative standard deviation for a single irradiation was $\pm 1\%$. Additional precision may be obtainable by simultaneous irradiation of samples and standards. In this case, the effects of variations in the neutron energy spectrum with time and the effects of minor differences in positioning in the reactor would be eliminated.

This neutron activation technique should also be useful in determining the fission yields of lanthanum-139, barium-138, iodine-127, and iodine-129. The technique is currently being investigated as a means of analyzing alkali metal mixtures. The precision of the results obtained to date for both sodium-potassium and sodium-cesium is very encouraging.