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SUMMARY

CHEMICAL ENGINEERING DIVISION
SEMIANNUAL REPORTI. Chemical-Metallurgical Processing (pages 45 to 142)

The first core loading of the EBR-II reactor will be processed for recycle to the reactor by the melt refining process. Development work on this process is complete, although it is expected that some plant assistance effort will be required after plant operations are started in the EBR-II Fuel Cycle Facility.

Study was continued of a halide slagging process, a melt-refining-type process, in which rare earth fission products present in discharged uranium or uranium-plutonium fuel alloys are preferentially oxidized and extracted from the molten fuel alloy into a molten, overlying halide salt phase. Potential advantages of this procedure are low operating temperatures ($\sim 1150^{\circ}\text{C}$), short liquation times (one hour or less), and high product yields ($\sim 99\%$). Previously demonstrated with uranium-fissium alloys, the procedure has been shown to be applicable to a uranium-plutonium-fissium alloy of a type being considered for a future EBR-II core loading, namely, a uranium-10% plutonium-10% fissium alloy. With 110% of the amount of MgCl_2 oxidant (in a $\text{BaCl}_2\text{-CaCl}_2$ carrier salt) required to oxidize all of the cerium from the metal alloy, cerium removals of 98% or greater were realized and were accompanied by plutonium extractions of 0.5% or less. The cerium-plutonium separation factor averaged 7300 in two runs. The plutonium extraction varied directly with the amount of oxidant employed. For the small scale of these experiments (700 g of metal alloy), product yields (as poured ingot) were high (97% or greater).

Various materials, principally high melting point carbides, borides, and nitrides, are being investigated for containing uranium and its alloys at temperatures from their melting point to several hundred degrees above their melting point. Of the materials tested to date for containing molten uranium at 1400°C (TiB_2 , CrB_2 , ZrB_2 , and TiC), only ZrB_2 was unattacked in a relatively short test (8 hr).

The purification of argon from nitrogen is frequently desired and may be required for future processing operations in the argon-atmosphere cell of the EBR-II Fuel Cycle Facility. Presently under study is a method whereby the nitrogen is gettered on hot titanium sponge. During the past report period, a 10-cfm pilot plant, designed to provide information on component design and reliability for large-volume purification systems, was operated for 1000 hours and then shut down for inspection and recharging of the titanium bed. Operation was trouble-free, and all components and instrumentation performed their design functions well.

Work was continued on the development of the skull reclamation process for recovery of melt refining crucible residues (known as "skull" material). In this process, the crucible residues are converted by controlled oxidation to oxide powders which are poured from the crucible. Plant equipment for this oxidation step has been built and installed in the Fuel Cycle Facility. Prior to installation of this equipment, it was tested by oxidizing the skull material in six full-scale melt refining crucibles. The uranium loss averaged $2\frac{1}{2}\%$ of the uranium originally in the skull material, which is equivalent to only 0.18% of the uranium charged to melt refining. An average introduction of zirconia crucible fragments equivalent to 1.3% zirconium in the skull oxide resulted. This amount of zirconium will not cause any problems in the skull reclamation process.

The rest of the skull reclamation process is conducted in molten metal (zinc-magnesium systems) and molten halide salt media. This portion of the process, which involves six process steps, is presently being demonstrated in a pilot plant which has a capacity of about 2 kg of skull oxide per process batch (which compares to a plant batch size of 7 kg of skull oxide). Thirteen runs have been made in the pilot plant to date; during these runs a variety of equipment and process problems have been worked on, and equipment operation has been markedly improved. The desired uranium recovery of 95% appears to be achievable. Efficient and reliable separation of waste metal and salt phases are now consistently demonstrated. Major remaining problems are the evaluation of various containment materials, the control of salt fumes, and the elimination of residual waste salt from a uranium product solution prior to retorting this solution for isolation of uranium metal.

In the EBR-II skull reclamation process, a flux consisting of 47.5 m/o CaCl_2 , 47.5 m/o MgCl_2 , and 5.0 m/o MgF_2 has been used in the reduction of uranium oxides by Zn-Mg solution. Determinations of the solubility of MgF_2 in CaCl_2 - MgCl_2 mixtures showed that the temperature coefficient of MgF_2 solubility is negligible. It was also found that the MgF_2 in this flux is at or very near its solubility limit. Because MgF_2 is hydrated, CaF_2 , which may easily be obtained without water of hydration, is being substituted for MgF_2 .

Development work has continued on pyrometallurgical methods for reprocessing fast breeder reactor fuels. The primary effort is devoted to metallic fuels. The basic separations in the current process concepts depend upon differences in the partition behavior of the fuel constituents between liquid metal and molten salt solvents.

Since mechanical removal of cladding from highly irradiated metallic fuels may not be feasible, chemical decladding methods are being investigated. In the case of vanadium-titanium alloy, a promising cladding material, scouting studies indicate that chlorination procedures may prove useful. The resulting chlorides of vanadium and titanium appear to be easily separated from the fuel by volatilization.

Further studies have been conducted on the use of Cd-Mg-Zn alloys as process solvents. The cadmium-rich region of this system, because of reduced operating temperatures and low zinc concentrations, might permit the use of stainless steels instead of tantalum or tungsten process vessels. Measurements of the solubility of uranium over the entire composition range of this solvent have been completed. Two regions of maximum uranium solubility are evident in the ternary diagram, one at about 52 a/o zinc and 48 a/o magnesium, and the other at about 83 a/o cadmium and 17 a/o zinc. At 600°C, the solubilities of uranium at these two points are approximately 0.75 a/o and 3.5 a/o, respectively.

Plutonium solubility measurements have also been made in solvent composition regions where the solubility of uranium is sufficiently high for process purposes. In general, the solubility of plutonium in these regions is three to six times greater than that of uranium. Since fast breeder reactor fuels contain a much higher proportion of uranium than plutonium, the solubility of uranium will dictate the choice of solvent composition.

Plutonium showed only a small tendency to coprecipitate with uranium from a solvent consisting of 69 a/o Cd, 16 a/o Zn, and 15 a/o Mg. Doerner-Hoskins coefficients were 0.068 and 0.164, compared to a value of 0.66 in 100% zinc solution.

Further distribution coefficients for praseodymium were determined, using Cd-Mg-Zn alloy as the metal phase and 30 m/o NaCl-20 m/o KCl-50 m/o MgCl_2 as the salt phase. By varying the composition of the metal phase, the distribution coefficient of praseodymium (a representative rare earth fission product) can be adjusted to different values.

Using information now available on uranium and plutonium solubilities, corrosion rates of stainless steel, distribution coefficients of pertinent elements, and melting point data, it has been possible to select composition regions in the Cd-Mg-Zn system that are suitable for use in various process flowsheets.

Brief studies of the distribution behavior of einsteinium and californium between liquid Zn-Mg alloys and molten MgCl_2 showed that both of these elements tend to seek the salt phase. With increasing magnesium concentration above about 30 a/o, the distribution coefficient of einsteinium increases while that of californium decreases, suggesting the possibility of additional transuranium element separations by this method.

The ternary systems, LiCl-NaCl-MgCl_2 and LiCl-KCl-MgCl_2 , offer promise as effective salts for the extraction of rare earth fission products from liquid metal solutions of uranium and plutonium. Liquidus temperatures of the system LiCl-NaCl-MgCl_2 have been determined over the entire composition range. In order to obtain satisfactory distribution coefficients

for the required separations, it is desirable for the salt to contain at least 50 m/o MgCl_2 , and for the remainder to be as rich in LiCl as possible. A liquid region was found to exist below 550°C with a minimum of 50 m/o MgCl_2 and LiCl concentrations up to about 30 m/o. Thus a satisfactory region appears to be available for the desired operating temperature of 600°C .

Work has been started on a program to develop engineering technology required for the separation of plutonium and uranium from rare earth fission products by multistage extractions between molten metal and molten salt systems. Preliminary engineering studies have been made with a low-temperature extraction column in which Wood's metal (a bismuth-base alloy melting at 70°C) was contacted with water. Observations were made on the flow patterns of the discontinuous metal phase, and measurements were made of the hold-up of the metal phase in the column for two different types of column packing. Work is now pointed toward the development of a packed extraction column and associated equipment for contacting molten metal and salt phases.

In a study of the nonturbulent vaporization of mercury (vaporization from the free liquid surface without bubble formation), the existence of a steep temperature gradient ($115^\circ\text{C}/\text{in.}$) in a thin (~ 0.2 -in. thick) surface layer, which had been previously shown, was confirmed by additional measurements made during the past report period. However, the rate of molecular heat transfer calculated from this gradient accounts for less than 20% of the total heat transfer represented by the mercury vaporization rate. It has therefore been postulated that the primary mechanism of heat transfer is one of convection whereby superheated eddies from the pool penetrate to the surface and lose a portion of their sensible heat (superheat) in vaporization. The surface temperature gradient then results from the mixing of superheated and lower temperature eddies near the surface. Surface temperature explorations made with an experimental liquid metal thermocouple showed nonconstant temperatures across the vaporizing surface.

Work was continued on a program to determine the critical constants of alkali metals. The densities of metal and vapor phases are to be measured from room temperature to the critical temperature by measuring the gamma radiation of an alkali metal radioisotope emanating from the vapor and liquid regions of the alkali metal held within a small capsule. Equipment for this program has been constructed and is now being put into good operating condition.

The catalyst in the argon purification system became poisoned by mercury which accidentally spilled into the Argon Cell from an overhead seal. Because of the impairment of catalyst activity, a buildup of H_2 , O_2 , CO , and CO_2 impurities in the argon gas occurred. During February 1964, the Argon Cell was purged with air to permit entry of personnel for removal of the mercury spread on cell surfaces and for repair and maintenance of

equipment in the cell. The poisoned catalyst was replaced with fresh catalyst and the Argon Cell was refilled with argon, following which the oxygen and water concentrations in the argon were reduced to 10 and 60 ppm, respectively. The rate of air in-leakage to the cell is low, 0.007 scfm at a cell pressure of minus 2.5 in. of water.

Operation of the transfer locks by means of motorized drives had caused extensive wear of the drive gears. These gears were replaced with hardened gears and the drives were modified to increase their reliability.

Operation of the in-cell cranes had indicated need for modifications. The crane hoists were provided with new gears to double the hoisting speed. Slip clutches were installed on the hoists to prevent damage from overloads. Arcing had twice caused failure in a mineral insulated cable in the crane hoist circuit. To overcome this difficulty, the mineral insulated cable was replaced with asbestos insulated wire.

The manipulators were modified to increase their reliability. New shafts were installed in the bridge drives. Several changes were made to prevent difficulties with the hoist cables; circuits were modified to prevent arm rotation while hoisting; cable anchorings to the hoist drums were modified; and slip clutches were installed on the hoist drives. The original brushes in the grip-drive motors became excessively worn in the dry argon atmosphere; these brushes have been replaced with brushes of a type which have proven to be superior. The brushes in the other drive motors have operated without trouble. A short occurred in a 64-lead conductor to a manipulator. Since it is believed that the short resulted from simultaneous operation of two drive motors, the circuits have been modified to prevent such simultaneous operation.

The shielding windows of the Argon Cell have been modified by adding a 1/4-in. thick glass cover plate on the inner cell-side of each window. The cover plates will prevent bruising impacts on the thick window panes and resultant disruptive discharges of gamma-induced electrical charges in the shielding windows.

Nineteen runs with unirradiated, uranium-fission alloy have been carried out by remote means in the melt refining furnaces in the Argon Cell. The purpose of the runs was to prepare ingots suitable for use in the injection casting furnace. The poured yields varied from 83 to 97 w/o, twelve of the yield being greater than 94 w/o.

Concentric shielding plugs are provided in the floor of the Air Cell to permit the transfer of materials. These plugs have been modified to provide shielding between the bottom of the cell floor and a shielded coffin during the transfer of irradiated fuel subassemblies. Careful alignment between the coffin and the floor opening is required; this alignment has been achieved.

The fuel transfer coffin has been used for the in-situ removal of sodium from four mock-subassemblies which had been in the sodium-filled reactor vessel. Analytical results of the washings from the sodium removal procedure showed that the sodium adhering to a subassembly amounted to 32 to 41 g. The amount of sodium remaining on the subassembly fuel pins after the sodium removal procedure was estimated to be 3 g.

A disposal container for burying solid radioactive wastes from the Fuel Cycle Facility was tested in a series of tests, one of which involved filling a container by dropping materials into it, and another of which involved dropping a loaded container onto a metal surface. The tests showed that the container is adequate for the proposed usage.

An argon atmosphere enclosure system is being installed in the Chemical Engineering Division to investigate the effect of a dry argon environment on the operation of equipment items which will be used in the Argon Cell. Initially, the system will consist of two gloveboxes and an argon purification system comprised of a compressor, catalyst and dryer. Test results of the purification system show that it can provide argon to the gloveboxes with oxygen and water concentrations less than 5 ppm.

The skull oxidation furnace, furnace control system, and the skull oxide dumper were successfully tested in six runs (with unirradiated uranium-fissium alloy) and have been installed in the Fuel Cycle Facility. In the skull oxidation runs, the skulls were processed in the oxidation times of 78 to 88 hr and with oxygen utilization of 70 to 83 percent. In the dumper tests, the maximum loss of oxide powder was 7 g from approximately 1 kg of skull oxide.

The skull reclamation process involves a number of heating and cooling operations. Self-heating (4 to 5 kw) of fission products imposes a special problem in cooling operations. Tests were made in a simulated process furnace to determine the effect of this self-heating on the cooling rate of the furnace. The results of the tests showed that in the furnace design special considerations must be given to means for facilitating cooling.

A furnace, enclosed in a water-cooled bell jar, has been used to investigate the distillation and uranium consolidation steps of the skull reclamation process. Experiments in which the furnace was operated in air resulted in poor uranium yields. The poor yields were attributed to contamination of furnace components when the furnace bell jar was removed prior to or after furnace operation. Therefore, the furnace is being installed in a glovebox containing a dry argon atmosphere.

The solubility of krypton in sodium has been measured. Krypton was found to be about one-half as soluble as argon, but the heats of solution for both are 16 kcal/mole. The theoretical implications are briefly discussed.

Experiments on the analysis of sodium for oxygen by the fast neutron method are proceeding. To reduce the interference caused by the oxygen content of the sample-encapsulating material, a technique has been devised wherein the sample is irradiated at one end of a capsule but is counted at the nonirradiated end.

The dry oxidation method for analysis of sodium for carbon is now giving good recoveries with low blanks.

The apparatus for the determination of thermodynamic functions of alkali metals and their alloys by optical resonance absorption spectrophotometry is now functioning satisfactorily. The measured heat of vaporization of sodium is in good agreement with the literature. The activity coefficient of sodium in a 33 a/o Na-K alloy is 1.59 at 150°C. The excess entropy in this system is small but definitely not zero.

Thermodynamic properties of the lanthanum-cadmium system have been obtained by both the emf cell and the effusion pressure methods. At 400°C the free energies of formation of the intermetallic compounds, as determined by the latter method are (in kcal/gram atom La): LaCd_{11} , -45.7; $\text{La}_2\text{Cd}_{17}$, -42.3; $\text{La}_3\text{Cd}_{13}$, -35.5; LaCd_2 , -24.1; LaCd , -14.9. For LaCd_{11} the corresponding value determined by the emf cell method is -43.0.

Refractory compounds of the actinide elements show promise as reactor fuels capable of withstanding high temperatures and large burnups. Methods are being investigated for the preparation of these refractory fuels. The more promising methods are being used to prepare sufficient quantities of these refractory fuels for use in fuel element fabrication and irradiation tests. The liquid-metal precipitation process for the preparation of UC has produced a product with good pressing and sintering properties. This process involves the addition of carbon to uranium dissolved in a Zn-Mg solution, reacting the mixture for about 8 hr at 800°C, removal of the supernatant solution, and retorting of the precipitated UC to remove residual zinc and magnesium. Twelve UC production runs using the liquid-metal precipitation process have been completed on a 500 to 1000 g scale of uranium metal. The oxygen content of the UC product has been reduced (~ 0.2 w/o) to the point where the primary source of oxygen contamination is the oxygen content of the carbon used in the process. The carbon contents of the UC products have varied from ~ 5.2 to 6.0 w/o (theoretical carbon content for UC = 4.8 w/o); however, recent changes in process variables (longer reaction times and lower C/U ratio of reactants) show promise of producing a UC product with < 5.2 w/o carbon.

A fluid-bed method for the preparation of UC from powdered uranium metal and a hydrocarbon gas is being studied. The work to date is primarily limited to the design and construction of laboratory equipment.

Additional work has been done on the use of Mg_2C_3 for the preparation of metal carbides. In this method, fused salts are used as the solvent for Mg_2C_3 and actinide compounds such as UCl_3 and PuCl_3 . Upon heating, a double decomposition reaction results in the formation of the metal carbide which can be recovered by filtration and distillation of the residual salts. Recent results indicate that a solid solution of uranium and plutonium monocarbides can be prepared by this process. The product, however, had a high oxygen content; and additional studies are required to make certain that a solid solution of the monocarbides was actually produced.

A new experimental program has been initiated to study slurries and pastes consisting of fertile, solid compounds suspended in liquid metals for use as blanket materials in fast breeder reactors. The work to date has been limited to the evaluation of the economic potential of slurry and paste blankets and the selection of systems for the initial experimental work.

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (pages 143 to 202)

Fluid-bed fluoride volatility processes are being developed for the recovery of uranium and plutonium from spent nuclear fuels. Laboratory support work for these processes is continuing with a study of the fluid-bed fluorination of mixtures of U_3O_8 , PuO_2 , and fission product element oxides, simulating the concentrations present in a spent fuel element. The U_3O_8 and PuO_2 in the mixture represent the product that would be formed by the oxidation of UO_2 - PuO_2 fuel pellets. The U_3O_8 - PuO_2 mixture, mixed with alumina, is conveyed to the reactor in the fluidizing nitrogen stream and is contacted with a dilute fluorine stream at a point just above that at which the U_3O_8 - PuO_2 powder enters. The fluorination reaction occurs as the streams mix. This portion of the reaction is called the feeding-fluorination period and results in the conversion of most of the uranium and about 50% of the plutonium to their respective hexafluorides. The gas phase composition during this period is 20 v/o F_2 and 80 v/o N_2 and the alumina bed temperature is 450 or 500°C. Once-through gas flow is used during the feeding-fluorination period; the gas from the reaction vessel is passed through a series of cold traps to remove the hexafluorides, an activated alumina trap to remove the excess fluorine, and is then vented to the box atmosphere. In order to remove the remaining plutonium, the system is next operated under total recycle using 100% fluorine for one or more recycle-fluorination periods at temperatures from 450 to 550°C.

Several experiments were performed in which an alumina bed was used for the fluorination of several additions of U_3O_8 - PuO_2 -fission product mixture. In the first experiment, six additions of 300 g of a U_3O_8 - PuO_2 -F.P. mixture containing about 0.4 w/o plutonium were made to a single alumina bed. The feeding-fluorination periods were carried out at 500°C with 20 v/o fluorine as the fluorinating agent. This was followed by two

recycle-fluorination periods with 100% fluorine: a 10-hr period at 500°C and a 10-hr period at 550°C. The plutonium content of the alumina bed was 0.10 w/o after the first addition, rose to 0.42 w/o after the fourth addition, and then decreased to 0.23 w/o after the sixth addition. After the recycle-fluorination period at 500°C, the plutonium concentration on the alumina was 0.19 w/o; after the recycle-fluorination period at 550°C, the plutonium concentration on the alumina was 0.18 w/o. In the second experiment, two additions were made to a single alumina bed. The feeding-fluorination periods were carried out at 450°C with 20 v/o fluorine. This was followed by recycle-fluorination periods of 5 hr at 450°C, 4 hr at 500°C, and 10 hr at 550°C, all with 100% fluorine. After the first feeding-fluorination period, the alumina bed contained 0.13 w/o plutonium and after the second feeding-fluorination period the alumina bed contained 0.19 w/o plutonium. After the three recycle-fluorination periods, the alumina bed contained 0.13 w/o plutonium. In a third experiment only PuO_2 (1.5 g) and fission products (2.6 g) were fed to the reactor. Four additions were made to a single alumina bed, using a feeding-fluorination period at 500°C (20 v/o F_2) and a recycle-fluorination period of 10 hr at 550°C (100% F_2) for each of the four additions. After each recycle-fluorination period, samples were withdrawn from the bed for plutonium analysis. The plutonium concentration on the alumina was 0.005 w/o after the first addition, 0.014 w/o after the second, 0.015 w/o after the third, and 0.024 w/o after the fourth addition. These results show that a significant fraction of the plutonium remains in the alumina and that further fluorination would be required to reduce the plutonium losses to acceptable values.

Two feed materials were evaluated. One feed material was prepared by oxidizing a solid solution of UO_2 - PuO_2 to a mixture of U_3O_8 and PuO_2 ; the other feed material was prepared by physically mixing U_3O_8 and PuO_2 . The use of a physical mixture rather than a solid solution would afford a significant saving in material costs for the pilot plant. In the tests, the two types of feed materials did not show a significant difference in plutonium retention on the alumina.

In a series of experiments, PuO_2 alone or PuO_2 -fission product mixtures were fluorinated. These experiments were performed to determine the variation in the plutonium content of the alumina bed with quantity of plutonium feed to the reactor and with quantity of fission products present. In these experiments, 1.5 or 10.5 g of PuO_2 alone or mixed with 2.6 or 19.4 g of a fission product mixture was fed into the reactor in 170 g of alumina. These concentrations of PuO_2 and fission products correspond to those in U_3O_8 - PuO_2 -F.P. mixtures containing 0.4 or 3 w/o plutonium, respectively. The feeding-fluorination period was carried out at 500°C using 20 v/o fluorine followed by a recycle-fluorination period for 10 hr at 550°C using 100% fluorine. The results showed a 20- to 30-fold increase in plutonium retention on the alumina for a 7.5-fold increase in plutonium fed to the reactor. The plutonium retention in the absence of fission products was

0.009 w/o for the small (1.5 g) addition of PuO_2 and 0.12 w/o for the large (10.5 g) addition. The plutonium retention on the alumina in the presence of fission products was 0.005 w/o for the 1.2-g addition of PuO_2 and 0.190 w/o for the large addition. Increasing the fission product level 7.5-fold resulted in an increase in plutonium retention on the alumina by a factor of between three and four; 0.005 to 0.014 w/o for experiments with low plutonium concentrations, and 0.19 to 0.71 w/o for experiments with high plutonium concentrations. Blank experiments in which alumina alone was fed into the reactor indicated that an average value of 0.003 w/o plutonium on the alumina could be considered as the background level in this reaction system.

Since knowledge of the location of the plutonium, whether on the surface of the alumina or dispersed throughout the body of the particle, is important in guiding further efforts toward lowering the plutonium retention on the alumina or in devising means of removing the plutonium retained on the alumina, autoradiographic experiments were performed to determine the location of the plutonium. These experiments showed, by the alpha tracks produced in the autoradiographic emulsion, that the plutonium was located exclusively on the surface of the alumina particles.

Studies of the decomposition of gaseous PuF_6 to fluorine and PuF_4 by alpha radiation were continued. The effects of several variables on the extent of decomposition were investigated. These variables included (1) duration of the decomposition, (2) initial pressure of PuF_6 , (3) temperature, (4) presence of PuF_4 at the beginning of the decomposition, and (5) surface-to-volume ratio.

The results of the studies were as follows:

- (1) The average rate of decomposition of PuF_6 at an initial pressure of 100 mm Hg in 125-cc nickel spheres at 26°C decreased nonlinearly with time. In 5.6-day experiments, the average rate was 0.38% per day; in 571-day experiments, the average rate was 0.091% per day.
- (2) Tests of long duration (571 days) indicated that the decomposition rate of PuF_6 increases when the initial pressure of PuF_6 is increased.
- (3) The decomposition rate of PuF_6 at 80 to 83°C (0.65% PuF_6 per day) is higher than the decomposition rate at 26°C (0.19% per day). When PuF_4 is initially present (from a previous experiment), a lower decomposition rate (0.53% per day) is obtained at 80 to 83°C .
- (4) An increase in volume of the container, that is, a decrease in the surface-to-volume ratio, caused the PuF_6 decomposition rate to decrease. In 75-day experiments, the decomposition rate decreased from 0.19% PuF_6 per day to 0.11% per day when the container volume was increased by a factor of about 50.

When the surface-to-volume ratio was increased tenfold (by packing 127-cc nickel spheres with nickel wool), the average rate of PuF_6 decomposition increased from 0.19% per day to 0.30% per day. However, when the packed spheres were re-used (i.e., when PuF_4 was initially present), the average decomposition rates of PuF_6 in two experiments were 0.13 and 0.18% per day.

Lattice constants for UF_6 , NpF_6 and PuF_6 were calculated from available powder pattern data, using a computer program. The unit cell volumes calculated for UF_6 , NpF_6 and PuF_6 were 466.0, 463.8 and 461.4 Å³, respectively (see ANL-6176). The volumes of the unit cells thus decrease in the series UF_6 , NpF_6 and PuF_6 , showing the effect of the actinide contraction.

An engineering-scale facility is being installed to permit the study of the main steps in the fluid-bed fluoride volatility processing scheme for the recovery of plutonium and uranium from spent uranium dioxide fuels. The experimental work will be conducted with nonirradiated UO_2 - PuO_2 sintered pellets containing fission product oxides. A fluorination pilot plant for demonstrating the processing of mixed oxide pellets to hexafluorides and a converter system for converting the mixed hexafluorides to dense mixed oxide particles are to be operated in this facility. The equipment for fluorination of oxide pellets has been installed and preconditioned with fluorine in preparation for shakedown experiments with UO_2 pellets. The converter reactor is in the final stages of fabrication; the main converter auxiliaries and control panel have been installed and electrical and piping work is in progress. Both systems are expected to be ready for studies with plutonium-containing materials by the end of 1964. Plans call for the later addition of a fractional distillation column in the same facility to study the separation and distillation behavior of UF_6 - PuF_6 mixtures.

Studies on the hydrolysis and filtration of airborne PuF_6 were continued. The experimental program is directed toward establishing the behavior of PuF_6 in releases of dilute PuF_6 gas streams into cell or glovebox atmospheres. From this information efficient gas cleanup systems can be designed. In order to facilitate planning of experiments with PuF_6 , experiments were conducted with diluted UF_6 in a system consisting of a packed bed of glass spheres backed up by AEC-type filter segments. Very low concentrations of UF_6 (less than 0.03 mm Hg) in nitrogen were used; ambient conditions of humidity and temperature were simulated. The hydrolysis of UF_6 was found to be catalyzed by any solid surface contacted by the gas stream. The construction of new experimental facilities for measuring hydrolysis rates of PuF_6 gas is nearing completion.

An investigation of a method of decladding stainless steel-clad fuel by corrosion with aqueous hydrochloric acid in an air-fluidized bed of inert solids has begun. The fluidized particles were -30 +50 mesh sintered alumina grain. In the initial tests which were made in a small Monel column, the corrosion specimen was a Type 304 stainless steel thermowell (1/2 in. in dia.). The HCl concentration in the acid added to the column was about 30 w/o, and the liquid content in the bed was estimated to be 10 w/o. For these test conditions, the corrosion rates were 1.0 and 8.5 mils/hr at 25 and 60°C, respectively. In tests in which no fluidizing material was present in the column, the corrosion rates were 0.5 and 1.0 mils/hr at 25 and 60°C. This suggests that the fluidized bed increases the rate of corrosive penetration, perhaps by abrasive action which removes a film of corrosion products.

In subsequent tests conducted in a 1½-in. dia. glass column a rod (1/2-in. dia.) of Type 304 stainless steel was used as a corrosion specimen. The test results indicated that the rate of attack on the stainless steel increases with acid content in the bed. For liquid (20 w/o HCl in water) contents in the fluidized bed of 2.7 and 26 w/o, the dimensional corrosion rates were 0.5 and 8.7 mils/hr, respectively, at bed temperatures varying from 75 to 100°C.

In experiments conducted in the glass column, severe channeling of the bed was observed and particles of the bed adhered to the wall in those tests in which the liquid content of the bed ranged from 3 to 20 w/o. It is believed that the poor fluidization at high liquid fractions may be reduced by decreasing wall effects with use of a larger diameter column. The construction of a 3-in. dia. glass column is underway.

Studies on the preparation of high-density particles of UO₂ directly from UF₆ were completed this period. Results of these studies will be applied to mixed uranium-plutonium hexafluoride systems as part of the fluid-bed volatility reprocessing studies on low-enriched uranium oxide fuels.

The process involves reaction of the hexafluoride with a mixture of steam and hydrogen in a bed of the product oxide maintained at temperatures of 650°C or above. Current work, conducted in the 3-in. dia. Monel column that has been used throughout this program, was concerned with the development and demonstration of an oxidative-fracturing method for the preparation of uranium oxide seed material. Such material is used to offset particle growth which occurs as a result of the gas-to-solid conversion reaction occurring preferentially on the surface of the bed particles. The oxidative-fracturing method appears preferable to grinding since it is carried out in situ and minimizes handling of the material, a feature of particular advantage for the forthcoming work with plutonium.

In exploratory tests, two concentrations of air were used, 10% and 20% (in nitrogen), at fluid-bed temperatures of 400°C and 650°C to oxidize the UO_2 and effect particle breakup. Reduction of the material back to the dioxide was achieved in periods of 30 to 60 min with hydrogen at 650°C. Better results [mainly the formation of lesser amounts of fines (-325 mesh)] were achieved when the lower temperature and the higher air concentration were used. After reduction, the material had a somewhat lower density than that of the starting material; typical values for starting and final material were 8.9 g/cc and 8.3 g/cc. It was observed that the material appeared to become friable after oxidation; particle breakup continued during the subsequent purge and reduction periods in which the bed was fluidized.

Satisfactory use of seed material prepared by the oxidation-reduction method was made in UF_6 -to- UO_2 conversion runs of 12- and 17-hr duration. The seed material was fed as a side stream at given intervals. In subsequent tests a cyclic procedure was used in which UF_6 -to- UO_2 conversion runs were followed alternately by the oxidation-reduction treatment to re-size the entire oxide bed in situ. Three complete cycles were carried out followed by a final fourth oxidation-reduction treatment. Hexafluoride feed was stopped when the average particle size of the bed material reached about 400 μ . Resizing of the bed particles to an average diameter of about 200 μ was then carried out, and the cycle was then repeated. Sufficient breakup was achieved during the oxidation step with as little as 0.25 times the amount of oxygen required to oxidize the bed of UO_2 to U_3O_8 . The hexafluoride feed periods ranged from 10 to 17 hr, during which an average of 2.7 bed equivalents of UO_2 were produced.

A topical report summarizing the study of UF_6 conversion to dense UO_2 particles is being issued (ANL-6902). A study of the conversion of mixed uranium-plutonium hexafluorides to oxides is planned in a 2-in. dia. unit now being installed in the engineering-scale alpha facility.

A basic investigation was started of the fluidization of fine powders in the particle size range of less than about 50 μ . The difficulties in fluidizing fine powders are related to interparticle frictional and adhesive forces. Channelling and poor solid mixing exemplify the difficulties in fluidizing fine particles. The objective of this work is to quantitatively describe the effect of these forces on the fluidizability and quality of fluidization. This information will be useful for such process applications as the fluidization of U_3O_8 fines, preparation of UC, and coating of fuel particles.

In the current experiments the following particulate materials were used: iron with an average particle diameter, $\bar{d}_p$, of 3.3 and 1.6 μ , alumina with a $\bar{d}_p$ of 11 and 27 μ , and nickel with a $\bar{d}_p$ of 18 and 137 μ . The interparticle adhesive force and the interparticle friction coefficient were determined by the inclined-plane method. Fluidization experiments were performed in 8.2-cm ID and 14-cm ID Lucite columns. The pressure drop

across the bed of particles and heat transfer coefficients between the bed and an electrically heated plate immersed in the bed were measured to determine experimentally the minimum gas velocity for incipient fluidization.

The ratio of a calculated minimum fluidization velocity to the velocity observed at incipient fluidization is being used as an index describing the fluidizability of a particulate material. The results to date show the index of fluidizability depends mainly on the adhesive force; the effect of the interparticle friction appears to be insignificant. It was shown that the index of fluidizability decreases when the ratio of gravitational force to the sum of gravitational and adhesive forces of a particle, expressed as $G_p/(G_p + F_p)$, decreases, i.e., the adhesive force becomes large in comparison with the weight of the particle. A state of fluidization was generally achieved when this ratio was larger than about 10^{-3} . For cases where the ratio was smaller than about 10^{-3} , very stable gas channels formed in the bed and no particle motion occurred due to the relatively large adhesive forces exerted by the particles.

Development studies on the hydrochlorination and fluorination steps of a fluid-bed volatility process for the recovery of enriched uranium from uranium-alloy fuels were continued in a $1\frac{1}{2}$ -in. dia. fluid-bed reactor (nickel-200) system. Experiments were performed with normal uranium-aluminum and normal uranium-Zircaloy alloy plate assemblies. Sintered alumina was tested as bed material and compared with the more expensive fused alumina tested earlier. Simulated fission products were added, in one case, as separate elements or compounds, in another case, in alloy form. The process cycle included hydrochlorination, hydrofluorination, and fluorination steps. Process conditions for achieving the desired high (99%) recovery of uranium were essentially the same for both types of alloy fuel materials: hydrochlorination at bed temperatures of about 400°C, hydrofluorination at 350°C, and fluorination, starting at 250°C and 5 v/o fluorine and ending with 500°C and 95 v/o fluorine.

An improved fluorination procedure which requires very low fluorine rates and which may obviate the need for a fluorine recycle pump was investigated. The improved procedure involved two steps: (1) carrying out the reaction for 1/2 hr at 250°C with 5 v/o fluorine while the reactor bed was fluidized to remove the bulk of the uranium, and (2) completing the fluorination reaction under static bed conditions at 500°C with 90 v/o F_2 at low flow rate. Residual uranium concentrations in the alumina fluid beds and filter beds were consistently below 0.01 w/o, a satisfactory level. Extended fluorination at 500°C did not result in additional uranium removal.

The presence of inactive fission product elements in the fuel charge did not affect the process operation or the uranium recoveries. The reactant utilization efficiency and the alloy reaction rates were similar to those obtained previously. The presence of fission products did not result in any change in the relative distributions of the minor elements of Zircaloy.

Full-scale operations have started in the pilot plant facility installed to demonstrate the fluid-bed volatility process for enriched uranium alloy fuels. In the initial experiments, multiplate aluminum assemblies (no uranium present) weighing 12.3 and 12.1 kg and a Zircaloy assembly weighing 19.15 kg were successfully processed (hydrochlorinated) in periods ranging from 6.5 to 8.6 hr. Fluid-bed temperatures during hydrochlorination were maintained at about 370°C and 290°C for the two aluminum runs. A temperature of 370°C was used for the Zircaloy experiment. Average hydrochlorination rates ranged from 2 to 3 kg/hr for a typical Zircaloy charge and 1 to 2 kg/hr for an aluminum charge. Overall HCl utilization was about 50 to 60% for both fuels. The initial experiments included a 1- to 2-hr hydrofluorination at temperatures near 300°C.

The first demonstration run with a uranium-containing fuel assembly was also completed in the pilot plant. A 19.6-kg uranium-Zircaloy assembly containing about 182 g of uranium was processed through the hydrochlorination-hydrofluorination-fluorination cycle. The hydrochlorination and hydrofluorination conditions were similar to those employed during the shakedown experiments. The element was completely hydrochlorinated in a period of 10.9 hr.

Uranium removal from the alumina beds by fluorination was satisfactory using the two-step fluorination procedure established earlier in bench-scale studies: (1) fluorination for 2 hr with 6 v/o fluorine in nitrogen while the temperature is increased from 250 to 500°C, (2) followed by a final 2-hr period at 500°C with a high fluorine concentration (~80 v/o) and with the reactor bed in a settled (nonfluidized state). The residual uranium concentration in the alumina beds, both for the reactor bed and the packed-bed filter, was less than 0.01 w/o. About 94% of the uranium in the initial charge was collected using the NaF absorption technique. A high uranium loss (2.5%) during the hydrochlorination step is attributed to the high operating temperature of the packed-bed filter (400°C instead of the recommended 350°C) and possibly insufficient filter bed depth. Based on experience to date, projected time values for processing typical batch charges in the pilot plant are about 20 hr for uranium-Zircaloy assemblies and about 16 hr for uranium-aluminum assemblies.

The fluid-bed pyrohydrolyzer for converting the waste metal chlorides to oxides operated satisfactorily in series with the main fluid-bed reactor for all experiments. Recent modifications to this unit included a new cone-shaped bottom section and an overflow system for continuous waste product removal. These changes appear to have contributed to the smooth operation of this unit.

Bench-scale equipment for high-level-activity studies of the fluid-bed volatility process for highly enriched uranium-alloy fuels has been temporarily erected in a cave service area preparatory to shakedown runs with

unirradiated fuel specimens. A preliminary check-out of the operating procedure using manipulators has been completed. Permanent installation of the unit in the Senior Cave and start-up of operations with irradiated fuel specimens are planned for the fall of 1964.

A corrosion program in support of the fluid-bed volatility program is in progress. Two types of tests are being conducted, laboratory-scale tests in tube furnaces and in-plant tests. A test series has been completed in which nickel-200 plate and welded nickel-200 plate specimens were exposed for periods of 240, 480, and 960 hr to selected gaseous environments. The gaseous reactants were those employed in the processes under development for highly enriched uranium alloy fuels and the low enriched oxide fuel, namely, fluorine, fluorine alternated with HCl, and fluorine alternated with oxygen. The rates of corrosion for the unwelded plate specimens were low, between 0.9 and 4.1 mils/yr. The corrosion rates for specimens of nickel-200 plate welded with nickel-200 filler metal were also found to be low, between 0.6 and 5.0 mils/yr whereas the corrosion rates for specimens of nickel-200 welded with nickel-61 filler metal were very high, between 70 and 1315 mils/yr.

III. High Temperature Reactor Materials Development (pages 203 to 220)

A program for the study of certain high temperature reactor materials is under way, the objective being to build up a reservoir of basic data which may be used for screening and evaluation. The study will be concerned with the chemical stability of potential high temperature fuels, i.e., uranium oxides, phosphides, sulfides, arsenides, nitrides, and their solid solutions, and their reactions with hydrogen and its contaminants and with refractory structural materials, such as tungsten, rhenium, molybdenum, tantalum, and certain alloys. These studies will be done in a quantitative manner to yield thermodynamic and phase diagram information. Selected systems are to be investigated in an integrated way using five methods which are mutually supporting. Progress in the application of these methods is itemized below.

Effusion Vapor Pressure Studies. The total vapor pressure of uranium-bearing species over the two-phase system - uranium liquid (saturated with solid uranium dioxide) plus uranium dioxide solid (saturated with liquid uranium) - has been measured. The total pressures are higher than for pure uranium dioxide. Further measurements and assessment of the data will be carried out.

Mass Spectrometric Effusion Studies. Measurements of the relative concentrations of vaporizing species have been carried out for the same two-phase system noted in the preceding paragraph and also for stoichiometric uranium dioxide. Tentative calculations based on the two sets of data

show that the oxygen activity for solid uranium dioxide is reduced by a factor of 40 to 50 as it becomes substoichiometric. A value of 137.1 kcal/mole has been obtained for the heat of sublimation of stoichiometric uranium dioxide. This value is in good agreement with literature values, but it is subject to a possible error of 0.6 kcal/mole because of an incomplete temperature calibration. Further work will be carried out for both of these systems.

Transpiration Studies of Vaporization. The extension of the vapor pressure measurements to higher temperatures than those possible in the effusion measurements is to be carried out by use of the transpiration method. Most of the equipment for the work has been assembled.

Phase Diagram Studies. Studies of the uranium-uranium dioxide system have shown that a wide two-liquid immiscibility gap exists at elevated temperatures. The monotectic composition occurs at an oxygen-to-uranium ratio of approximately 1.30. An approximate phase diagram for the U-UO₂ system is presented. Further work on this system is in progress.

Interdiffusion Studies. Tungsten metal of high density has been shown to be highly compatible with both solid and liquid uranium monosulfide. There appears to be very little, if any, solubility of the sulfide in tungsten but a detectable solubility of tungsten in the sulfide.

IV. Calorimetry (pages 221 to 231)

The technique developed for calorimetric combustions of the diborides of zirconium and niobium in fluorine has been applied to the diborides of hafnium and tantalum. Preliminary data for hafnium diboride are presented. They lead to a value of -73.7 kcal mole⁻¹ for the enthalpy of formation of HfB_{2,01}.

A series of combustions (15) of silicon carbide in fluorine has been carried out. Four different samples, two of the alpha- and two of the beta-crystalline modifications, were burned. The preliminary results showed no difference between the enthalpies of formation of the two modifications, within the precision of the measurements; they also showed that the impurity corrections, which differed for each of the samples, could be reliably computed.

Preliminary experiments on combustions of uranium monosulfide and of graphite in a fluorine flow reactor have been performed. The results indicate that the reactions are suitable for calorimetric measurements. A fluorine flow calorimeter is being designed and will be built as soon as possible.

A new arrangement has been developed for burning metals which form nonvolatile fluorides in fluorine. The sample is suspended at the top of a bomb which is completely lined with the fluoride of the metal to be burned. With this arrangement the sample, once ignited, becomes hot enough to sustain combustion in the vapor phase even after dropping to the bottom of the bomb.

The 1500°C drop calorimeter has been completely assembled. It is being evaluated by making drops with a heated copper sample into the copper block calorimeter. The latter has been calibrated electrically.

Nearly all of the components of the 2500°C drop calorimeter furnace have been fabricated. Assembly has not yet begun because of the press of work on the 1500°C drop calorimeter.

V. Reactor Safety (pages 232 to 303)

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. In general, it has been found necessary to study the reaction of each metal of interest by several methods. Some of these techniques are designed to study the reactions under isothermal conditions. One such method is the levitation experiment which has been used to study the reaction of steam with pure aluminum (see ANL-6648, p. 196), with an aluminum-uranium-nickel-iron alloy (SL-1 composition), and with commercial aluminum alloy 6061 which contains 1.0 w/o magnesium as the principal alloying agent. In this method, a sample pellet is simultaneously heated and supported in flowing steam by a radiofrequency field within a levitation-induction coil. In the experiment, molten specimens were exposed to steam at a controlled temperature for a period of time ranging from 5 to 100 min. The extent of reaction was determined by selective dissolution of aluminum, leaving the oxide intact. At 1200 and 1300°C, the reaction could be best described by a cubic rate law for pure aluminum and for both of the alloys studied. The same cubic rate equation also described the reaction of the aluminum-uranium-nickel-iron alloy at 1400, 1500, and 1600°C, although the experimental results at 1600°C were about 50% higher than those predicted by the cubic rate law. The results with pure aluminum at 1400, 1500, and 1600°C were interpreted in terms of an initial cubic reaction followed by a linear reaction which commenced after 2.3 mg Al/sq cm reaction had occurred. At 1400, 1500, and 1600°C, values of the extent of reaction of 6061 aluminum alloy were scattered and were generally greater than those of pure aluminum. The results were interpreted on the basis that the protective oxide film formed on the surface of the alloy is disrupted by vaporizing magnesium during a portion of the reaction and that the rate of reaction during this period is thereby increased.

Another method of studying metal-water reactions under isothermal conditions is the volumetric method. The stainless steel-steam reaction was studied by this method. Steam was passed over inductively heated specimens, and the quantity of reaction was determined continuously by measurements of the volume of hydrogen produced. Significant reaction occurred at 1100°C where the rate could be described approximately by a parabolic law. The reaction rate at 1300°C was found to depend on the rate at which the sample was heated. Metallographic and electron probe micro-analyzer studies indicated that a protective coating, high in chromium and nickel content, formed over the surface of slowly heated samples. The coating formed sparsely over rapidly heated samples. Quantitative rate studies could not be performed at 1400°C, because the sample underwent rapid and extensive swelling and foaming.

A third method of studying metal-water reactions under isothermal conditions is under development. This method involves the construction of a high-temperature (1900°C), high-pressure (1000 psi) furnace which is especially intended for studies of the reaction of stainless steel and aluminum with steam. The furnace consists of two zones separated by an alumina tube. The outer zone is argon-filled and contains a tantalum heater winding. The central zone is steam-filled and contains the specimen. The furnace will also be used to simulate the temperature-pressure environment experienced by power reactor fuel following a loss-of-coolant accident.

A brief study has been completed of the thermal decomposition of steam over inductively heated surfaces. The rate of production of knallgas ($2\text{H}_2 + \text{O}_2$) over heated platinum and iridium samples was determined as a function of specimen temperature and steam flow rate. The apparent activation energy of the decomposition reaction was 32 to 40 kcal/mole, which is similar to the apparent activation energy for the equilibrium dissociation of steam, 41 kcal/mole. This, combined with the positive effect of increasing flow rate, led to the conclusion that an equilibrium of water dissociation products is rapidly formed and maintained at the hot metal surface and that the observed reaction rate is determined by the rate of diffusion of dissociation products through the thermal boundary layer.

Some of the experimental techniques used to study metal-water reactions were designed to observe the reactions with small particles under nonisothermal conditions. One of these methods uses the energy contained in the light beam from a ruby laser to heat single particles of metal in a water environment. The experiment is designed not only to study the chemical reaction of particles with water, but also to study the transient energy exchange and associated hydrodynamic effects. Results with an aluminum sphere, $360\ \mu$ in diameter, showed that the extent of metal-water reaction varied between 6 and 12% and was independent of the laser energy, while with a zirconium sphere, $620\ \mu$ in diameter, there was about 30% reaction which was also independent of laser energy. The result with zirconium had been predicted from previous studies by the condenser discharge

method for fully melted particles. High-speed motion pictures of particles undergoing laser-beam heating showed the rapid growth of the steam-hydrogen bubble. The pictures also showed that the bubble size oscillated at a regular frequency. The observed hydrodynamic effects are being studied mathematically.

Another method used to study water reactions with finely dispersed metal is the condenser discharge experiment. It had been reported previously that this method was not applicable to the heating of pure aluminum wires. A recent attempt has been made with aluminum wires encased in a thin-walled nickel tube. Composite nickel-aluminum wires of this kind were heated and dispersed in water by a surge current from a bank of condensers. The extent of reaction was determined by analysis of the quantity of hydrogen generated. Experiments were performed in room temperature water under helium at pressures ranging from 0 to 2000 psig and in water heated to 242 and 335°C under 500 and 2000 psig steam overpressures, respectively. The results, although complicated by the presence of nickel in the composite wire, indicated negligible reaction in room temperature water regardless of the helium overpressure but reaction of 20 and 60% in 242 and 335°C water in runs in which the wires were heated to temperatures of about 1500 and 2000°C.

The third general method of studying metal-water reactions involves nuclear heating of typical reactor fuel materials in TREAT. In these studies, small fuel specimens were submerged in water in high-pressure autoclaves which were then placed at the center of TREAT and subjected to severe nuclear transients. Additional experiments have been completed with oxide core Zircaloy- and stainless steel-clad fuel specimens. The total extent of reaction for both cladding materials increased in an approximately linear fashion as the fission energy input during the TREAT burst was increased. The extent of reaction for the Zircaloy-clad specimens reached a value of 80% for a maximum fission energy input of 770 cal/g of UO_2 core, while a stainless steel-clad specimen reached 35.5% reaction for a maximum fission energy input of 690 cal/g of UO_2 core. The residue in the more energetic runs had the form of one larger particle and a considerable quantity of powdered material. Pressure traces indicated that no explosive pressure rises had occurred.

Several experiments in TREAT with preirradiated fuel material have now been completed. Three runs with unclad metallic fuel pins having the composition 93.5 w/o uranium (20% enriched)-5 w/o zirconium-1.5 w/o niobium, which had been irradiated in MTR to 0.3% burnup of the uranium atoms present, and two runs with undamaged fuel plates salvaged from the SL-1 reactor have been performed. The SL-1 material had been irradiated to 2.2% burnup of the uranium present. For both types of fuel, the extent of metal-water reaction was identical with the extent of reaction found in previous experiments with cold, clean fuel. Analysis of the fuel specimens before and after irradiation in TREAT for fission products led to the conclusion that the release of the nuclides ^{137}Cs , ^{90}Sr , and ^{144}Ce was very extensive.

Studies of transient heat transfer have been initiated to provide further insight into the mechanism of reactor meltdown accidents. Initial efforts have been calculational in nature and were directed toward obtaining an understanding of the violent pressure surge produced during the meltdown of the SPERT-ID reactor core. An equation was developed to approximate the heat transfer rate and the energetics of the steam film formed on the surface of fuel plates within the reactor. Another equation was developed to describe the acoustic constraint imposed by the large column of water above the relatively small reactor core. The equations were programmed on the CDC-3600 digital computer and were solved using several assumptions concerning the nature of the core break-up and the quantity of compressible gas within the core at the time of the destructive pressure surge. Calculations were performed for each of three values of surface area created by fuel melting in the central 35% of the reactor core. The three values assumed: (1) that the surface area was equal to the original heat transfer area in the undamaged core, (2) that the new surface area was five times the original area, and (3) that the new surface area was ten times the original area. Calculations were performed on the assumption that the central core region contained 2.1, 0.21, and 0 liters of compressible gas at the start of the destructive (second) pressure pulse. The results showed that the nominal 3000-4000 psi pressure rise could be explained on the basis of a steam explosion, although it is presently uncertain which combination of gas content and surface area is most realistic.

Another experimental program involves studies of the kinetics of oxidation and ignition of reactor metals, such as uranium and plutonium. This program is nearly completed.

Further characterization of the ignition behavior of a uranium-30 a/o plutonium-6 a/o iron alloy, which is being considered for zero power experiments, indicated that the ignition behavior is sensitive to fabrication procedure and aging. In earlier work, a chill-cast sample did not ignite in dry air even though heated to 820°C, while in wet air it ignited at 300°C. In current work, injection-cast samples ignited at temperatures between 240 and 300°C in dry air. It was concluded that the addition of 6 a/o iron to the uranium-30 a/o plutonium alloy offered only a slight increase in resistance to ignition. An alloy with 6 a/o molybdenum added is not as sensitive to method of fabrication or presence of moisture as the iron-containing alloy is. Self heating is evidenced at 300°C, but ignition does not occur until the alloy is heated to 600°C. Study of ignition behavior of a uranium-18 a/o plutonium alloy indicates that the addition of 14 a/o iron offers no advantage. Only slight increase of resistance to ignition was provided by additions of 6 a/o titanium, 6 a/o vanadium, 4.5 a/o molybdenum, or 3 a/o molybdenum to uranium-20 a/o plutonium alloys (as was the case for additions of 6 a/o aluminum, carbon, copper, and zirconium to uranium-30 a/o plutonium, reported in ANL-6800, p. 376). The ternary alloy uranium-20 a/o plutonium-6 a/o molybdenum shows nearly as much resistance to ignition as unalloyed uranium.

A uranium-10 w/o molybdenum alloy is frequently considered for use as core material in nuclear assemblies. Rising-temperature oxidation experiments showed that no ignitions occurred with 1-cm cubes of the alloy up to the limit of the thermobalance apparatus, i.e., up to about 800°C. Because of the practical interest in this alloy and the relative inertness to oxidation exhibited in the rising-temperature experiments, a series of isothermal experiments were performed. The oxidations were performed in moist air at 300, 400, 450, 500, 600, and 700°C. At 300°C, the oxidation was initially linear at 1.74×10^{-3} mg $O_2/(cm^2)(min)$ for 80 to 100 min, after which the oxide coating (about 1.5- μ thick UO_2) became protective and an apparently parabolic oxidation ensued. At 400 and 450°C, the reaction was parabolic with rate constants of 5.5 and 14 (mg/cm²)²/min, respectively. At 500 and 600°C, the reaction was linear for the entire period of measurement (300 min) with rate constants of 0.039 and 0.31 mg/(cm²)(min). The oxidation rates for the uranium-10 w/o molybdenum alloy indicate a complex process characteristic of an alloy. In general, oxidation rates were at least an order of magnitude lower than those of unalloyed uranium.

Studies of the thermal conductivity of metal powders have been completed. Thermal conductivities of uranium and zirconium powders were measured as a function of temperature, gas pressure, particle size, and extent of prior oxidation of the particles. The limiting high pressure conductivity was found to increase linearly with temperature, to increase with particle diameter, and to decrease with extent of oxidation. This decrease of thermal conductivity with oxidation was rapid at first and more gradual as the particles approached complete oxidation. A theory for spherical powders in random stacking (void fraction = 0.40) was developed. The data for uranium, zirconium, and a number of other metal powders in several gases were compared with this correlating equation and found to give fair agreement. The measured thermal conductivities of the uranium powders were applied to ignition data through the Frank-Kamenetskii ignition criterion. Predicted ignition temperatures were somewhat higher or lower than the experimentally determined ignition temperatures, depending on whether first or second stage uranium oxidation kinetics were used.

Studies were continued of the U_3O_8 -aluminum thermite reaction. Experiments demonstrated that compacts fabricated from -400 mesh powders were more reactive than compacts fabricated from coarser powders, as measured by peak temperatures reached by the samples upon being plunged into a preheated furnace. Previously sintered specimens also achieved higher temperatures than those not so treated, with heating rates measured in thousands of degrees per second by an electronic two-color pyrometer. Concentrations studied were primarily at the 75-85 w/o U_3O_8 levels, where the potential for violent reactions was demonstrated. Preliminary experiments have now begun with cermet having U_3O_8 concentrations (40 w/o) in the range of fuel material. Tests in this composition range have indicated that self-heating rates are limited to a few hundred degrees per second.

VI. Energy Conversion (pages 304 to 329)

Work on the development of methods for the conversion of heat into electrical energy was continued. Two types of regenerative cells are being studied, bimetallic concentration cells and the hydride cell.

Regeneration studies of the sodium-bismuth bimetallic system have been made with the Knudsen effusion-mass spectrometer technique. No intermetallic species were found in the gas phase. The mass peak due to bismuth appeared after the sodium content dropped from the original 0.75 (in Na_3Bi) to 0.6 mole fraction and at about 690°K. The total pressure of bismuth($p_{\text{Bi}} + p_{\text{Bi}_2}$) and the sodium pressure are calculated as a function of temperature and composition of the condensed phase. The data indicate that separation of sodium from the bismuth is possible.

Experimental sodium-bismuth cells have been assembled in open-top crucibles and have been operated at temperatures from 575 to 685°C with sodium chloride-sodium iodide electrolyte and from 300 to 500°C with sodium hydroxide-sodium iodide electrolyte and at currents as great as 145 ma/cm² at 0.28 volt. Open-circuit voltages as a function of mole fraction of sodium in the bismuth cathode at 576°C were obtained.

The effect of the solubility of Li_3Bi intermetallic in the electrolyte on the previously reported emf-temperature-composition surface of the lithium-bismuth system has been investigated in detail. No error in the previous data resulted from this phenomenon. The emf of the cell:

was identical, within 2.0 mv, with the emf of a cell containing a pure lithium liquid anode.

The solubility of Li_3Bi in the fused LiCl-LiF eutectic for temperatures between 600 and 1000°C ranges from 0.05 to 1.5 m/o. A ΔH_f for Li_3Bi estimated from the solubility data is 9.4 kcal/mole.

Below 800°C, the solutions of Li_3Bi in lithium salts are a clear deep red. At 800°C, the solutions are virtually opaque to visible light. At 525°C, the absorption spectrum is characterized by an intense absorption band whose long wavelength edge is at 610 m μ . This edge shifts 40 m μ to lower energies for each 100°C rise in temperature.

Alloys of lithium-bismuth containing 50 a/o of each metal were equilibrated with a eutectic mixture of LiCl-LiF . The atom ratio of lithium to bismuth is not 3.0 (as it is when a 70 a/o lithium-30 a/o bismuth alloy is equilibrated with the same eutectic), but approaches 1.0, probably as a result of the dissolution of more than one species in the eutectic, e.g., Li_3Bi and LiBi .

The absorption spectrum of Li_2Te in LiCl-LiF eutectic mixture has been measured. The solutions are clear red and are relatively stable in silica absorption cells. The spectrum is characterized by a peak at $469 \text{ m}\mu$ and an intense charge transfer band whose long wavelength edge is at $377 \text{ m}\mu$. A molar absorptivity of about 25.0 was obtained for the Li_2Te species. The spectrum of Cs_2Te has been observed in CsCl . The solutions are blue with a strong peak at $635 \text{ m}\mu$, a weaker peak at $465 \text{ m}\mu$, and a charge transfer band whose long wavelength edge is at $340 \text{ m}\mu$. Saturated solutions in lithium and cesium halides are estimated to range in the 1 to 10 M concentration range from 400 to 700°C .

The lithium hydride cell as well as bimetallic cell combinations of various anode and cathode metals are being considered from an engineering viewpoint, both as concerns cell operation and electrode material regeneration.

Studies of the solid-liquid equilibria of lithium hydride binary systems with lithium chloride, lithium bromide, and sodium chloride have been completed as a part of the evaluation of electrolytes for the lithium hydride cell. Detailed data for the lithium hydride-sodium chloride system are reported. All three systems are discussed and the evidence for associated Li_2Cl_2 , Li_2Br_2 and NaCl species in lithium hydride solvent is presented.

Lithium hydride cell studies with a flag H_2 , H^- electrode and solid lithium hydride in the cell electrolyte have given stable, reproducible emf data suitable for thermodynamic calculations of data pertinent to the regenerative cell program. The cell represented as follows

gives 0.2908 ± 0.0002 volt at $813.0 \pm 0.5^\circ\text{K}$ and with one atmosphere of hydrogen. The cells were reproducible with temperature cycling over a range of 510 - 610°C . The $(\partial E^0/\partial T)_P$ was obtained as -7.29×10^{-4} volts/deg. The slope is constant over the 510 - 610°C temperature range.

The standard free energy of formation of lithium hydride calculated from these data using the best available heat capacity and enthalpy data for lithium metal, lithium hydride and hydrogen gas is $\Delta F_{f,298}^\circ = -15,850$ cal/mole. This is consistent with calorimetric data in the literature. From these data

$$\Delta H_{f,298}^\circ = -21,180 \text{ cal/mole and } \Delta S_{f,298}^\circ = -17.9 \text{ eu.}$$

Permeation of hydrogen through pure vanadium metal diaphragms has been found to be variable, but even the lowest rates observed would support over 100 ma/cm^2 current densities. The variability observed is believed to be due to intrinsic characteristics of vanadium metal as an exothermic occluding metal rather than surface contamination.

Vanadium metal diaphragms have been operated in cells and give open circuit voltages similar to iron metal diaphragms. A cell has been operated 540 hours using a vanadium diaphragm. The cell, operated intermittently under resistive load throughout the run, produced 130 ma/cm² at one-half the open circuit voltage. The diaphragm showed no signs of corrosion.

VII. Nuclear Constants (pages 330 to 334)

Preparations are being made for irradiations of uranium and plutonium isotopes in EBR-II to measure the ratio of capture and fission cross sections as a function of position in the reactor.

A new program has begun for the measurement of inelastic scattering cross sections as a function of neutron energy. Spectra have been obtained for the gamma rays associated with neutron inelastic scattering in zirconium, holmium, niobium, copper, and rhenium.

Neutron cross sections of various reactor materials are being studied as a function of neutron energy in the range occurring in fast reactors. Radiative capture cross sections are reported for ¹⁸⁵Re and ¹⁸⁷Re for neutron energies between 4 kev and 2 Mev.

VIII. Analytical Research and Development (pages 335 to 340)

A program for the development of methods for determination of burn-up on EBR-II fuel is being carried out. The fission product nuclides technetium-99 (2×10^5 year) and lanthanum-139 (stable) have been selected as the fission monitors. Technetium-99 will be determined spectrophotometrically after separation from the fission constituents and other fission products by the distillation of technetium sesquioxide from concentrated sulfuric acid. The uranium-235 fast fission yield of technetium-99 has been determined. The investigation of lanthanum-99 as a burnup monitor is being carried out by the Idaho Division.

The uranium-235 thermal fission yields of technetium-99, cesium-133, and cesium-137 have also been determined. Values of $6.07 \pm 0.08\%$, $6.75 \pm 0.07\%$, and $6.32 \pm 0.04\%$, respectively, have been obtained.

CHEMICAL ENGINEERING DIVISION SEMIANNUAL REPORT

January-June, 1964

I. CHEMICAL-METALLURGICAL PROCESSING*

Pyrometallurgical processes for the recovery of fissionable material from discharged reactor fuels offer promise of achieving a reduction in fuel cycle costs associated with nuclear power. Lower costs are expected to result from rapid recycle of the fuel and a consequent reduction in fuel inventory, a minimum of chemical conversion steps, small solution volumes and resultant compact equipment, direct production of solid wastes, decrease in criticality problems because of the absence of aqueous solutions, and possible retention of valuable alloying agents in metallic fuels. Since the major objectives of these processes are repair of radiation damage and restoration of fuel reactivity, high decontamination from fission products is unnecessary. For high-burnup plutonium fuels, the buildup of activity from the higher plutonium isotopes precludes direct handling of the fuel even if fully decontaminated from fission products.

Included in the pyrometallurgical processes currently under development are melt refining (a simple melting procedure for metallic fuels) and various processes for core and blanket materials which employ liquid metals and molten salts as processing media. Pyrometallurgical methods also show promise for the preparation of certain reactor fuel materials, such as carbides.

The melt refining process is presently in the most advanced state of development, and it will be used for the recovery of enriched uranium from the first core loading of the second Experimental Breeder Reactor (EBR-II),** located in Idaho.

A. Pyrometallurgical Development

1. Melt Refining (L. Burris, Jr., R. K. Steunenberg)

The fuel for the first core loading of EBR-II, which is approximately 50% enriched uranium alloyed with about 5 w/o noble fission product elements (fissium), will be declad, chopped into about 2-in. long segments, and melt refined in a zirconia crucible. Work on this melt refining process

*A summary of this section is given on pages 19 to 26.

**The melt refining operation will be conducted in the Fuel Cycle Facility, which is adjacent to the EBR-II reactor building.

has progressed as far as is possible without startup of plant operations. When processing of spent fuel in the EBR-II Fuel Cycle Facility begins, it is expected that some plant assistance effort may be required. No work on this process was done in the last reporting period. Previous work has been documented in preceding summary reports of the Chemical Engineering Division.

a. Halide Slagging of Uranium-Plutonium Alloys

(G. A. Bennett, W. H. Spicer)

Work was continued on a halide slagging process in which a molten chloride slag or flux is used to extract highly electropositive fission products from molten uranium-fissium* or uranium-plutonium-fissium alloys. Potential advantages deriving from the use of molten fluxes are a low operating temperature ($\sim 1150^\circ\text{C}$), a short liquation time (~ 1 hr), and high product yields ($\sim 99\%$). Corresponding characteristics of the present melt refining process, in which spent EBR-II fuel is melted in a zirconia crucible, are an operating temperature of 1400°C , a liquation time of about 3 hr, and a product yield (as a poured ingot) of 90 to 95%. In the melt refining process, fission product elements are removed by volatilization and selective oxidation by the zirconia crucible. In the halide slagging process, beryllia crucibles must be used to contain the molten flux-metal combination, but these crucibles give promise of being reliable and durable.

In the chloride flux-melt refining procedure, the rare earth fission products are preferentially oxidized and extracted into the molten flux phase. Currently, a flux is used which has a composition of 81 w/o BaCl_2 -19 w/o CaCl_2 and contains MgCl_2 as a rare earth oxidant. About 200 g of flux is used with 700 g of metal. Cerium is alloyed with the charge metal at a concentration of about 0.6 w/o as a stand-in for rare earth elements. The phases are heated together under argon to 1150°C , maintained at 1150°C for 1 hr to allow rare earth oxidation and extraction to proceed to near-completion, and then cooled to 860°C . At this temperature the metal phase is frozen, and the flux, which is still molten, is poured off. The metal is then heated to 1300°C and poured into a mold.

During this report period, this work was extended to plutonium-containing alloys of a type being considered for a future EBR-II core loading, namely, a uranium-10% plutonium-10% fissium alloy.**

*Fissium is a mixture of relatively noble fission products: ruthenium, molybdenum, palladium, rhodium, and zirconium.

**This alloy has a melting point estimated to be 910 to 920°C . The flux has a melting point of approximately 800°C . No concerted attempt has been made to optimize the composition of the flux, but it has the desirable characteristics of a melting point lower than that of the metal phase, of being readily separable from the metal when both are frozen together, and of having low volatility.

(Work with uranium-fissium alloys was reported in ANL-6648, p. 35.) The major objectives of the work with plutonium alloys was to determine the plutonium losses occurring by vaporization (probably as the trichloride) and by extraction along with cerium into the flux phase. The work was conducted in a melt refining furnace having an integral glovebox. A diagram of the equipment was included in the preceding summary report (ANL-6800, p. 54).

Experimental Results and Discussion

Four runs with plutonium-containing fuels have been conducted to date. Experimental conditions and results of these runs are given in Table I-1. The runs included a blank run in which no MgCl_2 oxidant was added to the flux, two runs with 10% excess MgCl_2 (i.e., 10% in excess of the quantity to react stoichiometrically with the cerium present), and one run with 100% excess oxidant. The percentage of excess oxidant was varied to determine the sensitivity of plutonium transfer to the amount of oxidant added.

Table I-1

MELT REFINING OF PLUTONIUM-CONTAINING FUELS BY USE OF HALIDE FLUXES

All runs liquated at 1150°C for 1 hr under argon,
flux poured off at 860°C, and ingot poured at 1300°C

Run No.	Metal Charge		Excess Oxidant (%)	Ingot Yield (%)	Ce Removal from Ingot (%)	Pu Transferred to Flux		Ce/Pu Separation Factor ^a
	Wt (g)	Ce (w/o)				(% of Pu in charge)	(% of Pu in charge)	
HVC-5	737	0.335	No oxidant added	97.1	62.3	0.05	0.09	-
HVC-7	743	0.335	10	98.3	98.2	0.45	~0.002	7400
HVC-10	716	0.468	10	97.5	97.6	0.29	~0.006	7200
HVC-11	691	0.751	100	96.9	99.1	1.88	~0.088	4100

Metal Charge Composition (w/o): 80.97 U, 10.02 Pu, 9.01 fissium plus cerium in amounts listed in column 3 of this table.
Fissium Composition (w/o): 2.87 Mo, 3.20 Ru, 0.54 Rh, 1.13 Pd, 0.93 Zr
Flux Composition: 81 w/o BaCl_2 , 19 w/o CaCl_2
Ratio of Charge to Flux: 7:2
Oxidant: MgCl_2
Crucible: Isopressed, high-density, high-purity BeO

^aSeparation Factor = $\frac{\text{Ce in Flux/Ce in Metal}}{\text{Pu in Flux/Pu in Metal}}$. Ce and Pu values are weight percent at the end of a run.

The results shown in Table I-1 are encouraging. Loss of plutonium by vaporization was negligible in all runs. A cerium extraction of 62% in the blank run probably resulted from the presence of oxidizing impurities in the flux, and, in conjunction with a very low plutonium transfer (0.05%) to the salt, indicates the ease with which cerium may be selectively removed.

In the runs made with 10% excess oxidant, plutonium transfer to the salt was also small (<0.5%). Of particular significance is the cerium-to-plutonium separation factor, which averages 7300 for these two runs. Both the ingot yields and the cerium removal were around 98%.

When the oxidant was increased to a 100% excess, both the plutonium transferred to the flux increased (to ~2%), and the cerium removal increased (to ~99%). The relatively high plutonium transfer in this run indicates that the amount of oxidant added will have to be controlled within rough limits which will depend on the amount of fission products formed. Since burn-up, and hence the amount of fission products formed, can be predicted with an accuracy of 20% or better by either routine analytical methods or calculation, the feasibility of the process for actual plant operation appears to have been established.

b. Materials for Containment of Molten Uranium and Its Alloys
(G. A. Bennett, N. Quattropani)

Materials are being investigated for containing uranium and uranium alloys at temperatures from near their melting points to several hundred degrees above their melting points. A number of crucibles, each approximately 1 in. high by 1 in. diameter with a 1/2-in. OD cavity extending 1/2 in. deep in the center, have been procured for this test program. These crucibles have been fabricated from high melting point carbides, nitrides, and borides.

Two methods have been used to test the materials: (1) molten uranium has been contained in the crucible, and (2) the crucible has been partially submerged (bottom down) in a bath of molten uranium. The first method has served only to indicate whether or not the material is wet by molten uranium under the test conditions. No measurable corrosion has ever been observed by this method, probably because a very small amount of corrosion product serves to saturate the small quantity of uranium in the crucible. This method also suffers the disadvantage that crucible destruction is necessary in order to determine whether uranium penetration has occurred. In instances where the crucible has been sectioned for examination, neither autoradiographs nor metallographs have proved definitive. Therefore, increasing reliance has been placed on the second method in which the crucible is, in effect, used as a short rod and partially inserted into a bath of molten uranium.

Table I-2 summarizes the information obtained to date. At 1400°C, TiB₂ and CrB₂ were attacked by molten uranium. At this temperature, only ZrB₂ in a relatively short test (8 hr) was unattacked. As would be expected, the tendency for the materials to become wetted increased with temperature. TiC, which was not wetted and was only slightly attacked by molten uranium at 1200°C, was wetted and attacked at 1600°C. In future work in this area, other materials will be evaluated and ZrB₂ will be further tested.

Table I-2

CONTAINMENT OF MOLTEN URANIUM AND URANIUM-IRON ALLOY
BY REFRACTORY BORIDES AND CARBIDES

Type of Test: A - Uranium contained in crucible cavity
 B - Crucible used as short rod and partially
 submerged in bath of molten uranium

Crucible Material	Type of Test	Temp. (°C)	Time at Temp. (hr)	Observations	
				Wettability	Corrosion Resistance
ZrB ₂	A ^a	900	500	Slightly Wetted	b
ZrB ₂	B	1400	8	Wetted	No Attack
TiB ₂	A ^a	900	500	Not Wetted	b
TiB ₂	B	1400	24	Wetted	Attacked
CrB ₂	A	1200	50	Wetted	b
CrB ₂	B	1200	6	Slightly Wetted	Crucible Cracked
CrB ₂	B	1400	24	Wetted	Attacked
TiC	A	1200	50	Not Wetted	b
TiC	B	1200		Not Wetted	Slight Attack
TiC	B	1600	24	Wetted	Attacked

^aUranium-iron eutectic employed instead of uranium.

^bNo definitive information on corrosion was obtained by the Type A test.

c. Removal of Nitrogen from Argon with Titanium Sponge
 (M. Kyle, J. Arntzen, N. Quattropani, W. Pehl)

A method is under development for removing nitrogen contamination from argon by gettering the nitrogen on hot titanium sponge. Although this method will have general utility for purifying argon from nitrogen, the major incentive for its development is a possible future need to remove nitrogen from the argon atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility. Two sets of experimental equipment have been constructed: (1) equipment for a study of the kinetics of nitrogen removal from argon on hot titanium sponge, and (2) a pilot plant for obtaining overall process performance data and information on component reliability. Studies are being conducted with argon containing initial nitrogen concentrations between 50 and 50,000 ppm.

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

The equipment and experimental procedure for this study were described in the previous summary report (ANL-6800, p. 54). As pointed out in that report, difficulties were initially encountered in the operation of equipment. These have all been remedied, and runs are now underway to obtain data on the kinetics of the nitridation of titanium sponge at 900°C by nitrogen-argon gas mixtures. Meaningful conclusions cannot be

drawn from the few data which have been obtained to date. However, initial results indicate that the reaction probably follows an exponential rate law at titanium sponge conversions below 50% (calculated as the mononitride).

(2) Pilot Plant for Nitrogen Removal from Argon

A pilot plant-scale unit designed to demonstrate the removal of nitrogen impurity from argon gas on a large scale has been placed in operation. Operating at a gas circulation rate of about 10 cfm, this unit will provide information on component design and reliability for large-volume purification systems. Nitrogen concentrations of between 50 and 50,000 ppm in the argon gas will be used. Detailed information on the design and flow pattern of this system was presented in the previous summary report (ANL-6800, p. 58). Figure I-1 is a diagram of the system.

Figure I-1

PILOT PLANT FOR STUDY OF NITROGEN REMOVAL FROM ARGON

108-7356

Continuous operation of the pilot plant loop began on March 13, 1964, and continued until 1000 hr of operation had been accumulated. At that time, the unit was shut down for inspection and recharging of the titanium sponge bed. During this initial period of operation of the loop, all components and instrumentation performed their design functions well. The loop was operated at a pressure of 3 psig at the blower outlet, the pressure drop around the loop being 1 psi. The temperature rise of the blower at its operating speed of 850 rpm was 30°C. Inspection of the loop at the completion of 1000 hr of operation disclosed no significant component deterioration except for the expected slight air oxidation of the external surfaces of the Hastelloy "X" (trade name of Haynes Stellite Division of Union Carbide) and type 310 stainless steel vessels and pipes which are exposed to air at elevated temperatures.

Figure I-2 shows the temperature pattern in the loop at the completion of a flow cycle, i.e., just before the position of the 4-way valve is changed to reverse the flow through the heated section of the loop in order to recover heat stored in one of the regenerative heat exchangers. The 45-lb titanium sponge bed is kept at a temperature of 895 to 905°C, the trickle heater on the gas inlet side being employed to bring the gas up to 900°C. For the usually employed cycle time of 4 hr (time between reversals in the direction of gas flow), the temperature difference across the regenerative heat exchanger receiving gas from the titanium bed was 515°C, and for the maximum cycle time of 6 hr the temperature difference was 650°C. For a 4-hr cycle, about 77% of the heat in the gas flowing into a regenerative heat exchanger was stored (40,000 of 52,000 Btu). The temperature of the 4-way valve would rise to 85°C in a 4-hr cycle and to 200°C in a 6-hr cycle. The maximum permissible operating temperature of the valve is 200°C.

Figure I-2

TEMPERATURE PATTERN IN THE PILOT PLANT UNIT FOR THE REMOVAL OF NITROGEN FROM ARGON

(Approximate temperatures prevailing throughout the system at the completion of a flow cycle are given.)

In this initial period of operation, the performance of the sponge bed was difficult to assess because the bed had been exposed to air and water vapor during startup operations. Even so, efficient removal of nitrogen was achieved for a period of between 72 and 120 hr. Conversions of the titanium sponge (to TiN) corresponding to these periods of operation were estimated to be 15 and 30%. During this 120-hr period, the nitrogen concentration in argon at the inlet side of the bed was maintained at 650 ppm. Information will be obtained in the next run on the percentage of titanium which can be converted to TiN before occurrence of a rapid rise in the nitrogen concentration of the circulating gas (as in the first run) due to a decrease in the rate of nitrogen removal.

If present, water vapor and oxygen also are removed by reaction with titanium sponge. The concentration of water vapor in the circulating gas remained at a very low level during the initial 1000 hr of operation. For the first 650 hr, the water vapor concentration was less than 1 ppm, after which it rose slowly to a final concentration of 13 ppm.

Operation of the pilot plant loop will be continued as long as possible to obtain information on the useful operating life of various components.

2. Processes Employing Liquid Metal Solvents

Several processes are being developed which employ liquid metals and salts as processing media. The skull reclamation process is under development for recovery of the fissionable material remaining in the crucible residue (skull) after a melt refining operation. Skull reclamation runs are now being conducted in a pilot plant which has a capacity of about one-fourth to one-half that required for plant equipment.

Laboratory and engineering work are also underway on the development of processes for recovery of advanced fast reactor fuels which contain plutonium as a fissionable material.

Fundamental chemical and engineering studies of molten metal and salt systems, which tend to undergird the process development work, are also in progress.

a. Development of the Skull Reclamation Process (R. D. Pierce)

The skull reclamation process is being developed as an auxiliary process to melt refining for processing the first fuel loading of the EBR-II reactor. The process has two purposes: (1) recovery of uranium from the skull remaining in the crucible after melt refining, and (2) separation of fission products from the uranium. The recovered and

purified uranium will be returned to the main EBR-II fuel cycle. The skull reclamation process provides for all disposal of nonvolatile fission products in the EBR-II fuel cycle.

(1) Uranium Loss and Zirconium Contamination in the Oxidation of Melt Refining Skulls
(R. D. Pierce, T. F. Cannon)

The first step in the skull reclamation process is oxidation of the skull to permit the subsequent removal of oxide powder from the crucible by pouring. The equipment for this oxidation step was tested before installation in the EBR-II Fuel Cycle Facility. Six uranium-fissium-cerium skulls contained separately in six full-scale melt refining crucibles and produced in normal melt refining runs were oxidized and the resulting oxide powders were dumped from the crucibles. The waste crucibles were processed to determine the efficiency of uranium removal, and the skull oxides poured from the crucibles were analyzed to determine the amount of crucible fragments present.

The waste crucibles were crushed, and a pulverized sample from each crucible was submitted for X-ray spectrochemical analysis for uranium. The results are presented in Table I-3. Uranium loss averaged $2\frac{1}{2}\%$ of that originally in the skull and 0.18% of that originally charged to melt refining. These values, which are similar to those obtained on crucibles processed earlier when the equipment was in the developmental stage (ANL-6800, pp. 62-63), are probably typical of the losses which can be expected for the oxidation step at the EBR-II Fuel Cycle Facility.

Table I-3

URANIUM LOSS IN MELT REFINING CRUCIBLES AFTER REMOVAL OF SKULL BY OXIDATION^a

Skull Oxidation Run No. b	Original Melt Refining Charge (g)	Composition of Original Melt Refining Charge	Weight of Unoxidized Skull (g)	Uranium Loss in Waste Zirconia Crucible	
				(g)	(% of Uranium in Skull) (% of Uranium in Melt Refining Charge)
SOF-36	9689	U-1.7% fissium-0.61% cerium	642	16.0	2.8
SOF-37	9271	U-1.7% fissium-0.67% cerium	554	9.1	1.9
SOF-38	9188	U-1.3% fissium-0.67% cerium	902	22	2.7
SOF-40	7451	U-1.3% fissium-0.72% cerium	592	8.5	1.6
SOF-41	9476	U-1.3% fissium-0.66% cerium	741	9.0	1.4
SOF-42	9693	U-1.6% fissium-0.62% cerium	840	34	4.4
Average				2.5	0.18

^aSee similar data in ANL-6800, p. 63, Table I-3.
bOxidation runs performed in the Mock-up Facility with equipment to be used in the EBR-II argon-atmosphere cell. The waste crucible from Run SOF-39 was not analyzed because the charge material had not contained cerium.

An effort was made to determine the extent of uranium migration into the walls of the crucibles. Prior to crushing of the crucible from one of the runs (Run SOF-40), two small samples were taken from the melt zone of the waste crucible. Loose uranium oxide was brushed off, and the samples were mounted with a cross section of the crucible wall exposed. Autoradiographs from the samples clearly indicated that there had been no significant migration of uranium into the crucible wall; a trace amount of uranium was noted at the original interface between the wall and the melt. It is believed that virtually all of the uranium lost in the crucibles was oxide powder which either failed to fall free from the surface during dumping of the oxide or was trapped in cracks.

The general condition of the zirconia crucibles after oxidation was extremely poor. The bottoms were separated from the walls and were broken. The walls were also broken, especially in the reaction zone. However, the pieces of the crucibles held together during the dumping operation, and surprisingly little skull oxide was trapped in the cracks.

The extent of contamination of the skull oxide by zirconia is summarized in Table I-4. The zirconium content of these oxidized skulls averaged 1.3 w/o, which is an amount that would not cause any problems in the skull reclamation process (see ANL-6687, pp. 32-35).

Table I-4

ZIRCONIUM CONTENT OF OXIDIZED MELT REFINING SKULLS

(Cerium-containing skulls within full-size melt refining crucibles were oxidized and poured in plant equipment.)

Skull Oxidation Run	Skull Oxide Weight (g)	Crucible Zirconium in Skull Oxide	
		(w/o)	(g)
SOF-36	733	3.2	23
SOF-37	634	1.44	9.1
SOF-38	1027	0.44	4.5
SOF-40	670	0.71	4.8
SOF-41	838	1.21	10.1
SOF-42	937	0.82	7.7
Average	807	1.30	9.9

(2) Pilot Plant Studies of the Skull Reclamation Process

(I. O. Winsch, T. F. Cannon, P. Mack, K. L. Nishio,
K. R. Tobias, G. Teats, L. Kirkel*)

Operation of a pilot plant for study and demonstration of the skull reclamation process on an engineering scale was continued

*CEN Machine Shop.

during the past period. About 2 kg of skull oxide (containing about 75% uranium) is processed in each run. (In full-scale operations in the EBR-II Fuel Cycle Facility, 7 kg of skull oxide will be processed in each run.) Six skull reclamation process demonstration runs were made during the past period, making a total of 13 demonstration runs that have been completed to date in the pilot plant.

(a) Flowsheet. The skull reclamation process flowsheet was given previously in ANL-6800, p. 61, and is depicted schematically in Table I-5. The flowsheet has not been significantly changed in some time and now has been described in detail in an ANL report (ANL-6818). A slight modification is presently under consideration which involves delaying the removal of the waste salt or flux until after the uranium precipitation step. This change would permit keeping the transfer tube in a fixed position throughout the process, thereby simplifying remote operation.

Table I-5

BEHAVIOR OF URANIUM IN SKULL RECLAMATION PROCESS RUNS

(b) Pilot Plant. The pilot plant was previously described in ANL-6687, p. 35. All process operations up to the final retorting step are being performed in a tungsten crucible (about 12-in. OD by 19 in. high) equipped with four mixing baffles. The crucible is centrally located within a large mild steel bell jar (inside dimensions of 24-in. dia. by 36 in. high) and is heated by radiation from a $\frac{5}{8}$ -in. thick graphite susceptor which, in turn, is heated by radiation-cooled induction coils.

Enclosure of the crucible within a bell jar allows an argon atmosphere to be maintained in the system and permits pressurization of the system for transfer of molten metals or salts through a pipe to either a waste container or, in the case of the product solution, to a product receiver. The bell jar cover has three nozzles: one is used for a stirrer and the other two are used for insertion of transfer pipes and other equipment used for sampling, liquid level measurement, and temperature measurement.

The equipment has been operated in an open glovebox. The glovebox is gradually being closed up. Initially, a dry air atmosphere will be maintained within it, but eventually an argon or nitrogen atmosphere may be used.

(c) Flux Preparation. The premelting of the halide flux used in the skull reclamation process (47.5 m/o CaCl_2 , 47.5 m/o MgCl_2 , and 5.0 m/o MgF_2 or CaF_2 *) has been carried out in quartz crucibles. These crucibles were subject to cracking upon cooling. Therefore, an Inconel crucible was tested as a possible container material for fusing the flux constituents. It appeared to be unaffected by the high temperature and flux. Spectrochemical analyses of the flux produced in the Inconel container and of flux produced in a quartz crucible are as follows:

<u>Crucible</u>	<u>% Cr</u>	<u>% Fe</u>	<u>% Ni</u>	<u>% Si</u>
Quartz	<0.01	0.002	<0.001	0.005
Inconel	0.02	0.02	0.003	0.001

The analyses indicate higher chromium, iron, and nickel concentrations in the flux produced in the Inconel crucible. However, since these values are low and the noble metal extraction step of the skull reclamation process will remove iron and nickel and most of the chromium, any contamination of the product uranium as a result of using fluxes prepared in Inconel would be insignificant. Therefore, Inconel crucibles will be used for fusing the flux constituents.

(d) Separation of Flux from Uranium Product Solution. Experience has shown that removal of the waste flux just prior to dissolution of the uranium product can be accomplished satisfactorily. Flux transfers of about 90% or slightly higher have been obtained. However, slight contamination of the uranium product with a portion of the residual flux heel still occurs. In the previous summary report (ANL-6800), a method of preventing transfer of flux with the uranium product solution was reported. This involved agglomeration of residual flux by the addition of MgF_2 prior to product solution transfer. Because CaF_2 has recently been substituted for MgF_2 , CaF_2 has also been tried as a flux-agglomerating agent in small-scale experiments. It was determined that if the flux heel is no greater than twice the weight of the CaF_2 , the flux phase agglomerates; with larger flux heels, some fluid flux remains. If flux transfer is 92% complete in pilot plant runs, the early addition of the CaF_2 required in the following run can be expected to prevent transfer of significant amounts of flux along with the product solution. This procedure has not yet been tried on a pilot plant scale.

* CaF_2 has been recently substituted for MgF_2 . MgF_2 is hydrated whereas CaF_2 may be easily obtained without waters of hydration.

Some consideration was given to transferring the molten flux and uranium product solutions together and later separating the solidified phases. While this is a mechanically attractive procedure, i.e., the solidified phases may be readily separated, the cerium distribution ratio between the flux and the 12% magnesium-12% uranium-zinc product solution is such that appreciable cerium is extracted from the flux into the product solution, thus appreciably reducing the percentage of cerium removed. Consequently, no further consideration is being given to this procedure.

(e) Uranium Recovery. The fate of uranium in

Runs SKR-4 through 8 is shown in Table I-5. (Analytical results for subsequent runs are not complete.) The uranium recovery in the product solution has been high, well over 90%. The high uranium recoveries are also indicated by the amounts of uranium found in the waste streams. The amount of uranium lost was equivalent to about 4% of the initial charge in Runs 4 through 6, 2% in Run 7, and 10% in Run SKR-8. The high uranium loss in Run SKR-8 was the result of an abnormally high entrainment of uranium-zinc intermetallic precipitate in the supernatant solution. The smallest loss of uranium was sustained in Run SKR-7. The losses in other runs were generally higher, but were still (except for Run 8) acceptable since the desired recovery of uranium in this process is only about 95%. Uranium material balances are near 100%.

Comments regarding uranium losses in each waste stream are as follows:

Waste Stream	% Uranium Lost	Comments
Waste Zinc (Noble Metal Extraction)	0.03 to 0.8	Generally higher than expected; uranium loss should be less than 0.1%.
Waste Flux	0.24 to 1.0	Magnitude about as expected from small-scale demonstration runs, in which losses of 0.4 to 0.6% were routinely experienced
Supernatant of Intermetallic Precipitation Step	0.7 to 9.0	Minimum losses (solubility losses) are about 0.4%, but because of some precipitate entrainment, losses of about 1% are expected. Losses of uranium greater than 1% in this waste stream should be reducible.
Supernatant of Uranium Pre- cipitation Step	0.6 to 1.35	Minimum losses of about 0.7% are expected. Therefore, losses in this step have been reasonable.

As the above commentary indicates, the only major concern is with uranium losses in the intermetallic compound precipitation step. Attention will be given to this problem.

(f) Fission Product Removal. Cerium and zirconium removals in these early pilot plant runs are not very significant since the concentrations of these elements in the various process solutions were too low for accurate analyses. In succeeding runs, the concentrations of these elements have been increased to eliminate this difficulty. In these runs, the removal of cerium has been shown to be about 90 to 95%. However, removal of zirconium has proved to be a problem since only about 60% has been removed in the 5 w/o Mg-Zn supernatant. This problem is receiving attention.

Ruthenium and molybdenum are insoluble in the zinc-noble metal extract at the phase transfer temperature of 525°C. Low removals of ruthenium and molybdenum in the waste zinc solution of the noble metal extraction step were realized (14 to 78% for ruthenium, 27 to 57% for molybdenum) in early runs when no agitation or a low agitation rate of about 70 rpm was used during the phase transfer operation. Subsequent work has shown that an agitation rate of 400 rpm keeps the ruthenium and molybdenum in suspension in the zinc during the phase transfer operation. This has resulted in good removals of ruthenium and molybdenum in the waste zinc solution (85 to 90% for ruthenium and about 60% for molybdenum). A 60% removal is satisfactory for molybdenum but not zirconium. A greater removal is required for zirconium because of its introduction into skull oxide as crucible fragments.

(g) Process Time. It is desirable that processing times be as short as possible. Beginning with Run SKR-8, all process steps have been performed in a continuous sequence without shutdown between steps. Initial runs required a total of about 32 hr for completion. The time period in some of the later runs has been reduced to about 26 hr. It is felt that this can eventually be reduced to less than 20 hr.

Cooling Times. A major portion of the processing time is spent in cooling the crucible from 800°C to 450°C or 525°C in the noble metal extraction and uranium precipitation steps. Forced circulation of argon gas through the bell jar is employed to hasten the cooling. The time required for cooling the melt from a temperature of 800°C to 525°C averages about $1\frac{3}{4}$ hr. Cooling from 800°C to 450°C in the intermetallic decomposition step requires about $2\frac{1}{2}$ hr.

The forced-gas cooling system has worked well in most of the runs, but occasional plugs of condensed flux vapors have formed in the circulating system. It is believed that this difficulty has been corrected by using coarser filter media and by periodically cleaning the areas which are known trouble spots.

Uranium Reduction. In Run SKR-4, uranium reduction was complete within about $1\frac{1}{2}$ hr at an agitator speed of 750 to 900 rpm. However, difficulty was experienced in maintaining these high

agitation speeds. In subsequent runs, the agitation rates were reduced to 500 to 600 rpm, under which condition uranium reductions have been complete in 1 to 2 hr.

Dissolution of Precipitated Uranium. The precipitated uranium of the uranium precipitation step is dissolved in a 12 w/o magnesium-zinc solution for transfer out of the crucible and eventually to retorting equipment. This dissolution step proceeds rapidly and, as shown by chemical analysis, is complete within about 1/2 hr.

(h) Molybdenum-30% w/o Tungsten Transfer Lines.
A number of modifications have been made in the molybdenum-30 w/o

tungsten transfer lines used to transfer flux and metal phases out of the tungsten crucible. The transfer pipe is 5/8-in. OD with a 5/16-in. tube through it. For transfer of material, it is heated to between 700°C and 800°C by several 600-watt, magnesia-insulated, stainless steel-sheathed, 1/8-in. OD heating cables which are wrapped around it. The transfer line is sheathed in stainless steel to protect it from air oxidation. The transfer pipe was initially assembled by means of threaded elbows, but a number of failures at the elbows have occurred. These failures have been attributed mainly to strain resulting from the differences in thermal expansion of the stainless steel sheath and the pipe.

Figure I-3

TRANSFER LINE FOR SKULL RECLAMATION PROCESS

(Material of construction of
transfer tube: molybdenum-
30 w/o tungsten alloy)

In a new transfer tube, fabricated as shown in Figure I-3, the tube was bent to eliminate elbows. Since the maximum length of Mo-W tubing then available, about 60 in., was too short, it was necessary to use a threaded Mo-W coupling to increase the length of the downleg of the transfer tube. Tantalum gaskets were used inside the coupling as a seal, and the coupling and transfer tubes were back-brazed. Two stainless steel bellows were used in the stainless cladding assembly to prevent a strain on the Mo-W tube during heatup of the line. This new line has performed very well, having been used for 26 transfers.

A second transfer tube of a similar design, but with a U-bend, is now being fabricated. In this design, the stainless

steel sheath covering the Mo-W tube has been eliminated. The electrical heaters will be wound directly around the Mo-W transfer tube, covered with insulation, and then covered with a leak-tight stainless steel tube. The annular space will be evacuated initially and then will be filled with argon to prevent oxidation of the Mo-W tube.

A third transfer tube of this type is planned using a 72-in. length of Mo-W tubing (3/4-in. OD by 3/8-in. ID). This length of tubing will eliminate the need for a coupling, and the larger inside diameter will reduce the likelihood of plugs forming in the tubes.

When the transfer pipe is not being used to transfer material, a very small flow of argon is passed through it into the solution to prevent formation of a plug of infusible material. This technique has worked well, but equipment operation would be simplified by elimination of the gas flow. Therefore, metal plugs were deliberately allowed to form in the line in one run and were melted out prior to transfer of a metal or flux phase. This technique worked satisfactorily for transfer of the noble metal-zinc extract, but not for transfer of the supernatant solutions of the two uranium precipitation steps, apparently because of precipitation of uranium within the transfer tube. Therefore, it appears essential to have a small gas flow or "blow-back" through the transfer tube during the precipitation steps. The rate of argon gas flow must be kept low (less than 1 cu ft/hr) since, as observed in Runs SKR-11, -12, and -13, foaming of the flux is caused by a too rapid flow rate (up to 5 cu ft/hr) of argon.

Agitator Modification to Provide Path for Pressurizing Gas. The transfer of metal supernatants is made by pressurizing the furnace with argon at 15 to 20 psi. Pressure was transferred through the flux phase to the zinc phase by a high-pressure-drop path along the agitator shaft. Higher pressures than theoretical were required to transfer the waste streams. In recent runs, a hexagonal agitator shaft has been used instead of the round shaft formerly used. With this agitator shaft, openings along the "flats" are large enough to pressure-transfer the waste streams at near theoretical gas pressures (5 to 7 psi).

(i) Tungsten Crucible Failure. Failure of a large (about 12-in. OD by 19-in. high) pressed-and-sintered tungsten crucible occurred in Run SKR-10. This crucible had been in service for about one year, having been used at a frequency of about twice a week for periods of 8 to 48 hr. Failure of a transfer tube occurred in the intermetallic decomposition step of Run SKR-10, during which step the crucible contents (flux and metal phases) were allowed to freeze. The failure occurred when the contents were remelted. The crucible failure was unexpected since metal had been solidified and remelted in the crucible many times, and molten flux had been frozen over liquid metal phase and subsequently remelted numerous times. However, this was the first time a flux-metal

combination had been allowed to freeze in the crucible and had been subsequently remelted. Since the overlying flux melts between 550 and 600°C and 50 w/o Mg-Zn alloy melts at 358°C, there is a possibility that a large stress was put on the crucible as the metal expanded during heatup. Although this failure is disappointing and indicates that such remelting operations should be avoided if possible, the crucible, nevertheless, performed very well.

An inspection of the crucible revealed numerous cracks in the bottom and a large circumferential crack. An attempt will be made to have the crucible repaired by an outside contractor.

All runs subsequent to Run SKR-10 have been completed in a repaired pressed-and-sintered tungsten crucible. Another pressed-and-sintered tungsten crucible has been ordered.

(j) Fuming. Vaporization of flux and metal phases or "fuming" has been a problem in the skull reclamation process runs. Deposits of flux are found on the inside of the bell jar wall at the conclusion of each run. A spectrographic analysis of the material deposited on the wall in one run showed a composition of less than 1% calcium and magnesium, 32% zinc, and 26% chloride ion. An X-ray diffraction analysis of this material will be attempted to determine if zinc chloride is the material being vaporized.

Zinc chloride is a highly volatile salt and is used only in the noble metal extraction step when needed to oxidize any uranium and magnesium added as recycled metal heels. Zinc chloride is not a flux ingredient in subsequent steps of the skull reclamation process, but small equilibrium amounts of the compound may continually be formed and vaporized in some of the subsequent process steps.

Because of the fuming problem, it is likely that some sort of fume trap will be required. The trapping of zinc chloride fumes on conventional filters and on reactive materials has been investigated. Fiberfrax, resin-impregnated glass wool, and a conventional AEC filter were ineffective. The use of reactive-metal turnings of calcium, magnesium, and uranium showed considerable promise. Shallow (about 2-in. deep) loosely packed beds of metal turnings were placed over a source of zinc chloride vapor. Zinc chloride was added to a liquid calcium chloride-magnesium chloride flux at 800°C to initiate vaporization. Immediately after each addition of zinc chloride, a bed of a reactive metal was placed over the fuming melt so that all escaping vapors would have to pass through the bed.

In four experiments, beds of magnesium, calcium, uranium, and iron were tried. Iron, however, was employed as a control since little chemical action was expected between it and zinc chloride. The

beds were originally at room temperature and remained at a fairly low temperature, estimated to be below 200°C, throughout the runs. In another experiment, a calcium bed was heated to about 680°C for the test. Visible fuming disappeared in all experiments except the one in which iron was used. Since the reactive metals appear efficient in fixing the zinc chloride fumes, possible application of these metals to the solution of pilot plant fuming problems will be considered.

(3) Procurement and Testing of Crucibles for the Skull Reclamation Process (G. A. Bennett, N. Quattropani)

Two different crucibles are required in the skull reclamation process: (1) a tungsten or tungsten-lined crucible in which the noble metal extraction, oxide reduction, and uranium precipitation steps are performed and (2) a beryllia or beryllia-lined crucible in which the retorting step is performed.

(a) Tungsten Crucibles. Skull reclamation process runs on a pilot plant scale have been carried out for the past year in large pressed-and-sintered tungsten crucibles (12-in. OD by 19 in. high). The first failure of such a crucible occurred recently during a remelting operation. Although this crucible performed very well, alternative fabrication techniques are being investigated. Among these techniques are spinning, forming by plasma spraying, and welding.

Spun Tungsten Crucibles. A small (4-in. OD by 6 in. high) spun tungsten crucible successfully withstood a single melt-freeze-melt cycle between 800°C and room temperature while containing zinc and a halide flux. It also withstood 12 similar alternate melting and freezing cycles with a 50 w/o magnesium-zinc/halide flux system. Because of the good performance of this crucible, bids have been requested for an engineering-scale tungsten crucible.

Tungsten Crucible Formed by Plasma Spraying. Leakage of flux and metal occurred through the bottom and sides of small unsintered tungsten crucibles formed by plasma-spraying (at Waukesha Foundry, Waukesha, Wisconsin) tungsten on a removable mandrel. A sintered crucible will be checked, but this material does not seem very promising since it is rather brittle and, even when sintered, its density is not expected to exceed 92% of theoretical.

Heliarc Welded Tungsten Crucibles. Tests of Heliarc welded tungsten sheet carried out about two years ago (ANL-6543, p. 66) showed considerable loss of strength at the weld. The breaking stress at the weld (50,000 psi), although only one-third that of the parent metal, should be sufficient to withstand process operation conditions. An

advantage of welded construction is that crucibles would not be limited in size. Therefore, an engineering-scale welded crucible (10-in. OD by 21 in. high) has been ordered for evaluation under process conditions.

Tungsten-lined Crucibles. The feasibility of using plasma-sprayed tungsten coatings on various substrate materials is being examined. Work reported in the previous summary report (ANL-6800, p. 112) indicated that tungsten-coated silicon carbide crucibles showed considerable promise. Therefore, various types of silicon carbide are being investigated. A cast silicon carbide crucible with internal baffles has been ordered. When received, it will be plasma-sprayed with tungsten and subsequently tested under process conditions.

(b) Beryllia Crucibles. In the EBR-II skull reclamation process, a beryllia crucible is required for the final uranium retorting step. Beryllia has the very desirable characteristic of not reacting significantly with the solvent metals, magnesium and zinc, or with molten uranium, the product of the retorting operation. In work to date, beryllia has also had the desirable property of being unwetted by molten uranium - a factor which could influence which method is chosen for removal of the retorted uranium product (e.g., pouring or physical removal as a solidified mass). The required dimensions of the beryllia retorting crucible are an 8-in. OD and 15-in. height.

Thixotropically Cast Beryllia Crucibles. Initially, isopressed beryllia crucibles were used in the development work on the retorting step of the skull reclamation process. These crucibles were subject to cracking. Therefore, in cooperation with manufacturers, considerable effort has been devoted to the development of thixotropic casting for fabrication of beryllia crucibles. Thixotropically cast beryllia crucibles are less subject to thermal shock than are isopressed beryllia crucibles and also can be fabricated in larger sizes. During the report period, two thixotropically cast beryllia crucibles, $7\frac{1}{2}$ -in. ID and $14\frac{3}{4}$ in. high, were received for testing in engineering-scale retorting operations. These are scheduled to begin in the near future.

Beryllia-lined Crucibles. As is the case for tungsten, plasma-spraying of beryllia on an inert substrate appears to be a promising technique. If practical, this technique would overcome the size limitations of present techniques for fabricating beryllia crucibles and also would materially reduce the cost of the finished crucible.

In a preliminary test reported in ANL-6725, p. 75, a beryllia coating sprayed on an Alundum coupon withstood 12 thermal cycles between 300°C and 800°C. This work has been extended to an evaluation of beryllia coatings on tungsten and silicon carbide. A plasma-sprayed beryllia coating on the inner surface of a 2-in. diameter 1-in. wide tungsten

ring suffered loss in thickness by flaking in six thermal cycles between approximately 900°C and 250°C (or lower) in an argon atmosphere. A similar beryllia-coated tungsten ring was not wetted or affected by a single 1-hr exposure to a 50 w/o magnesium-zinc solution contained in a tungsten crucible at 800°C, followed by cooling to room temperature, and reheating to 800°C, at which temperature the solution was poured. Although a beryllia coating on tungsten does not appear to be a particularly promising combination, further testing of it will be done.

Plasma-sprayed beryllia coatings on silicon carbide were evaluated for two types of silicon carbide, Type KT, a fine-grained silicon carbide manufactured by the Carborundum Co., and Crystalon 63, a somewhat coarse-grained, high-strength, oxynitride-bonded silicon carbide manufactured by the Norton Company. The coatings were applied to the concave surfaces of segments of approximately 4-in. diameter crucibles. With either combination, no deterioration by peeling or flaking was evident after six thermal cycles between 900°C and 220°C (or lower) in an argon atmosphere. The only observable change was the appearance of several small, dark or reddish-colored spots on the beryllia. On the basis of these preliminary tests, beryllia coatings on silicon carbide are judged to be very promising.

To permit further testing of these materials

(Alundum, tungsten, and silicon carbides), small (~4-in. OD by 4 in. high) crucibles will be coated with beryllia. These coated crucibles will be evaluated for the containment of the zinc alloy and halide flux systems of the skull reclamation process.

b. Processes for Fast Breeder Reactor Fuels
(R. K. Steunenberg, L. Burris, Jr.)

Pyrometallurgical methods for reprocessing fast breeder reactor fuels containing uranium and plutonium are being investigated. Although the major effort is aimed at the processing of metallic fuel alloys, modifications of the process flowsheets to accommodate other fuels such as carbides are also being examined. The basic separations in the present process concepts involve equilibration of fuel constituents between liquid metal and molten salt phases.

(1) Chemical Decladding Studies
(D. A. Wenz)

Vanadium-titanium alloys are currently receiving serious consideration as cladding materials for fast breeder reactor fuels (ANL-6880, p. 18). Since it appears unlikely that the cladding can be removed from high-burnup metallic fuels by mechanical means, chemical decladding may prove necessary. Although the clad fuel elements can very likely be dissolved in a liquid metal, e.g., zinc, subsequent separation of vanadium and titanium from uranium and plutonium by molten salt extraction of the liquid metal solution does not appear feasible. Therefore, other decladding procedures are being investigated.

Chlorination of the fuel to remove vanadium-titanium cladding material as volatile chlorides appears to be a promising possibility. Scouting experiments were conducted on the chlorination of uranium-fissium alloy and V-20 w/o Ti cladding alloy in the three following systems:

Chlorinating Agent	Temperature (°C)	Molten Salt Phase
Cl ₂ gas	~350	none
Cl ₂ gas	~600	75 m/o LiCl-25 m/o NaCl
CuCl ₂	~600	75 m/o LiCl-25 m/o NaCl

In all three cases, most of the titanium and vanadium was distilled from the system as volatile chlorides with little loss of uranium in the distillate. Further studies of this procedure are being made in order to obtain more definitive data on the behavior of cladding, fuel, and fission product elements.

(2) Solubility of Uranium and Plutonium in the Ternary System, Cadmium-Magnesium-Zinc
(R. von Ammon,* J. B. Knighton)

Cadmium-zinc-magnesium alloys are being investigated as process media for plutonium-bearing reactor fuels. Because of the low melting points and low corrosivity of some Cd-Mg-Zn alloys, they may permit the use of stainless steel equipment at relatively low temperatures (550 to 600°C). Stainless steel has the advantages of much lower cost and greater ease of fabrication than tantalum or tungsten.

In order to utilize the Cd-Mg-Zn system as a process solvent, uranium and plutonium must be sufficiently soluble that the process volumes do not become too large. Data on the solubility of uranium in this solvent over a temperature range from about 350 to 700°C, at magnesium concentrations from 10 to 20 a/o and zinc concentrations from 6 to 30 a/o, were reported previously (ANL-6800, p. 94). These measurements have been extended, using the same experimental techniques, and the results combined with data from other sources to show the solubility of uranium over the entire composition range of the ternary solvent. The solubility of plutonium has also been determined in the composition region of process interest, and the coprecipitation of plutonium with uranium has been examined briefly.

(a) Solubility of Uranium. One additional experiment was performed in which the solubility of uranium was determined by sampling a 74 a/o Cd-20 a/o Mg-6 a/o Zn alloy that was saturated with uranium at temperatures ranging from about 390 to 660°C. The results of this experiment and the results of the three experiments (ANL-6800, p. 94) for which analytical data were not previously available fit well into the solubility pattern described earlier.

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Figure I-4
SOLUBILITY BEHAVIOR OF
URANIUM IN Cd-Mg-Zn SOLUTION

Nominal Composition of Solvent:
74 a/o Cd, 13 a/o Mg, 13 a/o Zn

108-7952

A van't Hoff plot ($\log U$ solubility vs $1/T$) of results from a typical experiment (Run IV, ANL-6800, Figure I-16) is repeated in Figure I-4 to show the three characteristic temperature regions that exist in the system.

The following general observations can be made concerning the behavior of this system:

- (1) A region of retrograde uranium solubility (field a) exists at temperatures above about 600°C. The break, A, shifts to higher temperatures with increasing zinc concentrations and with decreasing magnesium concentrations in the solvent.
 - (2) The slope of the line in the intermediate temperature region (field b) varies strongly with changing solvent composition. The relationship between this slope and solvent composition is indicated in Figure I-5.
- The slope, initially corresponding to the heat of solution of U_2Zn_{17} in pure zinc solution, decreases sharply as the cadmium content of the solvent is raised to about 70 a/o, where the heat of solution becomes very small. The break, B, in Figure I-4 does not shift as much with varying solvent composition as does point A. Since the zinc concentration always shows a sharp break at the temperature corresponding to point A, field b appears to be a field of crystallization of the U_2Zn_{17} delta phase.

Figure I-5
CHANGE IN HEAT OF SOLUTION OF
DELTA PHASE U-Zn INTERMETALLIC
WITH INCREASING Cd CONTENT OF
Cd-Mg-Zn SOLVENT

Solvent: Cd-Mg-Zn; Cd and Mg concentrations as indicated, balance Zn

108-7954

(3) The uranium solubility line in the low-temperature region (field c) has a fairly constant slope that corresponds roughly to the solubility of UCd_{11} in the U-Cd binary system.¹ Although UCd_{11} is probably the primary equilibrium solid phase in field c, the zinc concentration continues to decrease with falling temperature, suggesting that additional U_2Zn_{17} may precipitate, or that zinc may be substituted for some of the cadmium in the UCd_{11} lattice.

(4) The uranium solubility generally decreases with increasing magnesium concentration and increases with increasing zinc concentration in the solvent. However, the latter effect prevails only up to about 20 a/o zinc, where the uranium solubility begins to decrease again.

(5) The fact that the magnesium concentration remains essentially constant with changing temperature indicates that magnesium is not incorporated into the equilibrium solid phase.

Comparison of these data with information already available on the solubility of uranium in the three binary solvents, Mg-Zn, Cd-Mg, and Cd-Zn¹ showed that a region of relatively high uranium solubility might exist in the cadmium-rich corner of the ternary diagram. Solubility information on the binary system, Zn-Mg, suggested that a second region of high uranium solubility might occur near that edge of the diagram. Four additional experiments were therefore conducted at constant temperature (600°C), starting with binary Zn-Mg alloys and adding cadmium in increments of 5 a/o, thereby proceeding along a tie-line toward the cadmium corner of the diagram at a constant Zn:Mg ratio.

In Figure I-6, the data from this investigation, the results of Martin,¹ and uranium solubilities obtained during the course of distribution coefficient measurements are combined into a ternary uranium solubility diagram. Two regions of relatively high uranium solubility are evident: one near the cadmium corner of the diagram on the Cd-Zn edge at 17 a/o zinc; the other at the Mg-Zn edge at 52 a/o zinc. The two maxima are connected by a saddle-shaped ridge with a minimum uranium solubility on this ridge at 38 a/o Cd, 38 a/o Mg, and 24 a/o Zn. This ridge of maximum uranium solubility also appears to be a boundary between fields of the quaternary phase diagram, as indicated by the fact that the addition of uranium causes the composition of the solvent to shift toward the ridge. Thus, a shift toward the Mg-Cd edge implies the consumption of zinc by precipitation of U-Zn intermetallic, and a shift toward the Zn-Mg edge indicates the precipitation of a U-Cd intermetallic. The solubility of uranium decreases rapidly as the solvent composition approaches the magnesium corner of the diagram, becoming almost nil in pure magnesium. The solubility also decreases rapidly, then levels out, on approaching the zinc

¹A. E. Martin, Private communication, August 31, 1960.

corner of the system. In the magnesium-rich and zinc-rich corners of the diagram, the uranium solubility is too low to be of process interest.

Figure I-6

SOLUBILITY OF URANIUM (WEIGHT PERCENT) IN
CADMIUM-MAGNESIUM-ZINC SYSTEM AT 600°C

108-7384

Further work has been done in order to obtain additional information on the solid phases in equilibrium with the saturated solutions. Metallographic examination of quenched samples from the intermediate temperature region (field b, Figure I-4) showed only the delta phase, U_2Zn_{17} , in the crystal bed that formed when the stirrer was stopped at the equilibrium temperature. However, both UCd_{11} and U_2Zn_{17} , which are formed during quenching, were found throughout the ingot. Similar experiments, in which samples were quenched from an equilibrium temperature just below point B (Figure I-4), showed two solid phases to be present in the low-temperature region: UCd_{11} and U_2Zn_{17} .

An attempt was made to isolate crystals formed in solvents of various compositions during quenching from the intermediate temperature region (field b). The matrix was dissolved selectively by an

aqueous 20% NH_4NO_3 solution; then the crystals were cleaned and submitted for chemical and X-ray analyses. The results, listed in Table I-6, show that the solid phase is U_2Zn_{17} . The stability range of this phase appears to be rather wide, since the atomic ratio $\text{Zn}(\text{Cd},\text{Mg}):\text{U}$ scatters considerably around the theoretical value of 8.50, although the average value is exactly that number. This result, coupled with the fact that the X-ray lattice constants were qualitatively proportional to the cadmium content of the U_2Zn_{17} , indicates that cadmium, and probably magnesium, can be substituted for some of the zinc in the crystals.

Table I-6

URANIUM INTERMETALLIC PHASE IN EQUILIBRIUM WITH
URANIUM-CADMIUM-ZINC-MAGNESIUM SOLUTIONS

Composition of Solvent (a/o)			Composition of Crystals (a/o)			Atomic Ratio (Zn + Cd + Mg):U
Mg	Zn	Cd	U	Mg	Zn	
10	10	80	10.27	0.58	81.84	7.31
10	13	77	10.53	0.37	82.28	6.83
10	20	70	10.56	0.28	86.17	3.08
10	30	60	10.89	0.72	83.93	4.27
13	13	74	10.74	0.45	83.28	5.53
13	20	67	10.53	0.44	85.12	3.91
16	7	77	10.32	0.32	84.39	4.97
20	6	74	10.35	0.30	85.90	3.46
20	20	60	10.52	1.13 ^a	84.00	4.20
						Average 8.50

^aQuestionable value.

The cadmium content of the delta-phase, U_2Zn_{17} , is shown as a function of the cadmium concentration in the solvent in Figure I-7. A general increase in the cadmium content of the solid phase with

Figure I-7

EFFECT OF CADMIUM CONCENTRATION
IN Cd-Mg-Zn SOLVENT ON CADMIUM
CONTENT OF DELTA-PHASE URANIUM-
ZINC INTERMETALLIC

rising cadmium concentration in the solvent is apparent. This result confirms the earlier observation that the heat of solution of U_2Zn_{17} decreases sharply with increasing cadmium concentration of the solvent in the region of 60 to 80 a/o (Figure I-5). Thus, the cadmium content of the solid phase appears to cause the large change in slope of the van't Hoff plots in the intermediate temperature range.

Only one satisfactory sample of UCd_{11} was obtained from a solution of low zinc content. X-ray data on the isolated crystals showed a decreased cell size, suggesting substitution of zinc in the lattice. However, a definitive result was not obtained because the sample was slightly contaminated with U_2Zn_{17} . An electron probe microanalysis of the UCd_{11} sample showed that the intermetallic crystals were not completely homogeneous, but that their composition varied slightly. This coring effect was not unexpected, since the equilibration temperatures were too low to achieve homogenization of the crystals through solid diffusion.

Inasmuch as it is felt that the solubility behavior of uranium in the Cd-Mg-Zn system has been sufficiently well defined for process purposes, no further investigation is planned.

(b) Solubility of Plutonium. Plutonium solubility determinations were limited to composition regions of the Cd-Mg-Zn system where the uranium solubility is high enough to permit process application. The alloy, 80 a/o Cd-20 a/o Zn, was chosen as a starting point. Magnesium additions to this alloy were made, and the solubility of plutonium was determined at various temperatures. Because of the large temperature coefficient of plutonium solubility and the fact that analytical results were not available until after the experiments were completed, it was not possible to achieve the accuracy obtained in the uranium solubility determinations. However, the relative error should not exceed $\pm 5\%$.

The solubility of plutonium was determined in the following solvents:

<u>Run Number</u>	<u>Mg (a/o)</u>	<u>Zn (a/o)</u>	<u>Cd (a/o)</u>
I	0	20	80
IV	10	20	70
III	15	20	65
II	20	20	60

The detailed data from Run III are given in Figure I-8, and in Figure I-9 all of the data are shown along with earlier results from the binary

Figure I-8
SOLUBILITY BEHAVIOR OF PLU-
TONIUM IN Cd-Mg-Zn SOLUTION
Nominal Composition of Solvent:
65 a/o Cd, 15 a/o Mg, 20 a/o Zn

108-7956

NOMINAL ALLOY COMPOSITION, a/o				RISING TEMP	FALLING TEMP	CURVE
Mg	Cd	Zn				
0	80	20		▲	●	a
10	70	20		▲	●	b
15	65	20		▲	●	c
20	60	20		Δ	○	d
0	0	100				e
0	100	0				f

Figure I-9
SOLUBILITY OF PLUTONIUM IN CAD-
MIUM, ZINC, AND Cd-Mg-Zn ALLOYS

108-7957

systems, Pu-Cd and Pu-Zn. The following conclusions may be drawn from these results:

- (1) In general, the solubility of plutonium in this solvent composition region is higher than that of uranium by a factor of about three to six. Since the plutonium content of a reactor fuel would be much lower than the uranium content (probably one-tenth to one-fifth as great), the solubility of uranium will undoubtedly be the limiting factor.
- (2) At temperatures of 550°C and above, the presence of zinc increases the solubility of plutonium in liquid cadmium. Increasing the concentration of magnesium in the solvent does not appear to affect the solubility of plutonium significantly, although above 600°C, a slight increase with rising zinc content was observed.

- (3) The slopes of the solubility lines in the van't Hoff plots are nearly constant with varying temperature and solvent composition. However, they differ from the solubility plots for plutonium in pure cadmium and in pure zinc. According to Figure I-8, the zinc content of the solvent decreased as plutonium was precipitated, but the atomic ratio of plutonium decrease:zinc decrease in solution varied from 0.5 to about 4. Thus, from these data alone it was not possible to determine whether a Pu-Zn intermetallic compound was formed in addition to a Pu-Cd compound, or whether zinc was being substituted in the lattice of a Pu-Cd compound.

To investigate further the nature of the equilibrium solid phase, one quenching experiment was performed, using a solvent of the composition 70 a/o Cd, 20 a/o Zn, and 10 a/o Mg. Only one field of the phase diagram was apparently involved under these conditions. Metallographic examination of the crystal bed and the solidified ingot showed only platelets with the characteristic shape of the delta phase, U_2Zn_{17} . Attempts to isolate intermetallic crystals by leaching the matrix with aqueous NH_4NO_3 solution were unsuccessful, since by this treatment the plutonium was converted to PuO_2 . X-ray examination of filings from the ingot, however, showed the predominant phase to be a solid solution with a hexagonal cell characteristic of cadmium metal. Several reflections of $\text{Pu}_2\text{Zn}_{17}$ were also observed, but there were no signs of the cubic PuCd_6 phase or of PuCd_{11} .

The apparent stability of the plutonium-zinc phase over a large temperature range in a cadmium-rich solution is somewhat surprising. However, in view of the fact that the atomic ratio of zinc to plutonium being precipitated from solution was much smaller than 8.5, as stated above, $\text{Pu}_2\text{Zn}_{17}$ cannot be the only phase precipitated. Either metallic plutonium or an undetected Pu-Cd intermetallic compound must have been precipitated, since it is not reasonable to expect that 50% or more of the zinc in $\text{Pu}_2\text{Zn}_{17}$ could be replaced by cadmium.

(c) Coprecipitation of Plutonium with Uranium. One experiment was conducted to investigate the coprecipitation of plutonium with uranium in a solvent composition of process interest. The composition of the solvent, 69 a/o Cd, 16 a/o Zn, and 15 a/o Mg, lies on the ridge of maximum uranium solubility (see Figure I-6). A uranium:plutonium ratio of about 4 at the point of maximum solubility was used, since this is approximately the ratio that might be anticipated in future EBR-II core fuel. Samples of the solution were taken after equilibration at each temperature.

The results are shown in Figure I-10. The uranium solubility was not affected by the presence of small amounts of plutonium. The amount of uranium in solution and the shape of the solubility plot were the same as those obtained in the absence of plutonium. Plutonium was coprecipitated with uranium to a small extent from the solution, which was unsaturated with plutonium. The coprecipitation followed the law of Doerner and Hoskins,² which is valid when the crystallizing layer does not equilibrate with the remainder of the solid. The Doerner-Hoskins plot in Figure I-11 shows a break where the crystallization field changes from U_2Zn_{17} plus UCd_{11} to U_2Zn_{17} alone. The coprecipitation coefficient, λ , however, is rather low in both fields (0.068 and 0.164, respectively). A much larger value (0.66) had been obtained previously in zinc alone (ANL-5789, p. 89). Thus, it may be possible to effect a separation of plutonium by selectively precipitating uranium from Cd-Mg-Zn solutions in this region of composition.

Figure I-10

COPRECIPITATION OF PLUTONIUM WITH URANIUM IN Cd-Mg-Zn SOLVENT

Nominal Composition of Solvent: 69 a/o Cd, 15 a/o Mg, 16 a/o Zn

108-7958

Figure I-11

COPRECIPITATION OF PLUTONIUM WITH URANIUM IN Cd-Mg-Zn SOLUTION

Nominal Composition of
Solvent: 69 a/o Cd,
15 a/o Mg, 16 a/o Zn

108-7959

(3) Distribution of Elements between Liquid Metals and Molten Salts

(J. B. Knighton, J. D. Schilb, J. W. Walsh)

Since the separations of fissile and fertile elements and fission products are effected through differences in the distribution behavior of these elements between liquid metals and molten salts, it is necessary to determine distribution coefficients that are pertinent to the process. Praseodymium was chosen as a representative of the rare earth fission products because it is one of the more difficult rare earths to separate from uranium and plutonium and because it is conveniently analyzed. In addition to praseodymium, some results have been obtained on einsteinium and californium with the thought in mind that this type of separation may be applicable to mixtures of transuranium elements.

(a) Praseodymium. The distribution behavior of praseodymium between 30 m/o NaCl-20 m/o KCl-50 m/o $MgCl_2$ * and various compositions of the Cd-Mg-Zn system has been determined at 600°C. It was considered advantageous to determine first the distribution of praseodymium alone over a wide composition range of Cd-Mg-Zn alloys,

*A ternary eutectic composition used at Brookhaven National Laboratory for the extraction of fission products from liquid bismuth alloy fuel.

thereby avoiding much difficult and costly work with plutonium in regions that would not be of process importance.

The experimental results are illustrated in Figure I-12. Praseodymium shows the same general type of distribution behavior with changing magnesium concentration in Cd-Zn solutions that had been observed previously in liquid zinc. A minimum in the distribution coefficient (w/o Pr in salt/ w/o Pr in metal) occurs in the region of 20 to 40 a/o magnesium in the metal phase. The distribution coefficient increases at both higher and lower magnesium concentrations. At the low magnesium concentrations, the distribution coefficients of uranium, plutonium and rare earths are so sensitive to slight variations in magnesium concentration in the metal phase that process control difficulties would be expected. At the high magnesium concentrations, the solubility of uranium in Zn-Mg and Cd-Zn-Mg solutions becomes very low. Because of these two effects, favorable compositions for process separations are limited to the magnesium concentration region of about 5 to 20 a/o.

Figure I-12

DISTRIBUTION COEFFICIENT (w/o Pr in Salt/ w/o Pr in Metal)
OF PRASEODYMIUM BETWEEN 30 m/o NaCl-20 m/o KCl-
50 m/o $MgCl_2$ AND Cd-Mg-Zn ALLOY AT 600°C

In Figure I-12 it is interesting to note that praseodymium strongly favors the metal phase in high zinc-low magnesium alloy (80 a/o Zn-20 a/o Mg). This behavior is significant in that it offers a means whereby rare earth fission product elements could be removed from the process salt by extraction with this alloy if cleanup of the salt for recycle is desired.

(b) Einsteinium. Determinations of the distribution of einsteinium (^{253}Es , $t_{1/2} = 20$ days) between molten MgCl_2 and liquid Zn-Mg alloys were made. The quantity of einsteinium (5×10^6 alpha counts/min) was insufficient to use the two-phase sampling technique employed in the other distribution studies. Instead, the following procedure was followed: The tracer einsteinium was coprecipitated from aqueous solution with LaF_3 on pieces of zinc foil, which were dried and charged to 5-ml Morganite recrystallized alumina crucibles. A total of 5 g of metal (zinc and magnesium) was then introduced into each crucible in proportions that would provide a range of magnesium concentrations from 2 to 67 w/o. Purified MgCl_2 (approximately 2 g) was then added, the charged crucible was placed in a graphite block, and the assembly was heated to 800°C under an argon atmosphere for a 2-hr period. After cooling overnight, the salt and metal phases were separated and analyzed for einsteinium. The magnesium content of the metal phase was also determined. Before the experiments were conducted, this procedure was tested, using uranium. Good agreement was found with the uranium distribution data that had been obtained earlier by the standard sampling procedure.

The results of this study are shown in Figure I-13. Because of the procedure used in these experiments, the distribution coefficients were measured at 710°C , the melting point of MgCl_2 . The data

Figure I-13

DISTRIBUTION OF EINSTEINIUM BETWEEN MAGNESIUM CHLORIDE AND ZINC-MAGNESIUM ALLOY

Conditions

Temperature:	710°C (melting point of MgCl_2)
Atmosphere:	Argon
Crucible:	Alumina, except where otherwise indicated
Time:	2 hr at 800°C

108-7960

showed considerable scatter at magnesium concentrations below 30 w/o but it is evident that einsteinium distributes strongly to the salt in this system. A minimum in the distribution curve occurs at about 30 w/o magnesium, compared to about 10 w/o magnesium for the other actinide elements.

(c) Californium. Two experiments were performed to determine the distribution of californium (^{252}Cf , $t_{1/2} = 2.5 \text{ yr}$) between molten MgCl_2 and liquid Zn-Mg alloys. Tracer californium was coprecipitated with LaF_3 and plated on zinc foil for introduction into the crucible.

In the first experiment, the conditions, procedure, and equipment employed were similar to those used for the determination of other actinide and lanthanide distribution coefficients in the same system (ANL-6543, p. 49). The californium content of the salt and metal samples was determined by counting spontaneous fissions.

In the second experiment, the technique used in the einsteinium distribution coefficient measurements was employed to obtain distribution data at magnesium concentrations of 14 and 66 w/o in the metal phase. The californium in the salt and metal was determined by gamma counting.

The results of the two experiments, given in Figure I-14, show californium distributing strongly to the salt phase at magnesium concentrations below about 20 w/o in the Zn-Mg phase. As the magnesium concentration in the metal phase was increased, the californium showed an increasing tendency to distribute to the metal phase. This effect was unexpected, since it had not been observed with any of the other elements that were investigated.

Figure I-14

DISTRIBUTION OF CALIFORNIUM BETWEEN MAGNESIUM CHLORIDE AND ZINC-MAGNESIUM ALLOY

Conditions

Temperature: As specified

Mixing Rate: 300 rpm (in 800°C experiment)

Crucible: Tantalum or alumina

Atmosphere: Argon

The results of the two different types of distribution experiments using different experimental procedures and counting techniques are in good agreement. These results open the possibility that separations of other transuranium elements might be achieved by liquid metal-molten salt extraction processes.

(4) Selection of a Liquid Metal Solvent (J. B. Knighton)

The ternary system, Cd-Zn-Mg, appears attractive as a solvent for liquid metal processes for metallic fast breeder reactor fuels. At low zinc concentrations and decreased operating temperatures, it may be possible to utilize Series 400 stainless steels instead of tantalum or tungsten as container materials. The principal criteria governing the choice of a liquid metal solvent are:

1. A solvent melting point lower than the desired operating temperature.
2. Low rate of corrosion of container materials by the solvent.
3. Adequate solubilities of the major fuel constituents in the solvent.
4. Distribution coefficients that will permit the necessary separations of fission products from plutonium alone or from uranium and plutonium.

Figure I-15 is a composite ternary diagram of the Cd-Zn-Mg system showing melting points of various Cd-Zn-Mg compositions, the corrosion rates of type 405 stainless steel by various compositions, the ridge of maximum uranium solubility in the Cd-Zn-Mg system, and the compositions for which the distribution coefficient of the rare earths (as represented by praseodymium) is unity. For an operating temperature of 600°C, the melting point of the solvent³ offers no restriction, except at very high magnesium concentrations (above about 85 a/o).

Rates of corrosion of type 405 stainless steel by Cd-Zn-Mg at 750°C are plotted in Figure I-15. These corrosion rates increase nearly proportionally with zinc concentration. Compositions are desirable which would give corrosion rates of less than 2 mils/1000 hr at 750°C (since such compositions would give much lower corrosion rates at 600°C).

Using the data from Figure I-6, a curve showing the ridge of maximum uranium solubility has been incorporated into Figure I-15. Although the uranium solubility at any point along this curve is probably

³E. Janecke, Z. Metallkunde 30, 424 (1938).

sufficiently high for process purposes, the solubility is higher at the two ends of the curve than at its midportion. The solubility of plutonium would not be a limiting factor at any point along the maximum uranium solubility curve.

Figure I-15

FACTORS AFFECTING SELECTION OF LIQUID METAL SOLVENT COMPOSITION FOR MOLTEN SALT-LIQUID METAL EXTRACTION PROCESS

108-7962

To achieve a satisfactory separation of rare earth fission products from plutonium by extraction of the liquid metal solution with a molten salt such as NaCl-KCl-MgCl_2 , it is desirable to operate in a composition region where the distribution coefficients for the rare earths are greater than unity, and the distribution coefficient for plutonium is less than unity. Fields in which distribution coefficients for praseodymium are respectively greater than unity and less than unity are separated by the curve shown in Figure I-15. The region below about 5 a/o magnesium is ruled out because of the extreme sensitivity of distribution coefficients of uranium, plutonium and rare earths to small changes in magnesium concentration.

Taking these various factors into account, the most satisfactory composition region in the Cd-Zn-Mg system for separations of rare earths from uranium and plutonium by molten salt extraction is at about 15 a/o zinc and 5 to 20 a/o magnesium.

(5) Development of Engineering Equipment and Procedures
(R. D. Pierce)

Pyrometallurgical procedures for recovering uranium and plutonium values from partially spent advanced-fast-reactor fuels consist of a sequence of oxidation and reduction reactions in liquid metal and fused chloride salt media. Process and equipment development effort is currently centered on the requirements for the separation of rare earth elements from uranium and plutonium. In one promising process, multistage contacting of molten metals and molten salts is required to achieve this separation. A program is in progress to develop a packed extraction column and associated equipment for this purpose.

(a) The Design of Molten Metal-Fused Salt Extraction Columns
(T. R. Johnson, V. G. Trice)

Evaluations of the feasibility of using liquid metal-fused salt extractions to separate rare earth fission products from actinides are being made. The experimentally determined distribution coefficients* of rare earths and actinides in solvent systems of Zn-Cd-Mg with salts containing MgCl_2 with Group I chlorides were used in making calculations on typical fuel processes. Equations have been derived to facilitate the extraction calculations for compound columns when the recoveries of two distributing elements (e.g., plutonium and a rare earth element) are specified. These evaluations have shown that the liquid metal-liquid salt extractions should have wide applicability to advanced fast reactor fuel reprocessing. Recoveries of uranium and plutonium of greater than 99% and rare earth removals of greater than 80%, which are adequate, can be achieved in a compound extraction device with two to four extraction stages and one or two scrub stages. The actinide fraction appears in the metal solution product, and the rare earth elements appear in the salt, from which they may be later stripped to permit reuse of the salt.

The evaluations have shown that for processes in which both uranium and plutonium are kept in solution, cadmium-rich metal solutions are preferable to zinc-rich systems. (1) Cadmium-rich metal solutions and the chloride salts of several alkali and alkaline earth metals can be contained in stainless steels but zinc-rich solutions cannot. With cadmium-rich solutions, temperatures below 650°C may be used for the

*ANL-6648, p. 48. ANL-6687, p. 41.

extraction operations; with zinc-rich solutions, higher temperatures are required. (2) For a given plutonium recovery and rare earth removal, the amount of waste salt generated is less for metal systems rich in cadmium. However, in any case, the quantity of the waste stream can be reduced if desired by extracting the rare earth fission products into a metal phase. The salt extractant could then be recycled.

(b) Operation of a Prototype Packed Extraction Column with Molten Metal and Water as the Immiscible Phases

(T. R. Johnson, V. G. Trice, E. D. Johanson,*
L. F. Dorsey, W. H. Spicer)

A prototype extraction column has been constructed of 1-in. ID glass pipe and is being used in the component development program. In the prototype column, Wood's metal (an alloy consisting of 50 w/o bismuth, 27 w/o lead, 13 w/o tin, and 10 w/o cadmium and melting at about 70°C) is contacted countercurrently with hot water. The prototype has proved useful in the development of engineering techniques. Observations have been made of operating characteristics and holdup of the phases with the column filled with two different types of packing.

A sketch of the prototype extraction facility is presented in Figure I-16. Since the column was operated with water as the continuous phase, the metal-water interface was at the bottom of the column. The level of this interface was controlled by a manually operated jackleg. Where necessary, the process lines and vessels were heated and insulated to prevent freezing of the metal phase. A variety of heating methods were employed, primarily to gain experience in alternative heating techniques. Thermostatically controlled in-line heaters were employed in both influent lines to provide close temperature control. The column was operated with the influent temperatures close to the boiling point of water.

The influents were fed to the column by pressurizing the feed tanks with nitrogen, the flowrates being controlled with throttling valves. The water flow rate was measured with a rotameter and the metal flow rate with a gravity flowmeter which was mounted on top of the column. Purge-flow dip tubes were successfully used to monitor liquid level in the feed tanks, and a resistance probe was also employed successfully to monitor the level in the metal feed tank.

The operation of the column was observed and photographed through a narrow slit in the insulation at metal flow rates of 10 to 210 cc/min and water flow rates of 100 to 500 cc/min with the column packed with perforated nickel saddles (3.5 mm dia. by 4 mm long)

*Research associate, Northwestern University.

and with 5-mm diameter glass spheres. Metal phase holdup estimates were obtained by injecting cold water to freeze the metal, after which the column was disassembled, the packing removed, and the frozen metal recovered for examination.

Figure I-16

METAL-WATER PROTOTYPE EXTRACTION FACILITY

108-7997

The data obtained in two holdup determinations appear in Table I-7. In the first run, in which a metal flow rate of 110 cc/min and a water flow rate of 100 cc/min were employed, the metal phase residence time in a column packed with perforated nickel saddles was 1.1 sec per centimeter of packed column. In the second run, the column

was packed with glass spheres, and at a metal flow rate of 80 cc/min and a water flow rate of 100 cc/min, the metal phase residence time was 0.36 sec per centimeter of packed column. The increased residence time which appears to be characteristic of metal saddles as compared to spheres is one of the factors that will be considered in the choice of packing for use in separations processes.

Table I-7

HOLDUP MEASUREMENTS IN PROTOTYPE EXTRACTION COLUMN

Column ID: 1 in.
 Dispersed phase: Wood's Metal^a
 Continuous phase: Water

Packing	Run 1	Run 2
	Nickel saddles (3.5 mm dia. by 4 mm long)	5-mm glass spheres
Packing Fraction (v/o)	6	70
Metal Flow Rate (cc/min)	110	80
Water Flow Rate (cc/min)	100	100
Metal Phase Holdup:		
Percent of Column Volume	20	9
Percent of Packing Void Volume	21	30
Estimated Surface Area of Metal Phase: ^b		
Small Spheres (cm ² /cm column height)	17	0
Agglomerates (cm ² /cm column height)	13	7
Residence Time of Metal (sec/cm of packed column height)	1.1	0.36

^aWood's Metal is 50 w/o bismuth, 27 w/o lead, 13 w/o tin, and 10 w/o cadmium; it melts at 70°C.

^bThe metal phase in the column packed with saddles consisted of small spheres and massive agglomerates. Spheres of metal were not present in the column packed with 5-mm glass spheres.

Differences were noted in the manner that the metal phase traversed the column when the column was packed with saddles and when it was packed with spheres. With saddle packing, the metal phase appeared to form a number of collection centers or pools which were randomly scattered through the packing. Metal droplets appeared to travel through the column by passing from pool to pool. Samples of the metal phase in the column, which were obtained by suddenly dropping the temperature of the column to freeze the metal, are shown in Figure I-17.

About 25 w/o of the metal in the samples was in the form of small spherical particles. The remainder consisted of agglomerates which apparently were the pools that were observed in the operating column. The pool effect was not observed when the column was packed with spheres. Instead, the metal phase appeared to traverse the column as small continuous rivulets.

Figure I-17

REPRESENTATIVE SELECTION OF WOOD'S METAL PARTICLES^a
RECOVERED FROM THE PROTOTYPE EXTRACTION COLUMN

Column packing: Perforated nickel saddles
3.5 mm diameter by 4 mm long

108-7963

^aThe samples were obtained by rapidly injecting cold water into the column to freeze the Wood's metal.

(c) High-Temperature Extraction Facility
(T. R. Johnson, V. G. Trice, A. Kelecus*)

A prototype high-temperature extraction facility is being designed to determine the engineering practicality of various types of extraction columns for separations of actinides from rare earth fission products in molten salt-liquid metal systems. Nickel-free stainless steels appear to be the best overall material of construction for this facility since they are reasonably resistant to corrosion by cadmium-base alloys and chloride salts if the salts contain no strongly oxidizing materials. These stainless steels are also resistant to air oxidation at 600°C, are available, and can be formed and welded.

The salts to be used in this equipment must be purified to remove oxidizing agents and insolubles. Contacting a molten chloride salt with a cadmium-30% magnesium alloy at 550°C and filtering just above the salt's melting point through a 30-micron filter produces a salt which is not appreciably reactive toward stainless steel and which contains less than 0.2% insolubles when dissolved in water. Upon melting, the purified salt is clear except for a trace of very fine insoluble material. A salt purification facility for use with the engineering test loop and the high-temperature extraction facility is being designed.

(d) Preliminary Extraction Studies
(T. R. Johnson, V. G. Trice, F. G. Teats)

Although the experiments with the metal-water column showed no mechanism that might indicate inherently low extraction rates in high-temperature metal-salt systems, further preliminary experiments are planned before the high-temperature demonstration facility is built. In these experiments, rough measurements will be made of the mass transfer rate of uranium or a rare earth between a cadmium-rich metal phase and a salt containing magnesium chloride. Metal containing the distributing element will be passed into a packed bed filled with molten salt. The salt will move only as it is displaced by the metal. After one to two column volumes of metal have passed through the column, the packed bed will be frozen rapidly and the two phases analyzed to determine the amount of solute transferred from the metal into the salt.

(e) Component Development Program

A program to develop components for service in the high-temperature fused salt-molten metal continuous solvent extraction facility is in progress. An engineering test loop now under construction will be used to test components under conditions similar to those expected in the continuous extraction facility.

*CEN Drafting Group.

Eddy Current Liquid Level and Interface Probe (F. G. Teats, T. R. Johnson, I. O. Winsch)

A device for determining liquid levels and interface height in a liquid metal-liquid salt system by use of an eddy current induction probe of the type developed by Davidson⁴ is being further developed. The probe is a bifilar winding of nichrome wire on an alumina form. The windings are insulated and held in place with a ceramic adhesive. When a high frequency voltage is applied to one coil, a voltage is induced in the second coil. The voltage induced is sensitive to the presence of an electrical conductor in the medium surrounding the coil and, therefore, to the immersion depth of the coil in liquid metals.

The probe and its operation are fully described in ANL-6800, p. 118, which also presents a circuit diagram and a photograph of the probe. To determine liquid level, the probe is inserted into a stainless steel well which extends into the liquid.

The probe currently in use is not completely satisfactory because the ceramic adhesive used to bind and insulate the coil (Mil-bond produced by Mel-Par Inc.) tends to flake off at high temperature.

Alternative adhesives are being sought, and a new grooved alumina core is being fabricated which should give the probe assembly greater mechanical strength and eliminate the need for the ceramic adhesive.

Figure I-18
LIQUID LEVEL CALIBRATION
FOR MAGNESIUM, CADMIUM,
AND CADMIUM-8 w/o MAGNESIUM

108-7964

A study has been made to determine the optimum frequency and voltage for the measurement of the liquid level of molten cadmium and cadmium-magnesium solutions. A frequency of 50 kc and a voltage of 7 volts were selected as most satisfactory for the present equipment.

The results of liquid level measurements for the probe immersed in cadmium at 403°C, cadmium-8 w/o magnesium at 613°C, and pure magnesium at 720°C are presented in Figure I-18. The molten metals were each contained in a 5½-in. ID stainless steel crucible, and immersion in the liquid was increased by lowering the probe in the well. Between immersion depths of 1 and 4 in., linear relationships with a slope of -2.0 mv per inch of depth were obtained for all three of the above metal systems. With

⁴Davidson, D. F., IGR-R/CA-255 (1957).

the cadmium solutions, no response was observed for about the first 3/4 in. of immersion, but an immediate response was noted when the probe was immersed in magnesium.

Pulse Pump (V. G. Trice, L. F. Dorsey)

A low-capacity pump for circulating corrosive metals and salts is needed for use with the high temperature extraction column. A gas-pulse pump which has been built for use with fused salts and liquid metals features two check valves as the only mechanical parts either in contact with the fluid or located in the high temperature zone. A sketch which illustrates the operation of the pump is presented in Figure I-19. The force necessary to pump the fluid is transmitted pneumatically. When the first cam-actuated valve in the gas line is open and the second is closed, air pressure forces the liquid down the pulse leg and

Figure I-19

PULSE PUMP

through the overflow pipe. When the first valve is closed and the second is open, liquid enters the pulse leg through the check valve between the reservoir and the pulse leg. The direction of flow of the liquid is thus controlled. The pumping rate is controlled by varying the dwell of the cams and the pulse frequency. In tests with a variety of fluids (with water and mercury as the extremes in density), flow rates over the range of 20 to 600 cc/min were demonstrated for all fluids.

Centrifugal Pump (T. R. Johnson, J. Nixon*)

A centrifugal pump for liquid metals or salts is being designed. The pump, which will have a $3\frac{3}{4}$ -in. dia. impeller and a maximum speed of 1800 rpm, will circulate somewhat more than 1 gpm against a head of 10 ft of fluid. The pumped fluid will discharge downward through a fitting which will make a slip fit joint between the tank and the impeller housing. A mechanical shaft seal comprised of a tungsten carbide stator rubbing against a hardened steel shoulder on the shaft will be capable of operating at temperatures up to 250°C and will be partially cooled by water circulating in the pump shaft. The pump, mounted in a tank, will be first tested in the Engineering Test Loop before it is used in the High Temperature Extraction Facility.

Engineering Test Loop (V. G. Trice, L. F. Dorsey)

An engineering test loop is under construction for use in the development of components for service in the high-temperature extraction facility. The suitability of several alternative heating techniques will be determined on this equipment. The loop will be used to test the performances of the pulse pump and the centrifugal pump and to evaluate different types of flowmeters and valves.

c. Supporting Chemical Investigations (R. K. Steunenberg)

Supporting studies dealing with molten salt and liquid metal systems are being pursued to supply data for process use and to elucidate the chemical aspects of various process steps. During the reporting period, this work has been concentrated mainly on physical properties and solubility relationships of multicomponent salt systems.

(1) Liquidus Temperatures of the System LiCl-NaCl-MgCl₂ (N. R. Chellev, J. T. Feeney)

In the selection of a molten salt for liquid metal processing of fast breeder reactor fuels, it is known (ANL-6596, p. 61; ANL-6648, p. 45) that favorable distribution coefficients for the separation

*Central Shops Drafting Dept.

of rare earth fission products from uranium and plutonium are obtained with salts containing a high proportion of MgCl_2 . When alkali metal chlorides are added to the MgCl_2 to reduce the melting point, better separations are possible if the lower atomic weight cations are used. Therefore, the criteria for selecting a salt system are (1) a high MgCl_2 content, (2) a sufficiently low melting point, and (3) dilution of the MgCl_2 with low atomic weight alkali metal chlorides. The systems LiCl-NaCl-MgCl_2 and LiCl-KCl-MgCl_2 appear attractive. Since the melting points of various compositions of these salt systems were not available in the literature, a determination of the liquidus temperatures of these two systems was undertaken. Results are presently available on the LiCl-NaCl-MgCl_2 system.

Anhydrous MgCl_2 was purified by triple sublimation at 775°C and at less than $50\ \mu$ pressure. Reagent grade LiCl was exposed to chlorine as it was slowly heated to melting; then the excess chlorine was removed by sparging with helium. Reagent grade NaCl ($>99.95\%$ purity) was heated to 825°C and cast into small rods. All salts were stored under a purified helium atmosphere.

Conventional thermal analysis procedures were used, in which 7 to 25 g of salt mixture was held in a tantalum crucible, and temperatures were measured by means of a chromel-alumel thermocouple with a 10-mil stainless steel sheath that was immersed in the melt. The system was sealed from the atmosphere, with provisions for heating the salt under vacuum or argon, adding salt to the charge, and withdrawing samples. All operations were carried out without exposing the salt to the atmosphere. The apparatus was calibrated with reagent grade recrystallized NaCl (m.p. 800.4°C) and with a Bureau of Standards sample of lead (m.p. 327.4°C). The precision of the measurements was $\pm 1^\circ\text{C}$.

In the thermal analysis determinations, the composition of the salt was varied incrementally by repeated additions of NaCl to fixed ratios of $\text{MgCl}_2\text{:LiCl}$ so as to provide data on composition lines radiating from the NaCl corner of the diagram. Liquidus temperatures for 60 compositions are listed in Table I-8. At the completion of each set of measurements along a composition line, the salt was sampled and analyzed. The results showed good agreement with the composition calculated from the quantities of salts added to the system.

A contour plot of the liquidus surface of the ternary diagram is presented in Figure I-20. This figure was derived from plots of the quasibinary systems in which NaCl was one component, and the second component was a fixed ratio of MgCl_2 and LiCl . The edges of the plot were characterized by literature data on the three binary systems, LiCl-MgCl_2 (ANL-6596, p. 78), LiCl-NaCl ,⁵ and NaCl-MgCl_2 .⁶ For the

⁵Akopov, E. K., Zhur. Neorg. Khim. 1, 1019 (1956).

⁶Klemm, W., and Weiss, P., Z. anorg. u. allgem. Chem. 245, 281 (1940).

LiCl-MgCl₂ edge, the initial liquidus determinations reported in Table I-8 were within 3°C of the earlier values (loc.cit.).

Table I-8

LIQUIDUS TEMPERATURES FOR THE SYSTEM LiCl-NaCl-MgCl₂

Section I		Section II		Section III		Section IV		Section V		Section VI	
Starting Mixture		Starting Mixture		Starting Mixture		Starting Mixture		Starting Mixture		Starting Mixture	
LiCl	Temp.	MgCl ₂	Temp.	MgCl ₂	Temp.	MgCl ₂	Temp.	MgCl ₂	Temp.	MgCl ₂	Temp.
(m/o)	(°C)	(m/o)	(°C)	(m/o)	(°C)	(m/o)	(°C)	(m/o)	(°C)	(m/o)	(°C)
0	685	0	656	0	not measured	0	616	0	591	0	593
10.9	656	9.1	629	34.0	480	7.7	599	9.6	560	9.6	566
19.9	624	17.0	598	36.1	471	14.3	563	18.9	526	17.4	544
30.5	572	26.6	549	44.0	447	22.5	527	30.9	487	28.9	518
41.8	488	36.0	492	47.2	452	31.8	486	36.2	478	39.7	530
45.1	466	37.0	483			40.9	452	41.9	483	50.6	583
49.2	455	39.7	468			50.6	474	50.2	541	60.4	637
51.3	456	44.4	453			60.7	567	59.8	601	70.1	683
54.1	452	49.6	437			70.7	647	69.2	637 ^b		
59.5	433 ^a	53.7	457					75.4	695		
61.0	461	56.4	483								
65.5	548	66.0	583								
70.1	597	70.8	626								
79.1	684	77.5	683								

^aMinimum of liquidus surface.

^bValue questionable because of suspected equipment malfunction.

Figure I-20

SYSTEM LiCl-NaCl-MgCl₂

(Temperatures in °C)

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The data indicate a minimum liquidus temperature in the ternary system at 59.5 m/o NaCl, 35.0 m/o MgCl_2 , and 5.5 m/o LiCl. From this point, the liquidus valley gradually rises toward the minimum in the LiCl-NaCl edge of the diagram (553°C at about 27 m/o NaCl).

For process use, the composition region of greatest interest is that in which the salt is liquid at temperatures below about 550°C and contains both a high MgCl_2 concentration and a larger proportion of the lower atomic weight alkali metal chloride (LiCl). It is evident from the diagram that the ternary salt containing a minimum of 50 m/o MgCl_2 has a liquid region at temperatures below 550°C with LiCl concentrations up to about 30 m/o.

(2) Solubility of Magnesium Fluoride in the System
 MgCl_2 - CaCl_2
(M. D. Adams, D. M. Meyer)

In the EBR-II skull reclamation process, a flux consisting of 47.5 m/o CaCl_2 , 47.5 m/o MgCl_2 , and 5.0 m/o MgF_2 was adopted for use in the reduction of uranium oxide by Zn-Mg alloy. During the preparation and handling of this flux, some indications were obtained that the MgF_2 might be near its limit of solubility in this system. The solubility of MgF_2 in the system MgCl_2 - CaCl_2 at various compositions and temperatures was therefore examined briefly.

In general, the solubilities were determined at several temperatures up to about 100°C, above the melting point of the solvent. However, within the precision of the data, no significant correlation between the solubility of MgF_2 and temperature was found. It appears that the temperature coefficient of MgF_2 solubility in this system is very small.

Smoothed solubility data for MgF_2 in MgCl_2 - CaCl_2 are shown as a function of composition in Table I-9. Although the experimental data

Table I-9

SOLUBILITY OF MAGNESIUM FLUORIDE IN MAGNESIUM
CHLORIDE-CALCIUM CHLORIDE MIXTURES

Solvent Composition (m/o)		Solubility of MgF_2 (m/o)		Solvent Composition (m/o)		Solubility of MgF_2 (m/o)	
MgCl_2	CaCl_2			MgCl_2	CaCl_2		
0	100	15.1		60	40	5.8	
10	90	13.1		70	30	6.8	
20	80	10.6		80	20	7.9	
30	70	6.7		90	10	9.2	
40	60	4.4		100	0	10.6	
50	50	5.0					

^aThe effect of varying temperature on the solubility of MgF_2 over this range was negligible within the estimated experimental accuracy of $\pm 10\%$ (relative).

showed considerable scatter, the results in Table I-9 are believed to be reliable within $\pm 10\%$. It is clear that the MgF_2 in the above-mentioned flux is very close to its solubility limit (5.0 m/o in equimolar $\text{MgCl}_2\text{-CaCl}_2$), leading to the recommendation that the concentration of MgF_2 in the process flux be decreased to 3 or 4 m/o .

d. Supporting Engineering Studies
(L. Burris, Jr.)

During the past reporting period, engineering studies were conducted in two areas: (1) liquid metal boiling, specifically, the nonturbulent vaporization of mercury, and (2) determination of the critical constants of alkali metals.

(1) Study of Mechanisms of Liquid Metal Boiling and Entrainment
(J. Wolkoff, J. J. Heiberger)

The boiling of liquid metals has been actively studied in recent years from the standpoints of heat transfer rates and technology. Aside from equipment development and corrosion studies, the major interest of most investigators appears to be measurement of boiling rates, and correlation of pertinent parameters for design purposes. Comparatively few studies have been devoted to fundamental investigations of the vaporization mechanism. The older field of aqueous boiling similarly contains relatively few fundamental studies, although studies have been more numerous. Liquid metal systems, partly because of greater experimental difficulties, lag behind aqueous systems in fundamental knowledge. The physical property differences between water and liquid metals are great enough that significant differences in their behavior would be expected.

The phenomena associated with the vaporization of pure mercury from the free liquid-vapor surface have been under study. Nucleation within the liquid has been avoided or minimized by operating at low pressure (< 5 torr) and by controlling the heat input. With this vaporization mode (here referred to as nonturbulent vaporization), there is no droplet formation and thus no droplet entrainment.

The all-glass boiling loops used in earlier work have been previously described (ANL-6596, p. 81; ANL-6648, p. 85); a later modification with pressure taps into the vapor space and with an internal liquid metal cold junction is shown in Figure I-21. As before, either induction or external resistance heaters could be used. The pressure in the vapor space immediately above the vaporizing surface was read with a McLeod gage. The liquid metal thermocouple system shown, which has hot and cold junctions, respectively, at the vaporizing mercury surface and within an ice bath Dewar, was used for most of the temperature explorations. The hot junction probe could be moved laterally or vertically.

Figure I-21
TUBULAR-POOL MERCURY BOILING LOOP

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Vertical temperature traverses taken with the liquid metal thermocouple system showed that a steep temperature gradient existed across a thin (~ 0.2 in. thick) surface layer of mercury. Gradients of up to $115^{\circ}\text{C}/\text{in.}$, increasing with vaporization rate, were reported in ANL-6800, p. 133; more recent measurements have given values which range up to $165^{\circ}\text{C}/\text{in.}$ Below the thin surface layer, the temperature was almost constant with depth. A composite plot of three vertical traverses made with the liquid metal thermocouple, shown in Figure I-22, illustrates the magnitude of scatter in the data. The temperature gradient in the surface layer is $120^{\circ}\text{C}/\text{in.}$, based on a least-squares fit of a straight line to the data.

The temperature gradients observed in the thin surface layer account, by molecular conduction, for less than 20% of the total heat flux corresponding to the mercury vaporization rate. It is therefore suggested that the primary heat transfer mechanism is one of convection where turbulent eddies from the core of the pool penetrate to the surface

Figure I-22

TEMPERATURE VS DEPTH COMPOSITE
PLOT OF THREE VERTICAL TRAVERSES
AT CENTERLINE

Runs NTV 47, 48; Thermocouple IV.

Vaporization rate 115,000 Btu/(hr)(sq ft)

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and undergo a short period of unsteady state molecular conduction during vaporization. Some of the sensible heat (and superheat) is lost before being displaced from the surface by subsequent eddies. With this model, the average rate of heat transfer at the surface depends on the exposure time of an eddy and its temperature. The temperature at a fixed point is a measure of time averages of eddy temperatures. Wide temperature fluctuations attributed to individual eddy temperatures were previously shown to exist (ANL-6596, p. 82). The surface temperature gradients with this model are then attributed to an increasing frequency of low temperature eddies as the surface is approached.

By extrapolation of temperature gradients, the surface has been found to be superheated above the vapor space saturation temperature (ANL-6800, p. 133). As pointed out in ANL-6800, this average surface superheat provides the driving force for mercury vaporization. During the past report period, surface temperature measurements were also obtained with a surface temperature probe which is described below. These measurements are compared in

Table I-10 with surface temperatures determined from vertical traverses. The direct surface temperature measurements show an average superheat

Table I-10

MEASUREMENTS OF SURFACE SUPERHEAT DURING
NONTURBULENT VAPORIZATION OF MERCURY

Run No.	Av. Heat Flux through the Vaporizing Surface [Btu/(hr)(sq ft)]	Pressure (torr)	Surface Temperature Obtained by Extrapolation of Vertical Traverses		
			Saturation Temp. (°C)	Surface Temp. (°C)	Surface Superheat (°C)
NTV-47B	20,900	0.40	107	129	22
NTV-45	114,000	2.26	145	164	19
NTV-47B	115,000	2.26	145	168	23
NTV-47C	115,000	2.26	145	169	24
Surface Temperature Obtained by Direct Measurement with Surface Thermocouple Probe					
NTV-48	30,300	0.58	115	150	35
NTV-48	77,000	1.48	135	172	37
NTV-48	115,000	2.18	144	178	34

of 35°C as compared to an average of 22°C obtained from the vertical traverses. With both types of measurement, there exists no apparent trend of superheat value with vaporization rate, although the surface temperature, bulk temperature, and pressure over the vaporizing surface all increased with increasing vaporization rate.

The surface temperature probe, which operates on the liquid metal thermocouple principle, i.e., with mercury as one element of the couple, consisted of a bare 13-mil dia. Chromel wire which, when inserted through the mercury surface, acted as the hot junction. The observed temperature was independent of the depth of submergence of the wire.

Surface temperature explorations were made with the thermocouple probe at several vaporization rates, and it was found that time-average temperatures differed from point to point on the mercury surface. Figure I-23 shows the surface temperature isotherms at a high vaporization rate, 115,000 Btu/(hr)(sq ft), and was constructed from traverses made along the four diameters shown. Considerable lack of symmetry is evident. As the vaporization rate was decreased, temperatures tended to become more symmetrical around the central axis, but the surface temperature was in no case constant over the entire surface. These surface temperature patterns probably result from the eddy temperature and flow patterns in the mercury pool and would, therefore, be expected to be dependent on the configuration of the mercury pool, method of heating, and heating rate.

Radial temperature traverses taken within the pool below the zone of the surface temperature gradient show the temperature to decrease from a maximum at the wall to a constant value across a central area of the pool.

Results of this work are now being prepared for publication.

(2) Determination of the Critical Constants of Alkali Metals
(I. G. Dillon,* P. A. Nelson**)

Study of the nature of liquid metals indicates that their behavior may be expected to be considerably different from that of the so-called "normal" liquid used as the basis of the original theorem of corresponding states. However, many thermodynamic and physical properties of a metal can be calculated or estimated from their critical constants for the entire range of temperature from the boiling point to the critical point.

Thermodynamic properties of alkali metals are of particular interest because of their use as heat exchange media in nuclear reactors. For most alkali metals, vapor pressures and liquid and vapor densities are generally known up to the vicinity of the boiling point. While many estimates have been made of the critical constants of alkali metals, no actual measurements of the critical constants, vapor pressure, vapor density, and liquid density are known for the entire range of temperature from the boiling point to the critical point. Therefore, it is proposed to make measurements of vapor and liquid density as a function of temperature for the alkali metals, sodium, potassium, rubidium, and cesium from room temperature up to the critical point. Densities will be determined by measurement of gamma radiation from the liquid or vapor phases of radioactive tracer-containing metal held in a high-pressure cell. As the critical point is approached, the densities of the two phases and therefore the gamma activities emanating from the vapor and liquid phase regions will approach each other.

As reported in the previous summary report (ANL-6800, p. 136), initial measurements will be made on cesium and rubidium since their estimated critical temperatures (about 1900°C) are much lower than those estimated for sodium and potassium (2200-2500°C). Mercury will be used as a calibrating material since density data are known for it over the entire temperature range from the melting point to the critical temperature.

Installation of Equipment. The latest designs of the equipment for the initial experiments are shown in Figures I-24, I-25,

*Ph.D. candidate from Illinois Institute of Technology.

**Argonne advisor.

Figure I-24

HIGH PRESSURE CELL FOR MEASUREMENT OF CRITICAL TEMPERATURE OF ALKALI METALS

108-7950

Figure I-25

FURNACE ASSEMBLY FOR CRITICAL TEMPERATURE APPARATUS

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and I-26. In Figure I-24 is shown the high pressure cell, which is made of Mo-30 w/o W. It is in three sections to permit separate handling of the center section and to avoid, thereby, frequent removal of the long section connected to the 1/4-in. collimation tantalum tubes (Figure I-25) which go through the end of the silicon carbide crucible at 5° and 8° angles with the axis of the crucible. The center section contains the capsule which holds the alkali metal while the critical temperature is being determined. The radiation from the alkali metal will be collimated by passing through the 4-in. long holes in the Mo-30 w/o W block. The capsule chamber has a 3/16-in. ID, a 1-in. inside length, and a 20-mil wall. This corresponds to a volume of 0.452 cc. The critical temperature, that temperature at which the gamma ray measurements will indicate equal vapor and liquid densities, will be measured by a tungsten-5% rhenium/tungsten-26% rhenium thermocouple. Calibration of thermocouples with optical pyrometer readings has shown good agreement over a wide range of power input (temperatures from 700 to 1800°C), as may be seen from Figure I-27. Heating will be accomplished by inductively heating the molybdenum-30 w/o tungsten block. Reaction of the block with the tungsten carbide insulation will be prevented by means of a tantalum can. The crucible which contains the high-pressure cell, tantalum can, and insulation is supported by an adjustable-height ceramic support resting on a steel plate. This furnace assembly is shown in Figure I-25. The furnace assembly is contained inside a vacuum tank which has two counting beam holes drilled in the side and vacuum fittings welded in place.

Figure I-26

CAPSULE CHARGING ASSEMBLY

Figure I-27
COMPARISON OF TUNGSTEN-
5% RHENIUM/TUNGSTEN-
26% RHENIUM THERMOCOUPLE
READINGS WITH OPTICAL
PYROMETER READINGS

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The capsule (ANL-6800, Figure I-41) containing the alkali metal must be sealed under high vacuum to avoid contamination by the inert atmosphere inside the glovebox used for weighing the alkali metal charged to the capsule. Several capsules have been successfully charged, using the capsule charging apparatus shown in Figure I-26. This design provides for pulling a vacuum after charging a weighed amount of alkali metal into the capsule. The capsule is then sealed by driving the plug through the tantalum gasket with a rod which passes through an O-ring fitting. The capsule may then be welded in the same glovebox or taken elsewhere for welding. After being welded, the capsules are leak-tested with a helium leak detector.

The counting equipment for measuring vapor and liquid density has been assembled and checked. This consists of two 1 by 1 in. NaI thallium activated crystals with preamplifiers, a positive high voltage source, a recorder, count rate meter, scaler, single-channel analyzer, and amplifier.

Preliminary Runs

Preliminary runs have been made with unirradiated mercury to check the reliability of the molybdenum-30 w/o tungsten capsules. Several failures have been experienced which may have resulted from either liquid metal embrittlement or fracture as a result of pressure forces. It is planned to test capsules made of tungsten-2% molybdenum, an alloy which is expected to be less susceptible to liquid metal embrittlement.

Various lubricants were used in the capsule chamber and in the threaded plugs to facilitate disassembly after heating. Tung-spray,*

*A product of Bemol, Inc., Boston, Mass.

a dry film tungsten-disulfide lubricant, was the most satisfactory in preventing galling and seizing.

Samples of cesium and rubidium have been received from various suppliers and are being analyzed by emission spectrographic methods to determine purity.

B. Fuel Processing Facilities for EBR-II (J. H. Schraidt, M. Levenson, L. F. Coleman)

A direct-cycle fuel reprocessing plant based on pyrometallurgical procedures was designed and is being constructed as part of the Experimental Breeder Reactor No. II (EBR-II) Project. Melt refining, liquid metal extraction, and processes involving fractional crystallization from liquid metal systems are methods being examined for the recovery and purification of EBR-II fuels. Based on these studies, process equipment is being designed and tested.

1. Status of Fuel Cycle Facility

a. Building and Building Services

(W. Holcomb,* J. O. Ludlow, M. A. Slawewski, H. L. Stethers)

(1) Argon Cell Purification System

In August 1963, mercury was accidentally introduced into the Argon Cell when mercury spilled from a seal used to isolate the enclosure (Blister) which houses the crane and manipulator removal hoist (see ANL-6068, pp. 28-29). Since the enclosure seal is at ceiling height (22.5 ft above the floor), the mercury which spilled was spread widely throughout the Argon Cell by spattering.

Subsequent to the mercury spill, the argon purification system⁷ became progressively less effective for the removal of oxygen from the Argon Cell atmosphere. The loss in effectiveness was attributed to the progressive poisoning of a catalyst (palladium) bed in the system by mercury. This bed catalyzes the reaction between added hydrogen and the oxygen contaminant in the gas stream from the Argon Cell. Analyses of samples of the cell atmosphere taken at the inlet side of the purification system showed mercury concentrations of 0.6 to 0.7 mg/m³. The catalyst bed was also sampled to determine if appreciable mercury was in the bed and if the mercury concentration was constant throughout the bed. Samples

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⁷Schraidt, J. H., Coleman, L. F., Holcomb, W. F., Levenson, M., and Ludlow, J. O., "Establishing and Maintaining a High Purity Atmosphere in EBR-II Fuel Cycle Facility Argon Cell," Proceedings of the Eleventh Hot Laboratories and Equipment Conference, New York, New York, November 18-21, 1963, pp. 181-190.

were taken at the bottom of the bed before and after successively removing 20, 40, 60, 80, and 100% of the bed. (The bed material was removed from the bottom of the bed.) The samples were analyzed by means of X-ray fluorescence, using fresh catalyst bed material as a standard. The results which are given in Table I-11 show that appreciable concentrations of mercury were present in the catalyst material, thus explaining the poisoning. Although the mercury concentration was generally higher in samples from the upper portion of the bed (the gas flow is downward) than in samples from the lower portion of bed, no significant concentration profile existed at the time of sampling.

Table I-11

ANALYSIS OF POISONED CATALYST SAMPLES FROM
THE ARGON PURIFICATION SYSTEM CATALYZER

Percent Bed Material Removed from Bottom of Bed ^a	Mercury-to-Palladium Atom Ratio in	
	Poisoned Bed Material ^b	
	Pellets	Fines
0	0.71	0.77
20	0.71	0.77
40	0.77	0.77
60	0.77	0.83
80	0.83	0.91
100	0.71	0.91

^aSamples were taken at the bottom of the bed after removing the amount of bed material indicated.

^bThe catalyst bed material, initially in the form of 1/8-in. right cylinders, consists of 0.5 w/o palladium on an inert carrier.

An appreciable quantity of fine particles was found throughout the catalyst bed. The active catalyst (palladium) is a thin (~0.005 in.) layer on 1/8-in. right cylinders of inert carrier; the palladium layer is dark gray and the carrier is white. The fine particles appeared similar to the palladium layer. Catalyst cylinders from which the palladium layer was partially or totally eroded were also found throughout the bed. Examination of a similar catalyst bed which had been in periodic use for six years showed no fine particles or eroded cylinders. Apparently, a secondary effect of mercury poisoning is to cause or accelerate erosion of the palladium layer.

The results of the analyses of the samples indicated that approximately 1.5 lb of mercury was present in the catalyst bed at the

time the bed was removed (February, 1964). The catalyzer unit contained about 110 lb of 0.5 w/o palladium catalyst.

As the poisoning of the catalyst progressed, it became necessary to feed hydrogen to the purification system at a rate in excess of that necessary to react stoichiometrically with the oxygen in the gas stream. This caused the concentration of hydrogen to increase in the Argon Cell atmosphere. The extent of increase in the hydrogen concentration was observed as an increase in the reading of the nitrogen meter which is a thermal conductivity meter sensitive to all impurities, but particularly to hydrogen and helium. To determine the concentration of hydrogen and other impurities in the argon atmosphere of the Argon Cell, samples were taken on October 31 and December 2, 1963, and were analyzed by means of a mass spectrometer. The results of the analysis are shown in Table I-12.

Table I-12

CONCENTRATION OF IMPURITIES IN ARGON CELL ATMOSPHERE
DURING OPERATION WITH MERCURY-POISONED CATALYST

<u>Contaminant</u>	<u>Concentration^a (m/o)</u>	
	<u>Oct. 31, 1963</u>	<u>Dec. 2, 1963</u>
N ₂	7.45	6.1
He	0.074	0.27
H ₂	0.012	0.13
O ₂	0.010 ^b	0.001 ^b
CO	0.025	0.026
CO ₂	0.003	0.014
Light		
Hydrocarbons	0.003	-
Freon	-	<0.001

^aAnalysis by means of mass spectrometer, except for oxygen.

^bAnalysis by electrolytic oxygen analyzer.

On October 31, the reading of the nitrogen analyzer in the argon purification system was 8.15%, and on December 2 the reading was 9.4%. These readings correlate with the mass spectrometer results if it is assumed that the nitrogen analyzer is eight times as sensitive to helium and hydrogen as it is to nitrogen.

The presence of helium in the Argon Cell (2700 ppm on December 2) was from the use of helium as a shroud gas during welding of the end caps on fuel element cans after the reconstituted fuel pins are

inserted into the cans. Its presence will not be detrimental to the operation of processes but will cause some difficulties with auxiliary equipment. Therefore, argon has been substituted as a shroud gas.

The presence of hydrogen (1300 ppm on December 2) in the cell atmosphere is attributed to the previously discussed poisoning of the catalyst. Since mercury is no longer being used in the enclosure seal, the conditions which led to the high concentration of hydrogen in the Argon Cell will not reoccur in future process operations.

The oxygen concentrations were maintained at low values (10 to 100 ppm) by continually adjusting the rate at which hydrogen was fed to the purification system.

The presence of carbon dioxide in the Argon Cell is attributed to the exhalations of personnel (wearing self-contained breathing masks) during entries made in late September 1963 (see ANL-6800, p. 153). The probable source of carbon monoxide is the conversion of CO₂ to CO on the catalyst bed in the presence of excess hydrogen. Although in future processing operations carbon dioxide will not be introduced by personnel entering the cell, some CO₂ and CO may be introduced from radiolytic decomposition of organic materials. Periodically, it may be necessary to monitor the cell atmosphere for CO₂ and CO and, if their concentrations are increasing, to operate the purification system dryer as a CO₂ and CO sorber. To do this, a freshly regenerated dryer could be operated for about one day without adding hydrogen to the purification system (precluding the formation of water which could hinder the sorption of CO₂ and CO). The sorbed CO and CO₂ could then be removed from the purification system by regenerating the dryer.

During February 1964, the Argon Cell was filled with air to permit direct maintenance of cranes and manipulators and to remove all observable mercury from surfaces in the cell. A mercury material balance showed that 63.7 lb of the 64 lb of mercury originally added to the seal could be accounted for: 58 lb from the seal, 4.2 lb from the cell surfaces and 1.5 lb in the purification system catalyzer. During this period, the poisoned catalyst was removed from the argon purification system and new catalyst was installed.

(2) Argon Cell Atmosphere Control and Cooling System

Two 15,000 cfm, vaneaxial fans with direct-coupled motors are installed as part of the atmosphere control and cooling system for the Argon Cell. The motor of fan B had previously failed after being in operation for several weeks in the argon atmosphere (see ANL-6800, p. 153). It was thought that the failure might have been caused partially by operating the motor in argon atmosphere. A motor that is operated in such an atmosphere is subjected to abnormal corona effects owing to the

poor dielectric strength of argon. Also, because of the poor heat transfer properties of argon as compared with air, the demand on a motor that is operated in argon should be limited to 70% of the rated capacity of the motor.

Because of these considerations, the second fan (fan A) was removed for inspection during the period that the cell was filled with air. The fan and the motor were disassembled and each part inspected. The motor windings apparently were not damaged. The upper and lower bearings on the fan were replaced since they did not operate smoothly when turned by hand. The blade settings on the vaneaxial fan were changed in order to lower the flow of argon through the fan and to reduce the load on the fan motor, after which the fan rotor was balanced. The fan was then reassembled and reinstalled in the cooling system. The bearing replacement and load reduction should appreciably extend the life of this fan. Examination of the motor of fan A did not reveal the cause for the failure of the fan B motor but it is possible that early evidences of corona attack might have been masked by the varnish on the motor windings. The corona problem is being studied.

(3) Argon Cell Fill

On February 27, 1964, the Argon Cell was purged of air and filled with argon. The addition of 118,000 standard cu ft of argon reduced the air concentration in the cell to approximately 3.3%. During most of the fill period, the circulating fans in the cell were not operated. The entering argon simply displaced an air-argon mixture through an opening in the cell roof. Only during the final portion of the argon fill (in which the last 2000 standard cu ft of argon was added) were the circulating fans in operation. The effluent gas mixture from the Argon Cell contained about 3.5% air immediately before the circulating fans were turned on and about 3.3% air after the fans had been on for ten minutes. This showed that an appreciable vertical concentration gradient did not exist in the cell at the end of the displacement step.

The opening in the cell roof was closed and the argon purification system was then used to reduce further the oxygen and water concentrations. During each day shift, the purification system was operated with high (but less than the stoichiometric requirement) hydrogen feed rates. During the night and over a weekend, the purification system was operated (unattended) with very low rates of hydrogen feed. After about 34 hr of the former type of operation and 112 hr of the latter type of operation, the oxygen and water concentrations in the cell atmosphere had been reduced to 10 and 60 ppm, respectively. The air in-leakage rate of the cell (during May 1964) was 0.007 scfm with the cell maintained at a pressure of minus 2.5 in. of water. These conditions are satisfactory for processing operations.

(4) Transfer Locks

Materials are transferred between the Air Cell and the Argon Cell by means of three transfer locks (see ANL-6648, pp. 102-105). There are two small locks and one large lock. The hinged closure lid at each end of each lock is actuated by a chain which is powered by a motorized drive assembly. Inspection of the transfer lock drives revealed badly worn gears on both the air-side and argon-side drives; the gears were of a nonhardened type. The drive assemblies on all transfer locks (Air Cell and Argon Cell sides) have been modified by installing hardened bevel gears and smaller chain sprockets to replace the original components. The smaller chain sprockets were installed to reduce loading on the system. In addition, slip clutches were installed on the lock drive motors. These clutches are adjusted to slip when a load of approximately 300 to 350 lb is applied to the drive chain. (Approximately 200 lb is required to lift either the small or large lock lids.)

b. Air Cell and Argon Cell Cranes (J. Graae, W. Voss, R. Vree)

One five-ton crane is installed in the Air Cell and two are installed in the Argon Cell. The design of the Air Cell crane differs from that of the crane in the Argon Cell in that the movement of the bridge in the Air Cell is rectilinear, whereas the movement of each bridge in the Argon Cell is radial about a central pivot. Electrical connections to the Air Cell crane are through bus bars which hang from the ceiling and through spring-loaded sliding collectors mounted on the crane bridge. Electrical connections to the Argon Cell cranes are through slip-rings mounted around the center post of the Argon Cell and through spring-loaded brushes mounted on the crane bridges. The trolleys for the cranes in both cells are identical in design and are interchangeable. Once reprocessing of radioactive fuel has commenced, direct personnel access to these cells will not be feasible. Therefore, a considerable effort has been spent on making the cranes (and all other mechanical equipment in the cells) reliable and remotely maintainable. As a consequence, modifications to the cranes have been made in the field when operating experience revealed the need for a change.

During the present report period the cranes have been modified as follows:

- (1) The crane hoist gear-motors have been provided with new high-speed gear sets which have increased the hoist speed by a factor of 2. This modification was made to save operating time and to reduce the forces on the drum shaft, gear and bearings resulting from the starting and stalling torque of the motor. The change in gearing was possible because the gear motors were oversized by a factor of two and

therefore adequate for the increased speed. The hoist speed is now 4 ft/min which is still considered satisfactory for positioning purposes.

(2) New slip clutches have been installed between the gear motor and the main hoist reducer on all three crane hoists. The clutches are set to slip at 150% of rated motor torque. This torque value could be exceeded if the up-limit switch failed or the lifting hook became overloaded (for instance, it may become caught on a fixed object). If such an overload should occur, the clutch will slip, and, after a few seconds, the motor breaker in the control cabinet will interrupt the current to the motor.

(3) Anti-plugging time delay relays have been installed in the crane control cabinets. The relays assure that a motor cannot be reversed before it has stopped and help to eliminate excessive mechanical stresses in the drive machinery which otherwise could result from the rapid reversal of the crane motors. High transient voltage peaks, which might develop due to rapid reversing, will also be eliminated.

(4) Crane hoist No. 2 failed when a large transfer basket which was hanging from the crane hook was partly inside the large air lock. The failure occurred while the Argon Cell was full of argon. The basket was unhooked remotely by lifting it with two manipulators, after which the crane was moved away from the air lock freeing it for making transfers of materials.

The cause of the failure in the hoist was a short between two of the conductors from the power inlet to the hoist motor. The short occurred where the conductors emerge from the mineral insulation in a seven-conductor cable; the 14-gage copper wires had partially melted (from arcing) and the copper had bridged between the two conductors. The end seal* on the cable was not filled with potting compound because radiation would make the compound conductive. The separation between the conductors is 1/16 in. and should be adequate for the applied voltage of 220 volts ac. However, some transient peak voltages may have occurred, probably as a result of the starting, stopping, and reversing of a motor. The anti-plugging relays (see item 3) may help to prevent such transients in the future.

This failure is the second to occur in a seven-conductor mineral insulated cable (14 gage wire) used for the wiring from the brushes around the center slip-rings to the bus bars and the terminals on the crane bridges. The mineral insulated cable in this wiring has now been replaced by a type AA asbestos insulated (12 gage) stranded wire which is run in conduit for mechanical protection. This type of wire has been tested for radiation exposures of 10^{10} rad without noticeable deterioration, other

*A product of the Advanced Vacuum Products Company, Stamford, Connecticut.

than slight powdering of the insulation. The minimum separation between wires in the asbestos insulated wire is $1/8$ in. which is twice the separation in the mineral insulated cables.

c. Air Cell and Argon Cell Manipulators
(J. Graae, W. Voss, R. Vree)

There are two electromechanical manipulators in the Air Cell and six in the Argon Cell. The designs are basically the same except that the movement of the bridges in the Air Cell is rectilinear, whereas the movement of the bridges in the Argon Cell is radial about a central pivot. Electrical connections to the Air Cell manipulators are through bus bars mounted on the cell walls and through spring-loaded sliding collector assemblies. Electrical connections to the Argon Cell manipulators are made through multiconductor cables which are suspended from a pivot tower in the center of the cell ceiling and plugged into the manipulator bridges.

Considerable effort has been directed toward making the manipulators reliable and remotely maintainable. However, the field modifications and corrective rework performed on the manipulators have not been as extensive as those done on the cranes. Major field changes on the manipulators were largely avoided by incorporating, in the final design, information that had been developed while operating the prototype manipulator in the mock-up facility of the Chemical Engineering Division. Most of the field work done on manipulators has consisted of correcting faulty workmanship and making minor changes in dimensions and materials.

When personnel entered the Argon Cell during February, a number of defects in the manipulators were found and corrected. Changes were also made to improve operational reliability of the manipulators. The modifications are summarized below:

(1) New vertical bridge drive shafts of improved design were installed. The shaft diameter on the driven clutch-half was increased to one in. (from $3/4$ in.); the shaft and clutch were keyed together and secured with a $1/4$ -in. dia. roll pin.

(2) Stackpole* grade 660 brushes have been installed on all (eight) grip drive motors (EEMCO**). These brushes are made of carbon-graphite containing 5% molybdenum disulfide and have a specific resistance of 0.060 ohm/cu in. Brushes of this type have shown no wear after service periods in dry argon of 1 hr and 8 hr on grip drives No. 4 and No. 5, respectively. For grip drive motors No. 1, 2, 4, 5, and 6, the Stackpole grade 660 brushes are the third sets of brushes that have been

*Stackpole Carbon Company, St. Mary's, Pennsylvania.

**Electrical Engineering and Manufacturing Corporation, Los Angeles, California.

installed. For grip motor No. 3 it is the second set of brushes; this grip drive motor was out of service for a part of the time and was not used much.

The Stackpole grade 596 brushes (electrographite, lithium-treated) which were previously used on grip drive motor No. 1 showed no wear after 20 hr of service (during most of this time the motor operated in an argon atmosphere); however, every second commutator bar showed burn marks. The Stackpole grade 56 brushes which were previously used on grip drive motors No. 2, 3, and 6 were worn out. These brushes are made for high altitude use and are composed of electrographite containing 8% barium fluoride. Both grades of brushes (No. 596 and 56) have rather low specific resistance, 0.002 ohm/cu in.

The brushes (Stackpole grade 687) on the other motors (Master* gearmotors) in the manipulators show no wear even after more than 100 hr of service, many of them in dry argon. The brush material is a low friction graphite and has a high specific resistance (0.045 ohm). The rated speed for the Master gearmotors is 1725 rpm, which is much slower than that (6000 rpm) for the EEMCO motors for the grip drives. The Master motors are provided with interpoles which the EEMCO motors do not have, due to the compact construction of the EEMCO motors. The lower speed and the interpoles of the Master motors provide superior commutation compared to that of the EEMCO motors. This difference in commutation characteristics probably explains the difference in brush wear rates between the two types of motors.

(3) A change in the control cabinet wiring of each manipulator now makes it impossible to operate simultaneously the arm rotation motor and the hoist motor. This prevents the build-up of high potentials between the leads to the arm rotation and hoist motors which might have led to a short in a connector (see item 9). It also reduces the tendency of a hoist cable to skip a groove on the hoist drum.

(4) A hoist cable tore loose from its anchor on the hoist drum of manipulator No. 4 when the dual hooks engaged an object which was bolted to the cell floor. To prevent similar mechanical overload accidents in the future, a multiple-disc-pack slip clutch has been designed by the Chemical Engineering Division at Argonne and tested successfully in the Division's mock-up facility. Installation of these clutches in the drive mechanisms of the manipulator hoists has begun.

(5) Collision bumpers have been added to the Air Cell manipulator bridges. These are necessary in order to reduce impact stresses on bridge drive machinery should the bridges collide.

*Reliance Electric and Engineering Company, Cleveland, Ohio.

(6) The cable incident (see item 4) and previous examinations showed that the method of anchoring the hoist cables to the drums was not satisfactory. All the hoist drums have therefore been reworked so that the cable anchoring now is greatly improved.

(7) Spring snubbers have been installed on all hoist cables. The snubbers permit down-limit switches to function, yet prevent cables from becoming slack which could cause them to skip grooves on the hoist drums.

(8) Manipulator No. 2 became inoperative because the arm rotation and the hoist would function simultaneously when either circuit was energized. This simultaneous operation resulted from a short in the 64-lead connector at the upper end of the control and power feed cable to the manipulator bridge. There was no evidence of faulty workmanship. The leads involved were the armature leads to the arm rotation and hoist motors. If these two motors are operated simultaneously, the potential between the leads to the two armatures might reach 320 volts dc for certain directions of operation. The connector has a rating (National Electric Code) of 250 volts dc. In addition, transient high potentials might have developed as a result of starting and stopping motors due to the inductive loads of the motors. With a high-speed recorder (Visicorder*) used to record voltage variations during the starting and stopping of the motors, occasional peaks of 10 to 15% over the supply voltage were noted. The change in the control cabinet wiring (see item 3) has eliminated the possibility of simultaneous operation of arm rotation and hoist and should prevent the repetition of failures of the armature leads to these two motors.

Means for preventing arcing and resulting shorts or failures in the other circuits are being studied.

- d. Cell Viewing and Lighting
(T. W. Eckels, P. Kelsheimer)

Shielding Windows

At the time that the shielding windows for the Fuel Cycle Facility were being designed, there had been only one reported case of damage to a shielding window by the discharge of a gamma-induced electrical charge within a thick slab of glass. Since that time, there have been several additional such incidents. Experiments performed at this Laboratory⁸ and elsewhere⁹ on shielding glasses (PPG** 4966, 6788, and 6792; 3.3 density, cerium oxide-stabilized glasses) have shown the following:

* Honeywell Industrial Products Group, Heiland Division, Denver, Colorado.

** Pittsburgh Plate Glass Co., Pittsburgh, Pennsylvania.

⁸ Hardtke, F. C., and Ferguson, K. R., "The Fracture by Electrical Discharge of Gamma-Irradiated Shielding Window Glass," *Proceedings of the Eleventh Conference on Hot Laboratories and Equipment* (November 1963).

⁹ Rizzo, F. X., Muller, A. C. and Zucker, M. S., "Electrical Discharge in Gamma Irradiated Lead Shielding Glass," *Ibid.*

(1) Spontaneous discharges occur in 10 in. by 10 in. by 8 in. thick glass samples irradiated, at room temperature, to integrated doses of 10^8 to 10^9 rad. (2) Discharges occur when 4-in. glass cubes are irradiated to integrated doses of 10^6 to 10^7 rad at room temperature, and then struck a bruising blow on the surface of the glass. (3) Measurements show significantly less electrical charge accumulation in 4-in. cube glass samples heated during irradiation to temperatures up to 140°F. A discharge did not occur when a sample, heated to 150°F during irradiation to an integrated dose of 1.6×10^7 rad, was struck a bruising blow.

The results of these experiments may not be directly applicable for predictions of the effect of irradiation upon the shielding windows (PPG 6792 glass on the irradiated side) in the Fuel Cycle Facility, owing to differences in temperatures and in glass geometry. However, the results indicate higher integrated gamma exposures will be permissible if the glass surface is protected from bruising blows and if the glass is maintained at elevated temperatures during gamma irradiation.

On the basis of these conclusions, the shielding windows have been modified by the addition of a 1/4-in. thick glass plate, 39 in. square. It is mounted to provide an air gap of about 1/8 in. between the cover plate and the "A" slab. (The 9-in. thick "A" slab which is the innermost shielding window section is mounted in a heavy, hinged steel frame to permit remote replacement of the "A" slab from within the cell. For a complete description of a shielding window, see ANL-6605.) The principal purpose of the cover plates will be to protect the "A" slabs from any accidental blow which could bruise the glass surface. A further beneficial effect may be anticipated from the use of cover plates. Because of the insulating effect of the gas space between the cover plate and the "A" slab, computation shows that with a gamma radiation exposure rate of 3×10^5 rad/hr, the temperature of the "A" slab will be raised about 40°F to a peak temperature of ~215°F. The protection afforded by the cover plate and the higher slab temperature should lengthen the useful life of the "A" slab.

e. Process Equipment Installation
(M. Slaweck, J. O. Ludlow)

Melt Refining

Two melt refining furnaces are installed in the Argon Cell of the Fuel Cycle Facility for the processing of spent fuel. Nineteen runs with unirradiated uranium have been made in these furnaces to test the mechanical operation of the furnaces and to make uranium-5 w/o fission ingots for use in shutdown operations of the injection casting furnace.¹⁰ The charges consisted of combinations of uranium,

¹⁰Jelinek, H. F. and Iverson, G. M., "Equipment for Remote Injection Casting of EBR-II Fuel," Nucl. Sci. Eng. 12, 405-411 (1962).

noble elements, and chopped fuel pins, with charge weights of 4 to 11 kg. In five runs, a part of each charge was sodium-coated fuel pins and in one run the charge contained a heel from the injection casting furnace. The liquation times were $1/2$ to 3 hr at 1400°C. (Melt refining runs with irradiated fuel will use a 3-hr liquation time at 1400°C.) The poured yields varied from 83.4 to 96.9 w/o, twelve of the yields being greater than 94 w/o. Although these preliminary runs are not representative of the actual melt refining runs that will be conducted in the cell with irradiated fuel, the results obtained in these runs do give some indication of the poured yields that can be expected. All the melt refining equipment performed satisfactorily.

f. Miscellaneous Cell Service Equipment

(G. Bernstein, R. Fryer,* J. O. Ludlow, M. Slaweki)

Air Cell Floor Plug

Transfers into and out of the Air Cell are made through concentric openings in the cell floor. A 9-ft square area of floor containing the openings consists of an 18-in. thickness of steel. The largest floor opening is 6 ft in diameter and is filled by means of a series of removable concentric shielding plugs 6 ft, 3 ft, 2 ft, and 6 in. in diameter.

When fuel subassemblies or radioactive wastes are transferred through one of the floor openings, it is necessary to provide additional shielding between the bottom surface of the steel floor and a shielded coffin in which the material is carried. This additional shielding has been provided by increasing the length of the 2-ft and 3-ft diameter shielding plugs to about 25 in. Hydraulic lifting rams have also been installed for raising the plugs about 2 in. (The rams are manually operated from a position which gives the operator a view of the plugs and coffin.) When a fuel transfer coffin (see ANL-6800, p. 162) is to be moved into position under the floor opening, the plugs are raised to clear the top surface of the coffin. After the coffin is in position, the plugs are then lowered so that they rest upon the top surface of the coffin. A grapple can be lowered through the 6-in. floor opening into the coffin opening to grasp and remove the subassembly. Careful alignment of the coffin is required to permit the grapple to enter the $4\frac{1}{8}$ in. dia. opening in the coffin. This alignment has been achieved.

2. Service Equipment Development

a. Interbuilding Fuel Transfer Coffin

(G. Bernstein, R. Fryer*)

The interbuilding fuel transfer coffin (see ANL-6800, p. 162) has been used for the in situ removal of sodium from four mock

*Idaho Division.

EBR-II subassemblies. Neither the subassemblies nor the adhering sodium were radioactive. These subassemblies are identical to those which will be used in the EBR-II Reactor, except that natural uranium was used as the fuel content in place of enriched uranium. After each subassembly was removed from the reactor vessel by the fuel unloading machine, the adhering sodium was allowed to drain back into the reactor. The subassembly was then transferred to the fuel transfer coffin.

The sodium removal operation followed a previously developed procedure for plant operations (see ANL-6687, p. 66). The procedure involves the conversion of the sodium to sodium hydroxide and the removal of the sodium hydroxide with a water wash. In all four tests, the various operations in the sodium removal procedure were performed without difficulty. Analytical results of the accumulated wash solutions showed that the four subassemblies had been coated with 35, 41, 35 and 32 g of sodium. (In the development of the sodium removal procedure, the quantity of sodium that would adhere to the subassembly had been estimated at less than 100 g.)

When one of the subassemblies was dismantled, it was noted that a small amount of sodium oxide (or hydroxide) remained on the pins. The pins which appeared to have the most sodium oxide on the surface were washed. The washings were analyzed for sodium and were found to contain less than 0.1 g of sodium. The total amount of sodium adhering to all 91 pins was estimated to be less than 3 g. The presence of these amounts of sodium would cause no difficulty in subsequent fuel processing operations.

b. Waste Transfer Coffin
(G. Bernstein, E. Johnston)

Solid radioactive wastes produced in the Fuel Cycle Facility will be loaded into special waste containers and transported to a burial ground in a top-loading, bottom-dumping waste transfer coffin. The waste disposal container is a steel pail 6 ft high and $11\frac{1}{2}$ in. in diameter. The lower 5 ft of the container is fabricated from 20-gage steel with welded side and bottom seams. The upper section is made by inserting a bottomless 5-gal pail body (22-gage steel) into the long section and attaching it with a circumferential weld. The top can be closed with a standard 16-lug crimp type cover.

Waste pails are kept in the Air Cell floor pits until they are filled with approximately 120 lb of waste. The waste may consist of stainless steel components removed from fuel subassemblies in the dismantling machine. The steel scrap from seven subassemblies will constitute a load. Other wastes produced in the Argon Cell will be placed in 3-gal pails. These pails will be filled with approximately 20 lb of wastes

before being capped and removed from the Argon Cell. Six such pails will be dropped into a 6-ft pail using manipulator-operated tongs. To prevent damage to the bottom of the 6-ft pail, it will be protected by 1 in. of padding covered by a 1/8-in. steel disk. When a waste pail is full, the cover will be attached using a standard closing tool adapted for use by the operating manipulator.

The waste pail will be loaded into the waste transfer coffin through the 24-in. diameter opening in the Air Cell floor using tongs which are held by the operating manipulator. The waste transfer coffin will then be transferred to the burial grounds where it will be placed above a prepared burial hole. The bottom door of the coffin is rolled out which permits the pail to drop into the hole. The pail is then covered with 6 ft or more of dirt to provide shielding.

Various tests have been performed to evaluate the damage which could occur to a waste pail during filling and dumping. Such damage would create the possibility of eventual loss and migration of radioactive materials in the ground.

In the first set of tests, a 6-ft pail was filled twice by dropping into it various pieces of steel to simulate loading with subassembly waste. No damage resulted. The pail was then filled three times by dropping into it six 3-gal closed pails, each containing about 20 lb of loose scrap. No damage resulted to any of the pails.

In the second set of tests, a loaded 6-ft pail was dropped under various conditions to simulate discharge into a burial hole. A pail loaded with six filled 3-gal pails was first dropped 5 ft and then 9 ft onto 1 ft of dirt without damage. Drops as high as 15 ft might be made at the burial ground, but the test facility did not allow for drops from such heights. Instead a much more destructive test was made in which the pail was dropped $9\frac{1}{2}$ ft onto a steel plate resting on solid concrete. This condition would produce much greater impact forces than would a 15-ft drop onto dirt. Some damage to the bottom of the 6-ft pail and some collapse of the lowest of the 3-gal pails occurred, but all covers remained tight and no cracks developed. Similar drops with the large pail loaded with 120 lb of steel bars failed to damage the pail further.

Since all these tests were made in sequence re-using the same pail and reclamping the same cover, it can be assumed that a new pail will not be damaged as a result of a single fall into a burial pit.

The design of the waste transfer coffin is complete. Detailed fabrication drawings are being prepared.

c. Miscellaneous
(M. A. Slawecki, W. Miller, H. Stethers)

Heat-up tests have been performed in the zinc cans that will be used as storage containers for the oxide formed in the skull oxidation step (see ANL-6800, p. 174). The can, along with the oxide, will be charged to the skull reclamation furnace as needed. The self-heating of the oxide from high burnup fuel may raise the temperature of the zinc can appreciably. A 1-kg skull resulting from melt refining 10 kg of fuel which has undergone 2 a/o burnup in 135 days and has cooled for 15 days will produce 750 watts of self-heating, based on absorption of all the beta energy and 20% of the gamma energy from fission product decay.

Tests were made in which an electrical heater was buried in about 700 g of skull oxide obtained from the skull oxidation step. The skull was from the liquation of unirradiated uranium-5 w/o fission in a zirconia crucible. The amount of oxide used formed a 1-in. layer in the zinc can. The power to the heater and the temperatures on the top, bottom, and side of the can were monitored. The zinc can was in air. The highest equilibrium temperatures recorded were at the bottom of the can. These temperatures and the respective power inputs (to the heater) were as follows:

<u>Power Input (watts)</u>	<u>Temperature of Can Bottom (°C)</u>
400	290
575	360
700	>390

Since the zinc can had softened (zinc m.p., 410°C), the test at a 700-watt input was concluded before temperature equilibrium was reached.

A small, compact test stand, for use in the EBR-II Argon Cell, has been built to measure the bottom temperature of a zinc can when skull oxide is stored in the can. The stand contains a spring-loaded thermocouple upon which the zinc can will be placed immediately after the skull oxide is added to the can. The temperature will be recorded on an instrument located in the operating annulus (see ANL-6875, Figure I-26, p. 61) of the Fuel Cycle Facility. In this way, it will be possible to monitor the effect of self-heating of skull oxide on the temperature of the zinc can as fuels of increasing burn-up are processed.

3. Process Equipment Development
a. Installation of Service Equipment
(J. O. Ludlow, W. Miller, J. V. Natale)

It has become evident from experience in the Fuel Cycle Facility and in argon atmosphere gloveboxes that there are a number of

problems uniquely associated with the operation of equipment in a dry argon environment. The performance of equipment in air as compared with performance in dry argon can be quite different.

The change in performance is due to a number of factors. The lubricating and wetting properties of certain materials are changed markedly when their environment is changed from air to dry argon. Heat transfer rates for natural or forced convection, under otherwise identical conditions, are much less in argon than in air. The electrical insulating strength of argon is less than air. These, and other properties of the gaseous environment, vitally affect equipment performance.

Chemical processes being carried out within enclosed equipment are sometimes influenced by the gaseous environment outside the equipment enclosure because it is necessary periodically to open the enclosure. This is especially true for a process such as the skull reclamation process. The process solutions (metal phases) are readily oxidized. The salt phases are extremely hygroscopic. The oxygen and moisture enter equipment (and are then absorbed by the process materials and equipment components) when the equipment enclosure is periodically opened in an air atmosphere. The oxygen and moisture then become processing variables which are not easily controllable, and whose effects may vary from run to run since their concentrations are varying from run to run.

In developing equipment for the skull reclamation process there are three objectives to be attained: (1) The equipment must perform satisfactorily in the dry argon atmosphere of the Argon Cell of the Fuel Cycle Facility, (2) The operation of the equipment must result in carrying out the process flow sheet, and (3) The equipment must be operable and maintainable by remote means. The design of equipment for remote operation no longer requires extensive development because of the considerable experience obtained from remote operations in the EBR-II Fuel Cycle Facility and in the mock-up facility of the Chemical Engineering Division. To attain the first two objectives, however, new facilities are required so that meaningful equipment development for the skull reclamation process may be carried out in a dry argon atmosphere.

The establishment of an argon atmosphere enclosure system has been undertaken in this Division (Building 310). Two gloveboxes are being installed for the development of equipment. The first of these will be used for retorting equipment (see Section 3d). A system has been installed to circulate and purify the argon used in the gloveboxes and similar enclosures.

Description of Argon Purification System

The argon purification system (see Figure I-28) consists essentially of a palladium catalyst, a Molecular Sieve* dryer and a centrifugal compressor that is contained in a 60-cu-ft gas-tight enclosure. The throughput of the system is approximately 110 cfm. Hydrogen is introduced into the purification loop at a point upstream of the catalyst. The hydrogen catalytically reacts with oxygen in the argon and the resulting water is removed in the dryer.

Following completion of the installation of the purification system, the purification loop was purged with argon until the nitrogen concentration was reduced to about one percent. The system was then operated to reduce the water and oxygen concentrations. The moisture and oxygen analyzers indicated that the oxygen in the system was reduced below 5 ppm and that the water concentration leaving the dryer was less than 5 ppm. Since these indications were influenced by sample line contamination and by diffusion in each instrument, the true effluent concentration in each case would have been less than the indicated value. The concentration of impurities that will exist in a glovebox will not be certain until actual glovebox operations begin.

b. Skull Oxidation Equipment

(G. J. Bernstein, W. E. Miller, M. A. Slawecki, R. Paul)

After the melt refining step is carried out, a skull of metal remains in the zirconia crucible. The skull is expected to contain 1/2 to 1 kg of metal, one-half of which is ²³⁵U. In order to remove the metal skull from the crucible (which is discarded as waste), the metal will be converted to an oxide powder which will be poured from the crucible. (The oxide powder is the feed material for the skull reclamation process.) Equipment that was developed for the skull oxidation step includes the following: an oxidation furnace, a remote process control system for the furnace oxidizing process and a dumper for transferring the oxide powder from the melt refining crucible to a storage container. Preliminary designs and concepts of the oxidation furnace are given in previous reports (ANL-6725, p. 93, ANL-6477, p. 86, and ANL-6333, p. 99). The oxidation furnace control system was described in ANL-6687, p. 70. A description of the dumper and its operation was described in ANL-6800, pp. 168-176.

Construction of the furnace, the control system and the dumper was completed. Testing of the equipment items was carried out by oxidizing separately six skulls from the melt refining of unirradiated uranium-fissium alloy (cerium content, 0.6 w/o) and dumping the resulting skull oxide powders. In each of the six test runs, the procedure was to unload the oxidized skull from the previous run, remove the crucible,

*Product of Linde Air Products Company, New York City, New York.

Figure I-28

FLOW DIAGRAM OF ARGON PURIFICATION SYSTEM, BUILDING D-310

108-7955

charge the furnace with a new skull and crucible, initiate the oxidation reaction from the control panel and then allow the automated control system to complete the oxidation cycle. The oxidized skulls were transferred from their crucibles to their storage containers by means of the dumper. The results of the six runs are shown in Table I-13. The skull oxidation furnace and the dumper worked satisfactorily. Each skull was oxidized to a high oxygen-to-uranium atom ratio with the use of a large excess of oxygen. The oxide was transferred to the oxide receiver in the dumper without a large dumping loss.

Table I-13

RESULTS OF PLANT SKULL OXIDATION AND OXIDE DUMPING EQUIPMENT
(Skull material from melt refining runs with unirradiated uranium-fissium alloy)

Skull Oxidation Run No.	Original Melt Refining Charge		Weight of Unoxidized Skull (g)	Skull Oxidation Step			Skull Oxide Dumping Step Oxide Loss ^c (g)
	Composition	Weight (g)		Oxidation Time (min)	Oxygen Utilization Efficiency (%)	Excess Oxygen ^a (moles)	
SOF-36	U-1.7 w/o Fissium-0.6 w/o Ce	9690	642	407	83	0.67	3
SOF-37	U-1.7 w/o Fissium-0.6 w/o Ce	9271	554	379	76	0.88	0
SOF-38	U-1.3 w/o Fissium-0.6 w/o Ce	9188	902	582	78	1.24	7 ^d
SOF-40	U-1.3 w/o Fissium-0.6 w/o Ce	7451	591	371	75	0.91	1
SOF-41	U-1.3 w/o Fissium-0.6 w/o Ce	9476	741	496	70	1.44	-1
SOF-42	U-1.3 w/o Fissium-0.6 w/o Ce	9693	840	534	77	1.17	(gain) 4

^aIncludes oxygen present in oxidation furnace at end of run.

^bCalculation assumed skull was metal of same composition as melt refining charge and that the noble metals and cerium were completely oxidized in the skull oxidation step. Since approximately 10% of the uranium in the skull is in the form of UO₂, the oxygen-uranium ratio is actually higher than shown.

^cEstimated by subtracting the weight of material transferred to the oxide receiver from the weight of material poured from the crucible.

^dHigh loss attributed to oversized (9-11/16 in. high) crucible. Dumper is designed for 9 1/2 ± 1/8-in. high (plant specification) crucibles.

A schematic layout of the skull oxidation furnace for the plant (used in the above described runs) is shown in Figure I-29. It consists of a base containing the freeze seal, a receptacle for receiving the crucible container, and a bell jar containing the furnace heater. Figure I-30 shows an overall view of the furnace and supporting stand. In this figure, the manipulator double hook is shown approaching the handle of the bell jar. Figure I-31 shows the bell jar hanging on the support column after being placed there by means of the manipulator. The figure also shows the method of handling the crucible when it is loaded into or unloaded from the furnace.

Operating manuals covering the operation of the furnace, control system and dumper have been completed. Development work on skull oxidation equipment is now complete and the equipment has been installed in the Fuel Cycle Facility.

Figure I-29
EBR-II PLANT EQUIPMENT FOR
SKULL OXIDATION STEP:
SKULL OXIDATION FURNACE

108-7080 Rev.

Figure I-30
SKULL OXIDATION
FURNACE:
FURNACE CLOSED

108-6950-A

Figure I-31

SKULL OXIDATION FURNACE: FURNACE OPEN

(Bell jar is removed. Remote handling of the crucible by means of the manipulator is shown.)

108-6951-A

- c. Skull Processing Equipment Development
 (G. Bernstein, W. Miller, D. Grosvenor, T. Eckels,
 M. Slawecki)

At the conclusion of the melt refining process for recovery and decontamination of EBR-II fuel material, a heel or skull remains in the processing crucible. A skull reclamation process is under development for

the purpose of recovering the fuel material from the skull and separating it from associated fission products. The recovered fuel material will then be returned to the EBR-II fuel cycle. The powdered skull oxide produced in the skull oxidation furnace (see previous section) is the feed material for the skull reclamation process.

The skull reclamation process involves a number of heating and cooling operations that are designed to separate uranium from fission products in a series of process steps in which liquid metals and salt fluxes are employed (see ANL-6800, p. 61). These steps require heating and cooling the processing media between temperatures of approximately 800°C and 425°C.

The plant-scale operation presently contemplated for the skull reclamation process will treat the skull oxides from five melt refining skulls (approximately 5 kg of skull material). On such a scale, the heat output of fission products will significantly affect the rate of cooling of the process vessel. When the EBR-II reactor is operating at its rated capacity, this charge will produce about 4 or 5 kw of heat.*

Figure I-32

APPARATUS FOR SIMULATED SKULL RECLAMATION FURNACE COOLING TESTS

108-7972

*Based upon an average cooling time of 21 days and an absorption of 100% of the beta energy and 80% of the gamma energy from fission product decay.

rate of heating. The temperature was measured by means of a thermocouple attached to the crucible wall 4 in. below the surface of the lead.

Two tests were made with the arrangement shown in Figure I-32. In the first test the lead charge was heated to about 600°C at which time the heating was terminated and the insulating sleeve was removed. The resulting temperature drop was recorded. The second test was a duplicate of the first, except that air from a fan was directed at the stainless steel cylinder wall to increase the rate of cooling.

Two further tests were made in which the stainless steel cylinder was removed with the insulation at the beginning of each cooling period. In the first test the furnace cooled by natural convection and in the second test a fan was used to increase the cooling rate.

Based upon cooling rate and the heat capacity of the system, calculations were made of the average rate of heat removal as the temperature dropped from 600°C to 400°C and of the instantaneous cooling rate at 425°C. These values are shown in Table I-14. The rate of heat removal at 425°C must be substantially greater than the fission product heating rate. In one of the process steps, the charge must be cooled to this temperature to permit a phase separation to be made. Other separations are made at temperatures only slightly above this temperature level.

Table I-14

HEAT REMOVAL RATES FROM SIMULATED
SKULL RECLAMATION FURNACE

(1000 lb of lead used to represent
process materials)

Apparatus as shown in Figure I-32;
cylindrical Fiberfrax insulator re-
moved before each cooling period.

Test No.	Heat Removal Rate (kw)		Special Cooling Condition
	Instantaneous (at 425°C)	Average (from 600-400°C)	
1	2.3	3.5	None
2	3.0	3.9	Cooling Fan Added
3	4.1	5.6	Steel Cylinder Removed
4	6.7	8.3	Steel Cylinder Removed; Cooling Fan Added

The tests show that in the design of the furnace particular emphasis must be placed upon achieving a high rate of heat removal. A gas stream directed on the furnace wall is relatively ineffective

for increasing heat dissipation. Therefore, the design will incorporate metal packing between the crucible and the furnace wall in order to improve the thermal conductivity between them. In addition, it may prove desirable to circulate a gas stream through the furnace and an external heat exchanger.

d. Collection of Metal Vapors

(J. F. Lenc, W. E. Miller, R. Paul, E. Johnston,
A. Chandler)

In the current flowsheet for the EBR-II skull reclamation process, the process stream from the uranium-zinc intermetallic decomposition step is a solution which has the following approximate composition: zinc-12 w/o magnesium-12 w/o uranium (see ANL-6800, Figure I-8, p. 61). After transfer of the solution from the decomposition crucible to a mold, the solution is allowed to solidify in order to produce an ingot suitable for charging to the final step of the skull reclamation process. Recovery of the uranium is achieved in a final process step in which the volatile zinc-magnesium is distilled at pressures below 50 mm Hg. The residual uranium product is then melted to consolidate the uranium.

A modified melt refining furnace which is enclosed in a bell jar has been used in the development of a remotely operable distillation unit (see ANL-6725, p. 98). In several tests, up to 6 kg of zinc-50 w/o magnesium have been successfully vaporized in this equipment. However, the recovered uranium product was invariably contaminated because the furnace was loaded and unloaded in an air atmosphere.

In an effort to eliminate the problem of atmospheric contamination, the distillation apparatus with its bell jar enclosure has been installed in a purified argon atmosphere glovebox (see previous section of this report). To prevent excessive heating of the glovebox atmosphere during operation of the distillation furnace, water cooling coils have been soldered to the bell jar. Figure I-33 shows the glovebox and furnace. The glovebox is a CENHAM¹¹ glovebox with a top blister added. The blister contains a hoist for raising the bell jar and provides storage space for the bell jar when the bell jar is raised to open the furnace.

¹¹Malecha, R. F., Smith, H. O., Schraidt, J. H., Natale, J. V., Ross, N. E., and Brown, H. L. Jr., "Low Cost Gloveboxes," Proceedings of the Eighth Conference on Hot Laboratories and Equipment, San Francisco, California, December 13-15, 1960, pp. 485-493.

Figure I-33
INERT ATMOSPHERE GLOVEBOX
Distillation Furnace Installed

108-7328-A

Leak testing of the glovebox and the distillation apparatus is in progress. When the leak testing of these items is completed, shutdown operation of the distillation apparatus will begin. Leak testing and shutdown operations will be completed in June, 1964, and distillation experiments will begin.

This facility will be first used to recover the uranium from Mg-Zn-U ingots produced in pilot plant runs for the demonstration of the skull reclamation process. For this work, beryllia (BeO) crucibles which will accommodate charges of about 7 kg have been obtained. The procedure will be to distill off the volatile magnesium-zinc under vacuum

(50 mm Hg absolute) and to attain a final melt temperature of 1250°C. The uranium product will thus be liquified in the distillation crucible and then, after cooldown and solidification, possibly removed as an ingot from the crucible. In the event the uranium ingot adheres to the BeO crucible, provisions have been made to reheat the uranium ingot and to tilt-pour the molten uranium into a graphite mold.

C. Chemistry of Liquid Metals (I. Johnson and H. M. Feder)

The chemistry and thermodynamic properties of liquid metal systems and metallic alloys are being investigated to provide basic data for the pyrometallurgical reprocessing of nuclear fuels and for liquid alkali metal coolant technology. The results of these studies also provide data for the testing of theories of liquid metal solutions.

1. Solubilities in Liquid Metals

Of prime importance in the design of fuel-reprocessing methods utilizing liquid metal solvents are the solubilities of substances whose separations are being attempted. Solubility should be known as a function of both temperature and solvent composition. The solubility of a substance in a given liquid metal and solvent is related to the difference between its free energy of formation and the partial excess free energy of the solute in the saturated solution. The temperature coefficient of solubility gives information on the corresponding enthalpy and entropy differences. The empirical systematization of such data for a wide variety of different systems will aid in the resolution of the factors governing the energetics of formation of solutions in liquid metals. For these applications of solubility data it is necessary to know the constitution and the thermodynamics of the phase in equilibrium with the liquid phase.

Solubility of Krypton in Liquid Sodium (S. K. Dhar)

The solubilities of the rare gases in liquid alkali metals are being measured. The data obtained are expected to be of use in determining the differences among the reactions of metallic, molecular, and ionic liquids toward an atomic probe. The rare gases, with their extremely stable, completely filled, electronic orbitals, are ideal atomic probes since they are not expected to form localized bonds which vary from liquid to liquid. The alkali metals are being used as solvents since their electronic structures are better understood than those of other metals.

The experimental procedure used to measure the solubility of krypton in liquid sodium was similar to that previously reported (ANL-6800, p. 183) for the measurement of the solubility of argon. The

only significant change involved the analytical method used for determining the amount of dissolved krypton. Radioactive krypton-85 was used to saturate the liquid sodium and a very sensitive counting method was used for the analysis.* The counting method permitted the analysis of samples containing smaller amounts of dissolved krypton than was possible with the mass spectroscopic method.

Data for the solubility of krypton in liquid sodium are given in Table I-15; they have been recalculated to the standard state and compared with the solubility of argon in Figure I-34. It is seen that krypton is about one-half as soluble as argon; the temperature dependences of the solubilities are approximately the same. The heats of solution, derived from these temperature dependences, are 16 kcal/mole. This equality of heats of

Table I-15

SOLUBILITY OF KRYPTON IN LIQUID SODIUM

Temperature (°C)	Krypton Pressure (psia)	Solubility (atom fraction Kr)	Temperature (°C)	Krypton Pressure (psia)	Solubility (atom fraction Kr)
205	18	2.3×10^{-12}	396	18.4	2.8×10^{-10}
200	19	2.7×10^{-12}	400	18	3.3×10^{-10}
200	18.5	2.25×10^{-12}	400	18	3.4×10^{-10}
300	18	4.3×10^{-11}	480	18	1.2×10^{-9}
300	18	5.6×10^{-11}	480	18.4	1.7×10^{-9}
300	18	4.5×10^{-11}	480	18	1.5×10^{-9}

Figure I-34

TEMPERATURE DEPENDENCE OF SOLUBILITY OF ARGON AND KRYPTON IN LIQUID SODIUM

Rare gas pressure: 1 atmosphere

108-7147

*The radiochemical analyses were done by James Grey and Anthony Quattrocchi of the Chemistry Division.

solution may be fortuitous; the greater energy required to make a suitable cavity for the insertion of the larger atom (Kr) may be approximately balanced by the greater energy of interaction between the surrounding metallic ions and the more easily polarizable atom (Kr). Preliminary calculations of the heats of solution which take into account only these two sources of energy change are in fair agreement with the experimental values. Data for additional systems and more refined calculations will be required to reveal the participation (if any) of the conduction electrons in the solution process.

2. Liquid Sodium Chemistry

The increasing utilization of liquid alkali metals as heat transfer media in high power-density, fast nuclear reactors, as well as in other power sources, makes essential a continuing advancement of alkali metal technology. To insure the soundness of such an advance, the support of fundamental research is needed. A program to elucidate the chemistry of the reactions that occur in liquid alkali metal solutions has been undertaken; special emphasis will be given to liquid sodium, since its practical importance is greatest.

Sodium of known, high purity is required for significant research. Therefore, studies are being made in the closely related areas of purification, analysis, and contamination during handling. Liquid sodium contaminated with oxygen or carbon has been found to be more corrosive to structural materials than pure sodium. The two impurities, when present together, may accelerate carburization and decarburization. Studies are being started to clarify the mechanism of carbon transfer in liquid sodium solutions.

a. Sodium Purification (G. Lutz and K. E. Anderson)

A stainless steel filter vessel and still assembly has been constructed and operated for the production of high-purity sodium. The metal is charged to the filter vessel and is degassed to a residual pressure of 10^{-4} torr at 200°C. The liquid is filtered through stainless steel wool to the still pot for further degassing at 300°C. The temperature of the still pot is then raised to about 500°C for the distillation. Distilled sodium is collected in a stainless steel hold-up tank where it can be stored under vacuum until required. A demountable transfer vessel with a plate glass top can be connected to the hold-up tank for tapping a desired amount of sodium. The transfer vessel can be taken into a helium atmosphere box for further manipulations.

Several kilograms of sodium have been purified and transferred in this way. The oxygen analysis of the distilled sodium is about 30 ppm and the carbon assays about 50 ppm. It is believed that

distilled sodium should have a substantially lower carbon content. Oil diffusing back from the vacuum pump is suspected as the source of contamination. A molecular sieve trap to preclude back diffusion has been designed and is being constructed.

b. Sodium Analysis

(i) Oxygen
(G. Lutz and K. E. Anderson)

A mercury amalgamation apparatus, similar to that of Pepkowitz and Judd, has been set up for determining oxygen in sodium. The analysis is made at a pressure of 10^{-3} - 10^{-4} torr and all stopcocks and joints are greaseless to preclude the carrying of stopcock grease into the amalgamation chamber. Triplicate analyses of samples show a standard deviation of 18 ppm at the 100 ppm of oxygen level and 11 ppm at the 30 ppm of oxygen level.

Another series of experiments for the determination of oxygen in sodium by fast neutron activation (ANL-6800, p. 189) is underway. One of the major difficulties in this rapid, nondestructive method is its requirement for a sodium encapsulating material which does not interfere via its oxygen content. To avoid this problem, tests are being made to establish the feasibility of irradiating a sodium sample while it is located at one end of a container and counting the sample while it is located at the other, unirradiated end of the container. Polyethylene containers which are about 20 cm long and which can accommodate an 8-mm dia. by 10-mm cylindrical sample of sodium are being used in the tests.

(ii) Carbon
(C. Luner and P. D. Hunt)

Efforts are continuing to develop "dry" oxidation to the status of an accurate and reliable method for the analysis of carbon in sodium. Because of the variability of the blanks which occur from time to time when a flow system is used, the initial combustion and high temperature oxidation are now performed in a static system. In addition, the single copper oxide furnace that had been used formerly for the purification of oxygen has been replaced by two furnaces, each containing platinum and copper oxide. With these changes the reagent blank has been found to be reproducible at about $2\text{ }\mu\text{g}$ of carbon. Table I-16 shows that the recovery of carbon from two different sources is good. The recovery of carbon from sodium carbonate in the presence of sodium, however, was erratic. The reason for this is not clear since the carbon content of sodium sampled from the solubility apparatus (see below) showed good reproducibility. Additional experiments are planned.

Table I-16

RECOVERY OF CARBON FROM DIFFERENT STANDARDS
USING A STATIC SYSTEM

Oxygen Pressure 15 cm Hg			
<u>Form of Carbon</u>	<u>Carbon Added (μg)</u>	<u>Carbon Found (μg)</u>	
Na_2CO_3	28.3	27.2	
	22.6	21.0	
	11.3	12.6	
	11.3	11.2	
"Leco" Standard	30	33	
	30	28	
c. <u>Carburization Reactions in Liquid Sodium</u> (C. Luner and P. D. Hunt)			

It has been established that various metals can be significantly carburized or decarburized when in contact with liquid sodium. This presents a potentially serious problem associated with the use of liquid sodium in nuclear reactors, since undesirable changes in the mechanical properties of structural materials, such as steel, may result from small changes in their carbon contents. Since the mechanism of carbon transport is not well understood, a basic study of solutions of carbon in liquid sodium has been started. An extensive redetermination of the solubility of graphite in sodium as a function of temperature and oxygen content of the sodium has been started. The apparatus has been built and tested, and a preliminary value, 33 ± 5 ppm, for the solubility of graphite in sodium at 250°C has been obtained. The oxygen content of the sodium was 100 ± 18 ppm.

3. Thermodynamic Studies

Three methods of obtaining thermodynamic information in metallic systems are currently in use. (a) Galvanic cells have proved to be especially useful for the measurement of activities in liquid metal solutions and for the determination of the free energy of formation of the equilibrium solid phase in solid-liquid two phase alloys. (b) For systems composed of several well-defined intermetallic phases, measurement of the decomposition pressures in the two phase regions by the Knudsen effusion method has been effective. (c) A vapor phase optical absorption method is being employed for certain systems not amenable to methods (a) or (b). In these systems there is only a small difference in the electrochemical potentials of the components and both components have nearly the same vapor pressure.

a. Thermodynamics of Lanthanum-Cadmium System
 (Emf Studies)
 (I. Johnson and R. Yonco)

The galvanic cell method is being used to systematically study binary plutonium alloys with the low melting B-subgroup metals and the most cadmium rich compounds in rare earth-cadmium systems. The thermodynamics of the cadmium-rich portion of the lanthanum-cadmium system have been studied by means of galvanic cells of the type:

The cell reaction consists of the dissolution of lanthanum in the fused salt at the pure lanthanum electrode and deposition of lanthanum in the saturated liquid alloy electrode. The two-phase alloy consists of a cadmium-rich liquid phase in equilibrium with the solid intermetallic compound LaCd_{11} . The overall cell reaction may be written

Figure I-35

EMF VS TEMPERATURE

Cell: $\text{La}/\text{LaCl}_3, \text{KCl-LiCl}/$
 $\text{La-Cd (2-phase alloy)}$

Therefore, the free energy of formation, ΔG_f° , of the intermetallic compound LaCd_{11} from solid lanthanum and pure liquid cadmium is related to the cell emf, E , by the equation

$$\Delta G_f^\circ = -nFE + 11RT \ln a_{\text{Cd}}$$

in which a_{Cd} is the activity of cadmium in the saturated, liquid, cadmium-rich phase. The value of the term $11RT \ln a_{\text{Cd}}$ is found to be negligible compared to the value of $-nFE$.

Values of the emf as a function of temperature are shown in Figure I-35. These data may be used to compute the following equation for ΔG_f° :

$$\begin{aligned} \text{LaCd}_{11} (400-530^\circ\text{C}): \Delta G_f^\circ (\text{kcal/mole}) = \\ -72.9 + 44.4 \times 10^{-3} T. \end{aligned}$$

At 400°C , the free energy of formation of LaCd_{11} is -43.0 kcal/mole.

b. Thermodynamic Properties of the Lanthanum-Cadmium System (Effusion Studies)
(E. Veleckis and E. Van Deventer)

The lanthanum-cadmium system is known (see ANL-6725, p. 110) to form five intermetallic compounds: LaCd_{11} , $\text{La}_2\text{Cd}_{17}$, $\text{La}_3\text{Cd}_{13}$, LaCd_2 , and LaCd . The thermodynamic activity of cadmium above each alloy containing a neighboring pair of compounds was calculated from measurements of its cadmium pressure with the recording effusion balance. In these calculations it is assumed that the evaporation coefficient of cadmium is sufficiently large (>0.01) to permit attainment of equilibrium in the effusion crucible.

Figure I-36 shows the data which are represented on a Clausius-Clapeyron plot for each heterogeneous region of the phase diagram. The results can be represented by linear equations which are listed in column 3 of Table I-17. Also plotted in the figure is the vapor pressure of pure liquid cadmium obtained from the equation given by Nesmeyanov,¹²

$$\log P_{\text{mm}}^{\circ} = 2.529 - 5181 T^{-1} - 8.496 \times 10^{-4} T + 2.056 \log T.$$

This equation was employed for the calculation of the thermodynamic properties of the system.

Figure I-36

DECOMPOSITION PRESSURES OF
INTERMEDIATE PHASES IN THE
SYSTEM LANTHANUM-CADMIUM

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¹²A. N. Nesmeyanov, "Vapor Pressure of the Elements," Academic Press, New York, 1961 (translated in 1963), p. 444.

Table I-17

DECOMPOSITION PRESSURES AND FREE ENERGIES OF FORMATION OF
INTERMEDIATE PHASES IN THE SYSTEM LANTHANUM-CADMIUM

Two-Phase Region	Δr	P_{mm}	$-\Delta G_{i,(i-1)}$ (cal/g-atom La)	Compound	Index (n)	ΔG_f° (cal/g-atom La)	Std. Dev. $\Delta H_f^\circ \quad \Delta S_f^\circ$
LaCd ₁₁ -La ₂ Cd ₁₇	2.5	9,166-6425 $\frac{1}{T}$	12.35 T-11,820	LaCd ₁₁	5	54.00 T-82,080	2,720 12.00
La ₂ Cd ₁₇ -La ₃ Cd ₁₃	4.167	8,894-6289 $\frac{1}{T}$	15.59 T-17,240	La ₂ Cd ₁₇	4	41.65 T-70,260	2,560 11.13
La ₃ Cd ₁₃ -LaCd ₂	2.333	9,436-7369 $\frac{1}{T}$	14.67 T-21,290	La ₃ Cd ₁₃	3	26.06 T-53,020	1,700 7.56
LaCd ₂ -LaCd	1	8,625-7744 $\frac{1}{T}$	2.70 T-10,940	LaCd ₂	2	11.39 T-31,730	1,110 4.05
LaCd-La	1	9,941-9904 $\frac{1}{T}$	8.69 T-20,790	LaCd	1	8.69 T-20,790	500 1.37

To illustrate the free energy calculations, it is convenient to consider a generalized case. Suppose that a system M-X in which only the component X is volatile forms a number of intermediate compounds having atom ratios $r_0, r_1, r_2, \dots, r_i, \dots, r_n, \dots$ (composition r_0 corresponds to pure M). The free energy, $\Delta G_{i,(i-1)}$, released in the course of the decomposition reaction taking place between the i th and $(i-1)$ th compounds, i.e.,

can be obtained from the equation

$$\Delta G_{i,(i-1)} = -\Delta r RT \ln \frac{P_{i,(i-1)}}{P^\circ} \quad (2)$$

where $P_{i,(i-1)}$ is the pressure of X over the alloy in the composition region between the i th and $(i-1)$ th compounds, P° is the pressure of pure liquid X and $\Delta r (= r_i - r_{(i-1)})$ is the difference in the atom ratios between the i th and $(i-1)$ th compounds.

The standard free energy of formation of the n th compound relative to the pure components in their normal state of aggregation at a pressure of 1 atm may be obtained from the decomposition free energies by the equation

$$\Delta G_f^\circ, n = - \sum_{i=1}^n \Delta G_{i,(i-1)} + RT \sum_{i=1}^n \Delta r \ln \frac{P_{i,(i-1)}}{P^\circ} \quad (3)$$

The results of the calculations applied to the lanthanum-cadmium system are listed in Table I-17. The free energies of formation of

the compounds are expressed in terms of linear equations, the coefficients of which correspond approximately to the entropy and the heat of formation of the respective compounds. The equation for the standard free energy of formation of LaCd_{11} is ΔG_f° (kcal/mole) = $-82.1 + 54.0 \times 10^{-3} T$. At 400°C the free energy of formation of LaCd_{11} is calculated to be -45.7 kcal/mole. This is in good agreement with the result of the preceding section.

The thermodynamic consistency of the results was tested by plotting the standard free energy of formation (kcal/g-atom) at 400°C of the intermediate phases against the atom fraction of lanthanum [ΔG_f° (kcal/g-atom) = $N_{\text{La}} \cdot \Delta G_f^\circ$ (kcal/g-atom La)]. The criteria of stability of an intermediate phase require that (a) the free energy of the phase must be more negative than the free energy of a heterogeneous mixture of pure components, (b) the free energy of the phase must be more negative than that of all possible two-phase mixtures. As may be seen from Figure I-37, all of the compounds meet these requirements.

Figure I-37

STANDARD FREE ENERGIES OF FORMATION OF VARIOUS INTERMEDIATE PHASES IN THE SYSTEM La-Cd AT 400°C

c. Thermodynamics of Binary Alkali Metal Solutions (F. Cafasso, V. Khanna and R. Murray)

The thermodynamic properties of binary alkali metal solutions are being determined by a vapor pressure method which utilizes the principles of absorption spectrophotometry. In this method, light of certain characteristic frequencies (resonance radiation) is passed through the vapor above a pure alkali metal or through the vapor above its binary alloy. The quantity of the resonance radiation which is absorbed is a measure of the concentration of monatomic alkali metal in each of the vapor phases. Comparison of the absorption by the vapor over an alloy to that over the pure

alkali metal is a direct measure of the thermodynamic activity of one of the components in the solution. A more complete description of this method was given in ANL-6725, p. 107.

The sodium-potassium system is the first binary being studied. The activity of sodium in the eutectic NaK alloy (atom fraction of Na = 0.33) has been determined. Pure sodium and this alloy were placed in two 2.54-cm long Pyrex absorption cells. (Recent tests have shown that Pyrex has good resistance to attack by sodium and potassium at 130-150°C, the temperature range of this study.) The two absorption cells containing the metal samples and a third empty cell were placed in a furnace block assembly which had been modified to house three cells simultaneously. This modification permitted absorption measurements to be made simultaneously for the alloy sample and pure sodium sample. (Measurements made in this manner greatly reduce the possible errors in an activity determination and the time required for such a determination.) The absorption of the 5890 Å line of the Na-D doublet by equilibrium vapor over pure sodium and over the NaK alloy was then measured from approximately 137 to 149°C. Absorption measurements were made during both cooling and heating cycles. These measurements are shown in Figure I-38, where $T \log(I_0/I)$, the

Figure I-38

PARTIAL PRESSURE OF SODIUM ATOMS IN VAPOR ABOVE PURE SODIUM AND NaK EUTECTIC AS A FUNCTION OF TEMPERATURE

(Note: The vertical scale is arbitrary)

108-7976

product of the absolute temperature T and the logarithm of the ratio of the incident intensity of the 5890 Å line to its transmitted intensity, is plotted against the reciprocal absolute temperature for both samples. The ordinate of this figure, $T \log(I_0/I)$, is a measure of the partial pressure of monatomic sodium in the vapor. The enthalpy of vaporization for the

reaction $\text{Na}(l) \rightleftharpoons \text{Na}(g)$ obtained from the slope of the measurements on pure sodium is 23.6 kcal/g-atom. Taking into account the shortness of the temperature range, the agreement with the best literature value at 150°C, 24.9 kcal/g-atom,¹³ is adequate.

The activity coefficients calculated from the absorption measurements are given in Table I-18. It is concluded from these results that over the temperature range of this

¹³M. Sittig, "Sodium, Its Manufacture, Properties and Uses," Reinhold Publishing Corp., New York, N. Y. (1956).

study (approximately 12°) the activity coefficient of Na (γ_{Na}) is constant, the small variation in γ_{Na} being within experimental uncertainty.

Table I-18

ACTIVITY COEFFICIENTS OF Na (γ_{Na}) IN THE
NaK EUTECTIC (MOLE FRACTION OF Na = 0.33)

<u>T(°C)</u>	<u>γ_{Na}</u>	<u>T(°C)</u>	<u>γ_{Na}</u>
149.3	1.59	136.8	1.61
146.1	1.59	141.2	1.58
141.1	1.57	146.5	1.58
137.3	1.60		

The excess partial molal entropy for Na ($\bar{S}_{\text{Na}}^{\text{xs}}$) was calculated from these results using recently published heat data.¹⁴ This calculation, however, is approximate since the value of the partial molal enthalpy of Na [$\bar{L}_{\text{Na}}$] used in this computation is that determined at 111°C. The value of $\bar{S}_{\text{Na}}^{\text{xs}}$ was found to be -0.11 cal/deg mole at 143°C.¹⁵ At room temperature $\bar{S}_{\text{Na}}^{\text{xs}}$ ($X_{\text{Na}} = 0.33$) was estimated by Hultgren et al.¹⁵ to be -0.05 cal/deg mole.

Absorption measurements on alloys richer in sodium are now in progress.

D. Reactor Materials
(A. D. Tevebaugh)

Refractory compounds of the actinide elements, such as carbides and sulfides, show promise as reactor fuels capable of withstanding high temperatures and large burnups. Methods are being investigated for the preparation of these refractory fuels. The more promising methods are being used to prepare sufficient quantities of these fuels for fabricability evaluations and irradiation testing by the Metallurgy Division.

Mobile blanket materials, such as slurries, pastes, molten salts, and molten alloys, have been evaluated on the basis of calculations and existing literature data as to their potential in fast breeder reactors. On the basis of these calculations and evaluations, slurries and pastes of ceramic compounds of uranium in liquid metals have been chosen for the initial experimental studies.

¹⁴T. Yokokawa and O. J. Kleppa, J. Chem. Phys. **40**, 46 (1964).

¹⁵R. Hultgren, R., Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons (1963).

1. Preparation of Uranium Monocarbide by a Liquid-Metal Process (E. J. Petkus, M. A. Bowden)

The liquid-metal process for the preparation of uranium monocarbide (UC) involves the following steps: (1) dissolution of metallic uranium in a zinc solution containing 14 to 18 w/o magnesium, (2) addition of a degassed carbonaceous material (usually activated charcoal) at about stoichiometric quantities to form UC, (3) reaction of the constituents with stirring for 8 to 12 hr at 800°C, (4) a phase separation to remove the bulk of the supernatant liquid metal (Zn-Mg) from the precipitated UC, and (5) vacuum distillation to remove the residual magnesium and zinc from the UC product. It has been demonstrated that an easily fabricable UC can be produced by this process. The main objective of this work was to produce carbide material with a carbon content near the theoretical value of 4.8 w/o for UC and as low an oxygen content as possible.

In earlier work utilizing this process, the UC was unloaded in air atmosphere and quickly sealed in a container. A vacuum, inert-gas glovebox was designed and built to permit loading and unloading of materials under controlled atmosphere conditions (see ANL-6725, p. 79).

Twelve UC production runs have been completed on a 500 or 1000-g scale of uranium metal; these runs were made to prepare UC for fabrication and irradiation tests by the Metallurgy Division. Analytical data are shown for most of these runs in Table I-19. Of the runs omitted from Table I-19, Run UC-1 was not included because a hole developed in the reactor shell, causing a high oxygen content (2.52 w/o) in the UC product. Runs UC-8 and UC-9, also omitted from Table I-19, did not use

Table I-19

ANALYTICAL AND PROCESS DATA FOR URANIUM MONOCARBIDE (UC)
PREPARED BY THE LIQUID-METAL METHOD
(Activated Charcoal Runs)

Run	UC-2	UC-3	UC-4	UC-5	UC-6	UC-7	UC-10	UC-11	UC-12
Scale (Uranium Charge)	500 g	500 g	500 g	500 g	500 g	500 g	500 g	1000 g	1000 g
Reaction Time, hr	8	8	8	8	8	12	8	8	12
Charge C/U	1.20	1.20	1.20	1.10	1.10	1.10	1.02	0.90	1.02
Phase Separation	Tilt-Pour	Tilt-Pour	Pressure-Siphon	Pressure-Siphon	Pressure-Siphon	Pressure-Siphon	Pressure-Siphon	Pressure-Siphon	Pressure-Siphon
Yield, g	393	233	474	398	332	407	343	444	714
Oxygen, w/o	0.39	0.60	0.61	0.29	0.30	0.20	0.14	0.29	0.18
Nitrogen, ppm	380	380	60	10	180	220	120	20	190
Total C, w/o	5.40	5.40	5.86	5.56	6.00	6.23	5.59	4.56	5.24
Free C, w/o	0.80	1.2	1.3	1.1	1.5	1.9	1.4	0.36	0.74
Free C/U	0.17	0.26	0.28	0.22	0.33	0.41	0.30	0.08	0.16
Uranium, w/o	92.0	90.0	92.5	93.8	90.5	90.6	90.4	94.2	93.0
Magnesium, w/o	0.19	1.02	0.20	0.15	0.20	0.26	0.12	0.01	0.08
Zinc, w/o	0.52	1.49	0.58	0.31	0.82	0.69	0.30	0.08	0.20
X-ray, Species	UC	UC, UO ₂ Minor	UC	UC	UC	UC	αU, UC	UC	UC
X-ray, Parameter	4.959 Å	4.959 Å	4.959 Å	4.959 Å	4.959 Å	4.960 Å	4.959 Å	4.960 Å	4.960 Å
Surface Area, m ² /g	2.73	1.86	1.49	0.28	3.75	0.96	0.58	Not Available	Not Available

activated charcoal as the carbonaceous material. The use of grade 38 Acheson graphite powder in Run UC-8 resulted in a high total carbon content (7.8 w/o). The use of Witco charcoal black in Run UC-9 resulted in a low carbon content (3.99 w/o).

In earlier work, UC with an oxygen content of about 0.4 to 1.0 w/o (see ANL-6543, p. 62) was produced, but later work resulted in substantially purer material with an oxygen content of 0.30 w/o or lower. Oxygen content of the UC product was lowered by more efficient degassing of the activated charcoal and lowering of the C/U ratio (1.20 to 1.02).

Apparently, the oxygen content of the UC cannot be reduced much below 0.14 w/o with the present degassing techniques. Heating activated charcoal to 850°C, with continuous evacuation, has produced a charcoal product containing about 2.0 w/o oxygen. (The activated charcoal contributes from 60 to 80 w/o of the final oxygen content of the UC product.) The low oxygen contents of the products from Runs UC-10, UC-11, and UC-12 may be partially a result of degassing of the transfer and retorting furnaces by heating and evacuation.

The UC material containing the least oxygen (0.14 w/o) was that from Run UC-10. Material with an oxygen content of 0.2 w/o or less probably can be consistently produced in future preparations.

The total carbon content of the UC products was generally higher than the maximum of 5.2 w/o desired by the Metallurgy Division and varied from 5.2 to 6.0 w/o. In Run UC-12, the total carbon content was 5.24 w/o. Run UC-11 had a substoichiometric carbon content of 4.56 w/o; however, this run was not typical because the UC product contained a large amount of unreacted uranium metal. This uranium metal residue may have been due to the low C/U atom ratio of 0.9, insufficient reaction time, or a larger scale run (1000 g vs 500 g normally). The C/U charge ratio has been progressively decreased from 1.20 to 1.02 in an attempt to decrease the total carbon content of the UC product.

The uranium monocarbide and degassed activated charcoal are stored in closed Mason jars in the vacuum, inert-gas glovebox for several months before the UC is fabricated into test specimens and the charcoal is reacted with uranium. Some concern was expressed about oxygen pickup by these stored materials. Samples were taken for oxygen analyses from two batches of these stored materials after 95 days of storage. The oxygen analyses of these samples indicated that there had been no oxygen pickup by the degassed activated charcoal or the UC during storage.

The particle sizes of the UC products for the activated charcoal runs were determined by screening and are summarized in

Table I-20. Each UC product was screened in an inert atmosphere, by hand shaking, for about 10 min. In Runs UC-2 through UC-5, activated charcoal of less than $149\ \mu$ (100 mesh) was used. In Runs UC-6 through UC-12, activated charcoal of less than $44\ \mu$ (325 mesh) was used in an attempt to decrease the particle size of the final UC product. A finer particle size of the UC product is desirable to enhance its sintering capability; i.e., a density of greater than 90% of theoretical density of UC is considered minimal. In order to obtain this particle size, UC material is normally ball-milled. This ball-milling step could be eliminated if the UC product was primarily less than $44\ \mu$. Runs UC-6 and UC-7 showed a significant increase in smaller size UC material (93.0 and 90.6 w/o less than $44\ \mu$). Runs UC-10 and UC-11 are not representative because both products contained significant amounts of unreacted uranium. Run UC-12 was not completely retorted.

Table I-20

PARTICLE SIZE DISTRIBUTION OF URANIUM MONOCARBIDE
(w/o ABOVE STATED SIZE) - ACTIVATED CHARCOAL RUNS

Particle Size (μ)	Particle Size Distribution (w/o above stated size) Batch Number									
	UC-2	UC-3	UC-4	UC-5	UC-6	UC-7	UC-10	UC-11	UC-12	
149	0.2	0.8	1.6	15.8	2.0	0.5	2.8	45.4	11.3	
74	13.7	14.5	6.0	37.5	3.6	1.5	9.4	59.7	25.2	
44	21.5	33.0	17.5	54.0	7.0	9.4	22.5	67.9	29.9	
<44	78.5	67.0	82.5	46.0	93.0	90.6	77.5	32.1	60.1	

Metallographic examinations of the UC products were made to determine the homogeneity of the UC particles. Typical particles are shown in Figure I-39. The individual particles were mounted, polished, and

Figure I-39
PHOTOMICROGRAPH OF
TYPICAL URANIUM
MONOCARBIDE PARTICLES

Run UC-6

108-7977

533X

etched before viewing. In most cases, the particles exhibited two phases, a light, shiny phase on the perimeter of the product and a gray phase in the center.

In an attempt to identify the two phases, exploratory work with an electron probe microanalyzer was performed. Data from these examinations indicated high uranium concentrations at the edges of the particles and variable concentration of uranium throughout the gray phase. Further work is required to verify these results. Additional work will attempt to correlate the sizes and shapes of the activated charcoal source material with the final UC product.

2. Preparation of Uranium Monocarbide by a Fluid-Bed Process (E. J. Petkus, J. P. Bartos, M. A. Bowden)

Work has been done at other laboratories on the reaction of powdered uranium metal with methane (CH_4) to produce UC.¹⁶ These reactions were carried out by passing CH_4 over a static bed of uranium metal powder. When this method was used, the reaction rate depended upon the thickness of the bed of uranium metal powder. Moreover, the powder sintered into a relatively dense mass which further retarded the reaction. A heterogeneous product was obtained. Near the top of the bed, higher uranium carbides, such as UC_2 , and free carbon were present, while near the bottom, UC and uranium metal were the major phases.

Because of these disadvantages of the static-bed reaction, a fluid-bed method for the reaction of powdered uranium metal with CH_4 to produce UC is being studied. The work to date has been primarily limited to the design and construction of laboratory equipment for the preparation of 100-g batches of UC by a fluid-bed process. A few, small-scale studies have been made of the fluidizing properties of UH_3 and powdered uranium metal; the results to date are encouraging.

The fluidized-bed process holds particular interest as a possible method for the preparation of a solid solution of uranium and plutonium monocarbides and other ceramic fuels and fuel mixtures, such as sulfides, nitrides, and phosphides. It may be possible to control the stoichiometry of these ceramic fuels by using the proper gas mixture, for example, H_2 and CH_4 for the carbides and H_2 and H_2S for the sulfides.

3. Preparation of a Solid Solution of Uranium-Plutonium Monocarbide (S. Vogler, J. Pavlik)

A method for the preparation of homogeneous uranium and plutonium monocarbide is being studied. In this method, fused salt mixtures

¹⁶Jakešová, L. and Jakeš, D., Atomic Energy Rev. 1(3), 18-19 (1963).

are used as the solvent for the actinide compounds and for a metal carbide which is less stable than the actinide carbides. When the reactants are heated, a double decomposition reaction results in the formation of the actinide carbide, which can be recovered by filtration and distillation of the residual salts. In the present work, the fused-salt solvent is magnesium chloride-lithium chloride (MgCl_2 -35 m/o LiCl), the actinide compounds are the chlorides (e.g., UCl_3), and the metal carbide is magnesium sesquicarbide (Mg_2C_3). This method has been found to be applicable for the preparation of many carbides, such as UC, ZrC, WC, VC, and TaC (ANL-6800, p. 145).

When the above method was applied to plutonium, the plutonium carbide product was identified by X-ray diffraction studies as the sesquicarbide, Pu_2C_3 (ANL-6800, pp. 146-147). This was disappointing since it was known that UC forms a solid solution with PuC, but not with Pu_2C_3 . The formation of such a solid solution is the primary purpose of these studies.

Since UC is produced by this method, it was decided to perform an experiment to ascertain if a solid solution of $[\text{U}_x\text{Pu}_{(1-x)}]\text{C}$ would be formed by reacting uranium and plutonium chlorides with magnesium sesquicarbide. In this experiment, uranium and plutonium metals (ratio of 4 U:1 Pu) were dissolved in liquid zinc at 640°C with the zinc in contact with molten MgCl_2 -35 m/o LiCl containing zinc chloride (ZnCl_2). As the uranium and plutonium metals were dissolved in the zinc, they were oxidized to the trichlorides by the ZnCl_2 and thence transferred to the salt phase. After this transfer was completed, the system was allowed to cool. The solidified salt and metal phases were separated physically. The salt was then reacted with Mg_2C_3 in a tantalum crucible at 625 - 650°C for approximately 1 hr. At this time, the reaction was considered complete and the salts were removed by volatilization under vacuum at 850°C . The residue from the distillation was a fine, black powder. Preliminary analytical and X-ray data for this black powder indicated that:

1. The dominant phase exhibited face-centered cubic crystal symmetry with a lattice parameter of $4.960 \pm 0.004 \text{ \AA}$. This is exactly the lattice parameter of UC and is the value to be expected for solid solutions of $[\text{U}_x\text{Pu}_{(1-x)}]\text{C}$ up to approximately 15-20 a/o plutonium.¹⁷ Possible very minor phases were PuOCl , UO_2 , or Mg. There was one arc of extremely low intensity which could not be accounted for by any of the above impurities or by the compounds Mg_2C_3 , PuC, Pu_2C_3 , or PuO_2 .
2. Based on the gross weight of the product, the yield was approximately 75 w/o of the charge weight.

¹⁷Rosen, S., Nevitt, M. V., and Mitchell, A. W.; J. Nucl. Mat. 9, 137-142 (1963).

3. The uranium content of the product was approximately 84.5 w/o, and the plutonium content was 6.5 w/o.
4. The total carbon was approximately 4.1 w/o, and the excess carbon was approximately 0.33 w/o.
5. The oxygen content was 1.3 w/o.

At this point in the program, precipitation of the solid solution $[U_xPu_{(1-x)}]C$ must be established.

The appearance of a single phase with face-centered cubic crystal symmetry and a lattice parameter of $4.960 \text{ \AA}$ is encouraging since it is indicative of the formation of the solid solution. The high oxygen content is unwelcome since it is known that compounds of the type $U[C_xO_{(1-x)}]$ and $Pu[C_xO_{(1-x)}]$ exist. The formation of such compounds during precipitation of the solid solution would complicate the interpretation of the data, especially the X-ray diffraction results. Thus it is appropriate to repeat the above experiment, with a special emphasis upon reducing the oxygen contamination.

Another problem relates to the plutonium content of the carbide product. In the starting material, the plutonium metal was 20 w/o of the total plutonium and uranium dissolved in the zinc. The plutonium content of the product was 6.5 w/o. This enrichment of uranium in the product is another factor which requires further investigation.

4. Paste and Slurry Blanket Fuels (P. A. Nelson, M. Chasanov)

An experimental program is being initiated to study slurries and pastes consisting of fertile solid compounds suspended in liquid metals for use as blanket materials for fast breeder reactors. Such blanket materials may have significant economic advantages over solid blanket fuels.

For solid blanket fuel, the average power density and average burnup of actinide elements just prior to discharge of the blanket material is a small fraction of the peak power density and peak burnup reached by the blanket elements adjacent to the core. The sodium coolant outlet temperature for radial blanket assemblies is considerably higher at the end of the period of residence of the blanket fuel in the reactor than the outlet temperature at the beginning of the period. These heat transport and fuel utilization inefficiencies can be partially avoided by periodic shuffling of the blanket assemblies but probably at the cost of additional reactor down-time.

A mobile blanket material, such as a slurry or a paste, would avoid all of the above problems if it could be circulated throughout the blanket region (or at least the radial blanket region) while the reactor is in operation. Pastes or slurries have been chosen for experimental study in preference to molten alloys or molten salts containing a uranium halide because corrosion would probably be more severe for the latter two types. In the case of molten salts, the uranium density would be quite low. For slurry and paste blanket materials, sodium appears to be the most attractive suspending medium because of its known compatibility with structural materials and its excellent heat transfer properties, and UN, UC, US, and UO_2 (in order of preference) appear to be attractive fertile materials from the standpoint of uranium density and chemical stability.

The main problem contemplated with the use of a slurry or paste is settling of the solid phase. Therefore, the first experiments will be studies of wetting of the solid by the liquid phase, flocculation phenomena, and settling rates.

II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES*

Development work on fluid-bed fluoride volatility processes for the recovery of uranium and plutonium from spent nuclear fuels was continued. In these processes, the uranium and plutonium are converted to hexafluorides which are volatile and which can then be further decontaminated and separated from fission products by means of distillation techniques. The basic reactions in these processes are highly exothermic and wide use is made of inert fluidized beds which serve as a heat transfer medium. Work is being carried out with two principal types of fuels which are of current interest. The first type is low-enrichment uranium dioxide-plutonium dioxide fuels which are clad in either stainless steel or Zircaloy. The second type is highly enriched uranium fuels which are alloyed and clad with Zircaloy or aluminum.

Details of the current conceptual process for UO_2 - PuO_2 fuels were described recently (ANL-6800, pp. 197-198). The four major steps in this process are: decladding, fluorination, distillation, and reconversion to oxides. These steps are to be investigated in an engineering-scale plutonium handling facility now nearing completion. The first steps to be studied will be the oxidation-fluorination of UO_2 - PuO_2 pellet feeds to a mixed hexafluoride product for recovery of the fissionable values, and the fluid-bed conversion by reaction with steam and hydrogen of the mixed hexafluoride product to dense spheroidal oxide particles.

Laboratory support work for these processes is continuing with the study of the fluid-bed fluorination of mixtures of U_3O_8 , PuO_2 , and fission product element oxides, simulating the concentrations present in a spent fuel element. Work has continued on experiments to develop procedures which will provide maximum removal of uranium and plutonium from the inert bed material. Other laboratory support work included:

- (1) a study of the decomposition of gaseous PuF_6 to fluorine and PuF_4 by alpha radiation,
- (2) calculation of the lattice constants for UF_6 , NpF_6 , and PuF_6 from available powder pattern data, and
- (3) a study of the cleanup of exhaust air from PuF_6 -handling facilities. Studies were initiated on the chemical decladding of stainless steel-clad fuels by the use of aqueous HCl in an air-fluidized system. Also, a fundamental study on the fluidization of fine particles was started.

Studies were completed on the fluid-bed process for the preparation of dense spheroidal particles of uranium dioxide by means of the direct reaction of uranium hexafluoride with steam and hydrogen. The results of this

* A summary of this section is given on pages 26 to 34.

investigation will be used in subsequent work on the preparation of dense UO_2 - PuO_2 particles from mixed hexafluoride feeds. A fluid-bed converter unit for work with plutonium materials is now being installed in the engineering-scale alpha facility.

Development of a fluid-bed volatility process for the recovery of uranium from highly enriched uranium-alloy fuels continued. Application of the process to uranium-zirconium and uranium-aluminum alloy fuels is being evaluated. In this process scheme, separation of the uranium from the alloying material and the cladding is carried out by means of a hydrochlorination step. The uranium is subsequently recovered as the hexafluoride during a fluorination step. In "cold" bench-scale studies in the $1\frac{1}{2}$ -in. dia. fluid-bed unit, sections of normal uranium-Zircaloy alloy containing inactive fission product elements were processed to study the effect of the fission elements on process operability. A bench-scale unit for high-activity-level studies of the fluid-bed volatility process has been installed in a cave service area. Preparations are underway for shakedown runs with unirradiated alloy fuel specimens.

Following a series of shakedown tests, the first of a series of runs with unirradiated, normal uranium fuel subassemblies was conducted in the pilot-plant facility installed to demonstrate the recovery of uranium from highly enriched uranium-alloy fuels. In the shakedown tests which were made with fuel assemblies of Zircaloy or aluminum alone (no uranium), only the hydrochlorination and hydrofluorination steps were carried out. In the subsequent demonstration run which involved a 19.6-kg uranium-Zircaloy assembly, the fluorination (uranium recovery) step was included in the reaction sequence. During the hydrochlorination step, the fluid-bed pyrohydrolysis reactor which converts the volatile waste metal chlorides to solid oxide wastes was in operation.

A corrosion program in support of the fluid-bed volatility program is in progress. Current emphasis is on the evaluation of nickel as a material of construction.

A. Laboratory Investigations of Fluoride Volatility Processes (M. J. Steindler, J. Fischer)

1. Fluid-Bed Fluorination of U_3O_8 - PuO_2 Mixtures

(R. L. Jarry, J. Stockbar, T. Baker, G. Redding, W. Gunther, W. Shinn)

In the fluid-bed fluoride volatility process, the decadal fuel elements are reacted with oxygen and then with fluorine at about 500°C to convert the oxides to the volatile compounds, uranium hexafluoride and plutonium hexafluoride.

In previously reported work (see ANL-6742 and ANL-6766, p. 82), small-scale boat experiments were performed in order to develop procedures applicable to mixtures of uranium dioxide-plutonium dioxide-fission product oxides and alumina. These procedures were designed for maximum removal of uranium and plutonium from the alumina. Subsequent experiments, reported in the previous semiannual report (ANL-6800, p. 199), and carried out in laboratory-scale fluid-bed equipment, evaluated the experimental conditions for removal of plutonium from alumina. Data were obtained on the rates of fluorination of uranium oxide (U_3O_8) and plutonium oxide, and on the retention of plutonium on the filters and the internal surfaces of the fluid-bed reactor after fluorination. In addition, measurements were made on the rate of fluorination of mixtures of U_3O_8 - PuO_2 obtained by oxidation of UO_2 - PuO_2 solid solutions, and on the rate of fluorination of similar mixtures prepared by mechanically combining U_3O_8 and PuO_2 powders.

This report presents the results of the following types of experiments. (1) Experiments were performed in which an alumina bed was used for the fluid-bed fluorination of several additions of U_3O_8 - PuO_2 -fission product mixture. These experiments were designed to determine the feasibility of using one bed of alumina for several fluorinations. (2) Feed materials were evaluated by comparing the results of tests in which the PuO_2 was initially present in the form of a solid solution with UO_2 and then oxidized to form a mixture of U_3O_8 and PuO_2 with the results of tests in which a physical mixture of PuO_2 and U_3O_8 was used. The use of a physical mixture rather than a solid solution would afford a significant savings in material costs for the pilot plant. (3) Tests were performed in which PuO_2 alone or PuO_2 -fission product mixtures were fluorinated to obtain information on the variation of residual plutonium content of the alumina with the quantity of plutonium fed to the reactor and the quantity of fission products present in the feed material. (4) Blank experiments using feed materials containing no plutonium were performed to determine the plutonium retention in the reactor system. This type of experiment would indicate the lowest level of plutonium that could be expected on the alumina of the fluid bed. (5) The use of bismuth as an additive to promote the removal of plutonium from a used alumina bed during further fluorination was evaluated. (6) The location of the plutonium on the alumina was determined by an autoradiographic technique. The position of the plutonium, that is, whether the plutonium is on the surface of the alumina particles or in the body of the particles, is of importance in devising schemes for removing the plutonium from the alumina.

Equipment and Experimental Procedure

The preparation of the U_3O_8 - PuO_2 -fission product mixtures was described in a previous report (ANL-6800, p. 200). In a single experiment, 300 g of the U_3O_8 - PuO_2 -F.P. mixture, containing about 0.4 w/o plutonium and 0.9 w/o fission products, was used. The fission product mixture, described in a previous summary report (ANL-6800, pp. 200-201), contained eleven fission product element oxides.

Commercial grade fluorine was used in the experiments after it had been passed through a sodium fluoride trap at 100°C to remove HF. Nitrogen, which was used as the fluidizing gas and also as the diluent for the fluorine, was passed through a trap containing Molecular Sieves to remove water. High-purity fused alumina was employed as the inert fluidized material.

The fluid-bed apparatus used in this work has been previously described (ANL-6725, p. 115, and ANL-6763). The entire apparatus was contained within an alpha box and manipulation of the apparatus was accomplished through glove ports. Photographs of the alpha box and of the fluid-bed reactor are contained in a previous report (ANL-6800, pp. 202-203).

The general operating procedure for the fluorinations was described in detail in a previous summary report (ANL-6800, p. 199). Briefly, the procedure is as follows: The feed material, consisting of 300 g of U_3O_8 , 1.4 to 9.2 g of PuO_2 , and 2.58 to 19.4 g of fission products, was mixed with 150 g of 120 mesh alumina and was fed into the fluid-bed reactor in the fluidizing nitrogen stream. The mixture was contacted in the fluid bed with a separate stream of fluorine. This portion of the reaction, designated as the feeding-fluorination period, was performed at 450 or 500°C and resulted in conversion of greater than 95% of the uranium and about 50% of the plutonium to their respective hexafluorides. During this portion of the reaction, the gas phase, containing 20 v/o fluorine in nitrogen, is passed through the reactor and a series of cold traps to remove the UF_6 and PuF_6 . The remaining gases are then passed through an activated alumina trap to dispose of the fluorine, after which the nitrogen is vented to the box atmosphere. After the feeding-fluorination period, the system is put on total recycle and the gas phase changed to 100% fluorine. During the recycle period, the gas phase is passed from the reactor through several cold traps to remove UF_6 and PuF_6 . A Lapp pump circulates the gases back to the reactor. One or more recycle periods may be used at temperatures of 450°, 500°, and 550°C. This part of the reaction scheme is designated the recycle-fluorination period.

Results and Discussion

a) Effect of re-use of Al_2O_3 on retention of plutonium. Two experiments were performed to show the effect of the re-use of one bed of alumina for several additions and fluorinations of U_3O_8 - PuO_2 -fission product mixture on the quantity of plutonium retained on the alumina. The primary objective was to reduce the overall fluorination time by conducting a single recycle fluorination after a series of feeding-fluorinations in the same alumina bed.

In the first experiment, one bed of alumina was used for the fluorination of six 300-g batches of U_3O_8 - PuO_2 -F.P. The six feeding-fluorinations were performed at 500°C. At the end of each feeding-fluorination period, the alumina bed, which weighed about 570 g, was removed from the

reactor and sampled for analysis. Subsequent to each sampling, 400 g of this alumina bed was replaced in the reactor and 150 g of the bed mixed with an additional 300 g of $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ mixture. After feeding the latter mixture of alumina and $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ the feeding equipment was "washed" with an additional 20 g of clean alumina. After the sixth addition of $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$, the alumina bed was subjected to two 10-hr recycle-fluorinations, the first at 500°C and the second at 550°C . The alumina bed was removed after each recycle-fluorination period and a sample removed for uranium and plutonium analyses.

Table II-1 lists the experimental conditions and the results obtained from this series of experiments. (The validity of these results is somewhat uncertain for the reasons given in a later paragraph.) The results show that the concentration of plutonium on the alumina increased rather regularly (from 0.10 w/o to 0.42 w/o) for the first four additions of $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$, and then decreased to a value of 0.23 w/o after the sixth addition. After the recycle-fluorination period at 500°C , the plutonium concentration on the alumina was 0.19 w/o; after the 550°C recycle-fluorination period, the plutonium concentration on the alumina was 0.18 w/o.

Table II-1

FLUID BED FLUORINATION OF U_3O_8 - PuO_2 -FISSION PRODUCT MIXTURES;
RE-USE OF AN ALUMINA BED FOR SEVERAL FLUORINATIONS

Reaction Conditions:																	
Feeding-Fluorination Period:																	
Total Gas Flow Rate:							12 liters/min										
Fluorine Concentration in							20 v/o										
Total Flow:							400 g										
Alumina in Bed:							170 g, 1U:2Al ₂ O ₃										
Alumina in Feed:							~300 g										
U ₃ O ₈ -PuO ₂ -F.P. in Feed:																	
Recycle-Fluorination Period:																	
Total Gas Flow Rate:							8 liters/min										
Fluorine Concentration:							100%										
Recycle-																	
Fluorination																	
Feed-Fluorination		Temp.		Time		U Fed		Pu Fed		U and Pu Concentrations in Bed							
(°C)		(g/min)		(hr)		(g)		(g)		w/o U		U (g)		w/o Pu		Pu (g)	
Experiment 1																	
500	5.0	-	-	-	-	-	254	1.18	0.16	0.93	0.10	0.57					
500	4.3	-	-	-	-	-	254	1.18	2.24	1.38	0.21	1.21					
500	4.8	-	-	-	-	-	250	1.15	0.17	1.02	0.28	1.71					
500	4.6	-	-	-	-	-	250	1.15	2.00	11.38	0.31	1.84					
500	4.6	-	-	-	-	-	250	1.15	1.90	11.0	0.30	1.74					
500	5.7	-	-	-	-	-	252	1.17	0.64	3.68	0.23	1.34					
-	-	500	10	Total	1510	6.98			0.13	0.71	0.19	1.06					
-	-	550	10						0.01	0.05	0.18	0.97					

The second experiment listed in Table II-1 was performed to show the effect of using a low-temperature, low feed-rate feeding-fluorination period on the retention of plutonium on alumina. Two additions of $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ were made to a single bed of alumina during the feeding-fluorination periods and the alumina bed was then subjected to recycle-fluorination periods at 450° , 500° , and 550°C . After each feeding-fluorination period and following the recycle-fluorination, the bed was removed from the reactor and sampled. The alumina bed after the first feeding-fluorination period contained 0.128 w/o plutonium and 1.67 w/o uranium, and after the second feeding-fluorination period contained 0.190 w/o plutonium and 4.36 w/o uranium. After the recycle-fluorination periods the alumina bed contained 0.127 w/o plutonium and 1.39 w/o uranium.

The re-use of alumina for a series of feeding-fluorinations with no recycle-fluorinations until the series is complete apparently resulted in increased retention of plutonium in the alumina bed. A comparison of the final result for experiment 1 (Table II-1) with a single experiment previously reported (ANL-6800, p. 205, Table II-2, Part 2, Entry 3) in which the alumina bed contained 0.029 w/o plutonium (0.165 g Pu) indicates that the total quantity of plutonium in the alumina bed after multiple use in this fashion was many times greater than the sum of plutonium retained in the same number of individual experiments using both fluorination periods. Similarly, for experiment 2 (Table II-1) the final result can be compared to that for a single experiment previously reported (ANL-6800, p. 205, Table II-2, Part 2, Entry 4) in which the alumina bed contained 0.007 w/o plutonium (0.040 g Pu).

The conclusions reached in these experiments are somewhat clouded by the poor uranium removal achieved in experiment 2 (1.39 w/o uranium). Since uranium is easily fluorinated from alumina, the results suggest that the operation of the laboratory-scale fluid-bed reactor may have been unsatisfactory for reasons not clearly understood. Results of experiments on re-use of alumina under somewhat different conditions reported in Table II-3, Part C, and results of recent experiments to be reported in the next semiannual report indicate that plutonium retention by the alumina can be reduced to much lower levels.

b) Evaluation of the source of plutonium. A series of experiments were performed to confirm the low value, ANL-6800, Table II-2, Part 2, Entry 4, (less than 0.01 w/o plutonium on the alumina) found for an experiment in which the feeding-fluorination period was performed at 450°C using a low feed rate (about 2 g/min), followed by recycle-fluorination periods of 5 hr each at 450° and 500°C and 10 hr at 550°C . In addition, these experiments were to show any effect of the source of PuO_2 on the plutonium retention on the alumina. For these purposes, $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ mixtures in which the PuO_2 was originally present as a solid solution with UO_2 , and mixtures in which U_3O_8 and PuO_2 were mechanically mixed, were used. The results of this series of experiments are listed in Table II-2. Comparing

the first four entries in Table II-2 indicates that the source of the PuO_2 does not affect the plutonium retention on the alumina. In one experiment the feed rate during the feeding-fluorination period was 5 g/min rather than the 2 g/min or less used in the first experiments. The former experiment resulted in a plutonium retention on the alumina of 0.022 w/o, indicating that the low feed rate may be important. In the last experiment listed in Table II-2, the $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ mixture contained about 3 w/o plutonium instead of the usual 0.4 w/o. This experiment resulted in a retention of 0.14 w/o plutonium on the alumina, indicating that the retention of plutonium is probably dependent on the quantity of plutonium fed to the reactor.

Table II-2

FLUID-BED FLUORINATION OF $\text{U}_3\text{O}_8\text{-PuO}_2\text{-FISSION PRODUCT MIXTURES: EFFECT OF LOW TEMPERATURE DURING FEEDING-FLUORINATION PERIOD AND SOURCE OF PuO_2 ON PLUTONIUM RETENTION ON ALUMINA$

Feeding-Fluorination Period:						
Temperature:		450°C				
Total Gas Flow Rate:		12 liters/min				
Fluorine Concentration in Total Flow:		20 v/o				
Alumina in Bed:		400 g				
Alumina in Feed:		170 g, 1U:2Al ₂ O ₃				
U ₃ O ₈ -PuO ₂ -Fission Products:		300 g				
Recycle-Fluorination Period:						
Recycle Periods:		(1) 450°C, 5 hr				
		(2) 500°C, 5 hr				
		(3) 550°C, 10 hr				
Total Gas Flow Rate:		8 liters/min				
Fluorine Concentration:		100%				

^a A - designates $\text{U}_3\text{O}_8\text{-PuO}_2$ mixture in which PuO_2 was obtained from $\text{UO}_2\text{-PuO}_2$ solid solution pellets containing ~5 w/o Pu. Pellets were oxidized to form $\text{U}_3\text{O}_8\text{-PuO}_2$ and additional U_3O_8 added to bring plutonium concentration to about 0.4 w/o.

^b B - designates $\text{U}_3\text{O}_8\text{-PuO}_2$ mixtures prepared by mechanically mixing U_3O_8 and PuO_2 to produce mixtures containing about 0.4 or 3.0 w/o Pu.

^c C - designates $\text{U}_3\text{O}_8\text{-PuO}_2$ mixture prepared by oxidizing $\text{UO}_2\text{-PuO}_2$ solid solution powder containing about 0.4 w/o Pu.

c) Effect of added bismuth. An investigation was made to determine the effect of adding bismuth metal and then refluorinating on the plutonium content of an alumina bed which had been used for the fluorination of a $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ mixture. Bismuth was added to the bed because it was believed that the fluorination product of bismuth, BiF_5 , which is highly reactive, might react with the plutonium residue, converting it to PuF_6 . An alumina bed containing 0.18 w/o plutonium was chosen for these tests. One gram of bismuth was mixed with 50 g of the bed material. This mixture was then fed into 400 g of the bed material contained in the reactor at 550°C . This addition was followed by a recycle-fluorination of 5 hr at 550°C . After this treatment the bed was removed from the reactor and sampled for analysis. The addition of bismuth and the fluorination cycle were then repeated. After the first treatment, the alumina bed contained 0.08 w/o plutonium, less than one-half the original plutonium content. The second bismuth addition and fluorination cycle did not reduce the plutonium content of the alumina bed further.

d) Fluorination of PuO_2 mixed with fission products; determination of residual plutonium levels in equipment. Additional fluid-bed fluorination experiments were performed (1) to investigate the effect of the quantities of plutonium and fission products fed to the reactor on the plutonium retention on alumina, (2) to determine the residual plutonium remaining in the reactor system, and (3) to determine the plutonium level on alumina with reuse of the alumina for several additions of feed material carried out under reaction conditions which have resulted in low levels of plutonium retention. These experiments were carried out with PuO_2 , PuO_2 -fission product mixtures, or alumina alone as the feed. A feeding-fluorination period at 500°C with a gas phase containing 20 v/o fluorine in nitrogen and a recycle-fluorination period of 10 hours at 550°C using 100% fluorine were employed. During the feeding-fluorination period, 150 g of 120 mesh alumina containing the PuO_2 or PuO_2 -fission product mixture was fed into the reactor containing 400 g of alumina at a feed rate of from 3 to 6 g/min. The experiments designated in Table II-3 as "low plutonium" experiments used about 1.5 g PuO_2 containing about 1.2 g plutonium; the corresponding quantity of the fission product mixture was 2.58 g. The ratio of plutonium to fission product as well as the quantity of plutonium are identical to those which are reported in Tables II-1 and II-2. The experiments designated in Table II-3 as "high plutonium" experiments contained about 10.5 g of PuO_2 containing about 9.2 g of plutonium. The quantity of fission products, 19.4 or 14.9 g, was dependent on whether the mixture contained MoO_3 , the larger quantity being for the mixture containing MoO_3 .* In the blank experiments, either alumina alone or alumina containing a quantity of the fission product mixture was fed to the reactor. In one series of experiments, four separate additions of the

* The presence of MoO_3 in the fission product mixture is believed to contribute to plugging of valves in the cold trapping system and hence is not used in some experiments. Analysis of solids removed from plugged valves showed the presence of molybdenum, plutonium, and bismuth. The bismuth was present as the result of experiments performed using that element to facilitate the removal of plutonium retained on alumina residues. The MoO_3 probably does not affect the experimental results.

low plutonium-low fission product mixture were made to one bed of alumina. The alumina bed was removed from the reactor after each reaction period and sampled for plutonium analysis; the remaining bed was then split into two parts: 150 g for the next feed mixture and 400 g for the next bed.

Table II-3

FLUID-BED FLUORINATION OF PuO₂:
EFFECT OF QUANTITY OF PLUTONIUM AND PRESENCE OF
FISSION PRODUCTS ON PLUTONIUM RETENTION ON ALUMINA

Feeding-Fluorination Period:							
Temperature:		500°C					
Total Gas Flow Rate:		12 liters/min					
Fluorine Concentration in							
Total Flow:		20 v/o					
Alumina in Bed:		400 g					
Alumina in Feed:		170 g					
Recycle-Fluorination Period:							
Temperature:		550°C					
Time:		10 hr					
Total Gas Flow Rate:		8 liters/min					
Fluorine Concentration:		100%					
Analytical Results							
Exp. No.	Feed Material		Alumina Bed		Disengaging Chamber		% Pu Volatilized ^a
	Wt. Pu (g)	Wt. F.P. (g)	w/o Pu	Wt. Pu (g)	w/o Pu	Wt. Pu (g)	
A. Low Plutonium-Variable Fission Product							
1	1.23	None	0.0085	0.044	0.77	0.014	96
2	1.23	2.58 ^b	0.0048	0.027	0.31	0.008	98
3	1.23	19.4 ^b	0.014	0.080	0.09	0.010	93
4	1.23	19.4 ^b	0.025	0.148	0.59	0.027	88
B. High Plutonium-Variable Fission Product							
5	9.24	None	0.12	0.632	2.70	0.052	93
6	9.18	2.58 ^b	0.19	1.100	22.8	0.802	88
7	9.13	14.9 ^c	0.71	4.340	13.9	0.483	53
8	9.13	14.9 ^c	0.71	4.409	-	-	52
C. Re-use of Alumina							
9	1.23	2.58 ^b	0.0048	0.027	0.31	0.008	96
10	1.21	2.58 ^b	0.014	0.078	-	-	97
11	1.21	2.58 ^b	0.015	0.085	1.94	0.037	98
12	1.22	1.94 ^c	0.024	0.143	-	-	97
D. Blanks							
13	None	19.4 ^b	0.0045	0.028	0.32	0.060	-
14	None	None	0.0007	0.004	0.50	0.006	-
15	None	None	0.0015	0.011	0.32	0.006	-
16	None	14.9	0.006 ^d	<0.036	-	-	-

^a Based on plutonium retained in bed alone.

^b Fission product mixture contained MoO₃. The F.P. mixture contained the following: La₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Y₂O₃, BaO, ZrO₂ and MoO₃. (For relative concentrations of the fission product oxides, see ANL-6800, Table II-1, p. 201.)

^c Fission product mixture did not contain MoO₃. Composition is that indicated in b, less the quantity of MoO₃ shown.

^d Estimation by X-ray fluorescence analysis.

In Table II-3, Part A contains the data for the low-plutonium content-variable fission product content experiments; Part B contains the data for the high-plutonium content-variable fission product content experiments; Part C contains the data for experiments in which the alumina was re-used; and Part D contains data on the blank experiments. For the experiments using small quantities of plutonium, an increase in the fission product level from 2.58 to 19.4 g resulted in an increase in the plutonium retention on the alumina from 0.0048 w/o (experiment 2) to 0.020 w/o (average of experiments 3 and 4). For the high-plutonium experiments, the plutonium retention on the alumina was 0.12 and 0.19 w/o for experiments in which fission products were not present and 2.58 g in tests in which fission products were present. When the fission product level was raised to 14.9 g, the plutonium retention on the alumina increased to 0.71 w/o. It is to be noted here that, for a plutonium concentration of 0.4 w/o in the $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ mixtures, the quantity of fission products was 2.58 g, and for a plutonium level of 3 w/o in the $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ mixture, the quantity of fission products was 19.4 or 14.9 g.

These results show a 20- to 30-fold increase in plutonium retention on the alumina for a 7.5-fold increase in the plutonium fed to the reactor for experiments in which fission products were not present (experiments 1 and 5) and for the experiments in which the small quantities of fission products were present (experiments 2 and 6). Increasing the fission product level 7.5-fold resulted in an increase in plutonium retention on the alumina by a factor between three and four (experiments 3 and 4 versus experiment 2 for the tests with low levels of plutonium, and experiments 7 and 8 versus experiment 6 for the tests with high levels of plutonium).

In the tests in which the alumina was re-used (see Part C, Table II-3), the plutonium concentration in the alumina after the first addition of the fuel mixture (experiment 9) was 0.0048 w/o, the plutonium concentration rose to 0.014 w/o after the second addition (experiment 10) and remained near this level for the subsequent two additions (experiment 11, 0.015 w/o and experiment 12, 0.024 w/o). If the plutonium concentration on the alumina were to remain at this level for a series of seven such additions to a single alumina bed, then the plutonium retained on the alumina would represent only one percent of the total plutonium fed to the reactor. This suggests that a similar experiment involving the feeding of seven batches of $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ mixture to a single alumina bed might result in the retention of only one percent or less of the total plutonium. An experiment is planned using the low feed rate 450°C fluorination, each to be followed by three recycle periods, 5 hr at 450°C , 5 hr at 500°C , and 10 hr at 550°C . These reaction conditions when used in previous experiments have resulted in low retentions of plutonium on the alumina.

A series of blank experiments (see Part D, Table II-3) were performed to determine the extent of retention of plutonium in the fluid-bed reactor. Some of these experiments were carried out after experiments had been completed with high levels of plutonium and some were carried out after experiments had been completed with low levels of plutonium. In the blank experiments, no plutonium was added to the bed during the feeding-fluorination period; the conditions of time, temperature, and fluorine concentration were the same as in the other experiments described in Table II-3. Experiment 14 was performed after a new manifold, new traps, and new disengaging chamber filters had been placed in the system. The plutonium concentration in the alumina of 0.0007 w/o found for this experiment can, therefore, be considered as the lowest level of plutonium likely to be observed in the reactor system. Experiment 15 was performed following a regular experiment in which a low level of plutonium was used, and the alumina in the blank experiment contained 0.0015 w/o plutonium. In two blank experiments performed after experiments with high levels of plutonium, the plutonium concentrations in the alumina were 0.0045 w/o (experiment 13) and less than 0.006 w/o (experiment 16, an estimation by X-ray fluorescence analysis). On the basis of these results it appears that an average value of 0.003 w/o plutonium on the alumina could be considered as the background level in this reaction system.

The amount of plutonium that would accumulate on the disengaging chamber filters is of interest in determining the plutonium material balance in the reaction system. Two 6-in. long sintered nickel bayonet filters, with an average pore size of $10\ \mu$ and with a total active surface area of 30 sq in., were removed from the reactor after 26 experiments. The material on the surfaces of the filters was removed and analyzed for plutonium and uranium. The analysis showed a total of 2.6 mg of plutonium and 132 mg of uranium. These quantities represent 0.09 mg of plutonium and 4 mg of uranium per square inch of filter surface. During the 26 experiments, about 26 g of plutonium hexafluoride passed through these filters at approximately 200°C. Therefore, about 3.5×10^{-3} mg of plutonium was retained per square inch of filter surface per gram of PuF_6 passing through the filters.

e) Autoradiography of alumina containing plutonium. Autoradiographic experiments were performed to determine the location of the plutonium retained on the alumina of fluorinated fluid beds. It is important to establish whether the plutonium is located on the surface of the alumina particles or dispersed throughout the body of the particle; this information is needed to guide further efforts toward lowering the retention of plutonium on alumina or devising means of removing the plutonium retained on the alumina. The autoradiographic method, using the alpha activity of the plutonium to indicate the location of the plutonium on (or in) the alumina particles was chosen as the experimental method. Adams and Steunenberg have shown that the location of the site of plutonium in a metal matrix can be determined by this method (ANL-6412). The tracks developed in a photographic emulsion by the alpha particles are readily distinguishable from the general darkening produced by beta radiation.

The alumina from two fluid beds was chosen for this work. One bed contained 0.12 w/o plutonium on the alumina, the second bed contained 0.005 w/o plutonium on the alumina. The bed materials were screened to select the largest particles of the nominal 120 mesh alumina. The fraction retained on a 100 mesh screen (about 5% of the original bed) was used in these experiments. Photomicrographs of the alumina contained in this 100 mesh fraction showed that the particles were very irregular in shape.

The procedure used for the autoradiographic experiments was as follows. A small quantity of alumina, about 1 to 3 mg, was mounted in clear plastic and polished through 600 grit emery paper to expose a cross section of the alumina granules. Each mount containing the alumina particles was then cleaned in an ultrasonic bath to remove loose radioactive particles. This procedure was performed in a special alpha-handling metallurgical facility. The mounts were next moved to an open-faced hood and cleaned again, using firstly a soap solution and then a solution of Versene. Swipes taken of the surface of the mounts after this cleaning procedure showed no loose radioactive particles. The surfaces of the mounts were counted and showed 10,000 dis/min for the mount containing the 0.005 w/o plutonium-alumina, and 500,000 dis/min for the mount containing the 0.12 w/o plutonium-alumina. All other surfaces of the mounts showed less than 2000 dis/min. As a final precaution, the mounts were dipped in a 1.5% solution of vinyl plastic in methyl ethyl ketone to cover the surfaces with a thin layer of plastic. The mounted specimens were then moved to a darkroom and AR-10 autoradiographic emulsions were placed in contact with the active surfaces of the mounts by the usual technique. Exposures of from 5 hr to 5 days were made, after which the radiographic emulsions were developed in place.

The emulsions were removed from the mounts and placed on microscope slides. Each autoradiograph of an individual alumina particle showed a dense band containing alpha tracks surrounding an area free of alpha tracks. Figure II-1 is a micrograph of the emulsion, mounted on a

Figure II-1

MICROGRAPH OF AUTORADIOGRAPHIC
EMULSION, FIVE-HOUR EXPOSURE
AR-10 AUTORADIOGRAPHIC
EMULSION, SHOWING ALPHA
TRACKS DUE TO PLUTONIUM ON
SURFACE OF FLUID BED ALUMINA

microscope slide, after a 5-hr exposure of the alumina containing 0.12 w/o plutonium. The dark outlines are due to alpha particles and mark the shape of the alumina grains; individual alpha tracks can be seen on the edges of the darkened areas. This micrograph clearly shows that the plutonium was present on the surfaces of the alumina particle.

2. Effect of BiF₃ on the Fluorination Rates of U₃O₈ and UO₂F₂ (W. Gunther, T. Baker, R. Wagner)

A thermobalance study of the effect of the addition of BiF₃ on the rates of fluorination of U₃O₈ and UO₂F₂ has been performed. The addition of small amounts of BiF₃ to the U₃O₈-PuO₂ mixtures used in the fluid bed experiments was considered as a means of obtaining better plutonium removal from the alumina during the fluorination.

This work was performed using the Sartorius thermobalance and covered the temperature range 400-450°C using a fluorine flow of 200 cc/min. The fluorination rates of BiF₃, U₃O₈, and UO₂F₂ and of the mixtures BiF₃-U₃O₈ and BiF₃-UO₂F₂ have been measured.

The BiF₃ used in these experiments was shown by chemical analysis to contain 79.4% bismuth and 15.3% fluorine (calculated: Bi-78.6%; F-21.4%). The low result for the fluorine analysis indicates the presence of a bismuth oxide.

The results obtained in these experiments are listed in Table II-4. The presence of 7.5 and 15% BiF₃ in U₃O₈ resulted in fluorination rates at 450°C of 6 and 14 mg/min, respectively. Concentrations of BiF₃ above 20% resulted in fluorination rates which were too rapid to follow on the recorder (>50 mg/min). At 450°C, BiF₃ and U₃O₈ each have fluorination rates of about 2 mg/min. The addition of BiF₃ to UO₂F₂ resulted in fluorination rates at 400°C lower than those obtained for UO₂F₂ itself. For UO₂F₂-BiF₃ mixtures, fluorination rates of 3.5 and 2.3 mg/min were obtained at 400°C for BiF₃ contents of 10 and 30 w/o, respectively. The fluorination rates of BiF₃ and UO₂F₂ at 400°C are 0.4 and 4 mg/min, respectively.

In summary, the presence of BiF₃ in U₃O₈ greatly increases the rate of fluorination of U₃O₈ in the range studied, 390°C to 450°C. The fluorination rate of U₃O₈ increases with an increase in BiF₃ content. The presence of BiF₃ in UO₂F₂, however, decreases the rate of fluorination of UO₂F₂ at 400°C. The UO₂F₂ fluorination rate decreases with an increase in BiF₃ content.

Since the addition of bismuth metal to an alumina bed which contained plutonium did not aid significantly in the further removal of plutonium and since the handling of BiF₅ in the present 1½-in. dia. fluid-bed reactor and auxiliary equipment was difficult, no additional thermobalance experiments are planned.

Table II-4

FLUORINATION RATES OF BiF_3 - U_3O_8 AND
 BiF_3 - UO_2F_2 MIXTURES ON A THERMOBALANCE

Temperature: As indicated $\pm 10^\circ\text{C}$

Fluorine Flow: 200 cc/min, 100% F_2

Material	Temperature ($^\circ\text{C}$)	Fluorination Rate (mg/min)
BiF_3	400	0.4
BiF_3	450	2
BiF_3	450	3
BiF_3	450	1.5
BiF_3	510	4
BiF_3	540	6
U_3O_8	390	0.8
U_3O_8	450	2
U_3O_8	450	2
U_3O_8	450	2
UO_2F_2	400	4
UO_2F_2	450	50
7.5 w/o BiF_3 -92.5 w/o U_3O_8	450	6-8
15 w/o BiF_3 -85 w/o U_3O_8	390	0.4
15 w/o BiF_3 -85 w/o U_3O_8	450	14
15 w/o BiF_3 -85 w/o U_3O_8	450	13
18 w/o BiF_3 -82 w/o U_3O_8	450	Too high to record
20 w/o BiF_3 -80 w/o U_3O_8	450	Too high to record
30 w/o BiF_3 -70 w/o U_3O_8	450	Too high to record
10 w/o BiF_3 -90 w/o UO_2F_2	400	3.5
20 w/o BiF_3 -80 w/o UO_2F_2	400	2.9
30 w/o BiF_3 -70 w/o UO_2F_2	400	2.3

3. Alpha Radiation Decomposition Rate of Plutonium Hexafluoride
 (R. Wagner, W. Shinn)

a. Introduction

Studies of the rate of decomposition of gaseous plutonium hexafluoride (PuF_6) to fluorine and solid plutonium tetrafluoride (PuF_4) caused by alpha radiation from the plutonium have been continued. The investigations are designed to obtain information applicable to the handling and storage of PuF_6 and to the handling, storage and analysis of the UF_6 - PuF_6 mixtures obtained by the fluorination of solid U_3O_8 - PuO_2 in a fluidized bed containing alumina.

Effects on the PuF_6 decomposition rate of such parameters as duration of experiment, initial PuF_6 pressure, container volume, temperature, surface to volume ratio, and additives such as PuF_4 are being determined. Results of previous experiments have been reported in ANL-6800, p. 216. The present report lists results obtained from decomposition experiments carried out over a long period (571 days) and with initial PuF_6 charges of 100, 75 or 50 mm Hg. These experiments were carried out both with and without PuF_4 initially present and with two sizes of spherical nickel vessels (22.55 liter and 127 cc). Results are also reported for experiments of 77-day durations in which an initial charge of 100 mm of PuF_6 was decomposed at 80 to 83°C with PuF_4 initially absent and with PuF_4 initially present. Experimental results are presented for experiments in which a charge of 100 mm of PuF_6 was allowed to decompose for 77 days at 26°C in nickel spheres which contained nickel wool and PuF_4 . Data were also obtained on the rate of decomposition of PuF_6 at 26°C over a 77-day period in a 5.96-liter nickel sphere.

b. Procedure

The experimental procedures for the decomposition experiments carried out in 125 to 129-cc nickel spheres were the same as those reported previously in ANL-6800, p. 217. In all tests the nickel spheres were prefluorinated to provide a protective nickel fluoride film on the inner surface of the sphere. Although the prefluorination conditions were varied among the tests, changing the conditions did not appear to affect significantly the rate of decomposition of PuF_6 . The amount of PuF_6 decomposed was determined by weighing the PuF_4 formed. In addition, some of the spheres were dissolved in nitric acid-aluminum nitrate solutions, after removal of the valves, in order to prepare the solid (PuF_4) for determination of the plutonium content by alpha counting methods. The valves were washed with nitric acid-aluminum nitrate solutions and the wash solutions were added to the solutions used for the dissolution of the spheres. Further, in the larger spheres, the undecomposed PuF_6 was determined by first passing the PuF_6 -fluorine mixture through a series of tared traps cooled to -80°C and then through an activated alumina trap. The PuF_6 in the traps was determined by weighing. The PuF_6 retained in the activated alumina was determined by alpha counting after dissolution of the sample of the alumina.

c. Long-term Experiments

The effects of long PuF_6 decomposition times (571 days) were investigated and the results are shown in Table II-5. The tests were performed at 26°C in nickel spheres of approximately 127-cc capacity, with PuF_6 pressures of 100, 75 and 50 mm Hg. The effect of the initial presence of PuF_4 on the PuF_6 decomposition rate was observed in three tests. In several instances both gravimetric and radiochemical analyses were performed on the same sample, and determinations of decomposition rates by radiochemical analysis of the plutonium residue in the spheres showed good agreement with the rates obtained by weighing the deposited PuF_4 .

Table II-5

DECOMPOSITION OF PuF_6 BY ITS ALPHA RADIATION (571 Days)

Spherical Nickel Vessels:	125 to 129 cc
Storage Temperature:	$26 \pm 2^\circ\text{C}$
Duration of Decomposition:	571 days
Prefluorination Conditions:	1) $1/2$ hr at 40°C with F_2 at 760 mm Hg and 18 days at 26°C with F_2 at pressures ranging from 760 to 1240 mm Hg.
	2) $1/2$ hr at 40°C with F_2 at 760 mm Hg, 20 days at 26°C with F_2 at 760 mm Hg, 4 hr at 26°C with PuF_6 at pressures ranging from 28 to 100 mm Hg, and 9 days at 26°C with F_2 at pressures ranging from 800 to 1100 mm Hg.

Pneumofluorination Conditions	Initial Quantity of PuF ₆		Initial PuF ₄ (mg)	PuF ₆ Decomposed (mg)	Average Rate of PuF ₆ Decomposition (% per day)		
	Weight (mg)	Pressure (mm Hg)			Method of Determination		
					By Weight of PuF ₄	Radiochemical	
2	234.0	100	-	56.8	0.044	0.045	
1	234.7	100	7.6	123.8	0.091	-	
2	230.7	100	3.8	118.2		0.095	
2	171.5	75	-	93.2		-	
2	173.2	75	4.8	88.5	0.090	-	
1	117.6	50	-	53.3	0.080	0.088	
1	118.4	50	-	49.1		0.072	-
2	115.6	50	-	47.1		0.071	-
2	116.5	50	-	43.3	0.067 ±0.008	-	
2	118.2	50	-	42.6		0.065	-
2	115.7	50	-	40.1		0.063	-
2	115.8	50	-	38.1	0.061	0.065	
					0.058	0.065	

In a single 571-day experiment with 100 mm of PuF_6 , a decomposition rate of 0.044% per day was obtained. With 75 mm of PuF_6 , a decomposition rate of 0.095% per day was observed in a test of the same duration. In a series of seven experiments with 50 mm of PuF_6 , an average decomposition rate of 0.067% per day with a standard deviation of 0.008% per day was obtained.

Radiation decomposition experiments carried out in the presence of PuF_4 formed in previous decomposition experiments gave decomposition rates that were different from those obtained in the absence of added PuF_4 . Two experiments, in which 7.6 and 3.8 mg of PuF_4 were present in nickel spheres during the addition of 100 mm of PuF_6 were found by weight measurements to give average decomposition rates of 0.092 and 0.090% per day, respectively. These rates may be compared with the rate (0.044% per day) obtained in an experiment carried out under similar conditions, but with PuF_4 initially absent. The finding that the decomposition rate increases when PuF_4 is initially present is contrary to the results of previous experiments (ANL-6800, p. 219) in which 100-mm samples of PuF_6 were decomposed over a 75-day period. In these earlier experiments, the rate of decomposition was 0.14% per day when PuF_4 was

initially present and 0.19% per day when the PuF_4 was initially absent. In a test in which 75 mm of PuF_6 was stored for 571 days at ambient temperatures in the presence of 4.8 mg of PuF_4 , an average PuF_6 decomposition rate of 0.090% per day was observed. This decomposition rate may be significantly lower than the rate, 0.095% per day, obtained under similar conditions but in the absence of initial PuF_4 .

In 571-day long experiments with pure PuF_6 (PuF_4 initially absent), decomposition rates of 0.044, 0.095, and 0.067% per day were obtained when the initial pressures of PuF_6 were 100, 75, and 50 mm Hg, respectively. These results are contrary to the results of previous, 75-day tests (ANL-6800, p. 218 and ANL-6687, p. 105) in which it was found that the decomposition rate was slightly lower when the initial pressure of PuF_6 was 50 mm Hg than the rate when the PuF_6 pressure was 100 mm Hg.

The two anomalies reported here depend on the reliability of the single experiment with 100 mm of pure PuF_6 (no PuF_4 initially present). The reason for the two anomalies reported here has not yet been established.

d. Short-term Experiments

Data on experiments carried out for 77 days are shown in Table II-6. Two series of PuF_6 decompositions were carried out at 80 to 83°C with 100 mm (measured at $26 \pm 2^\circ\text{C}$) of PuF_6 in 127 ± 2 cc nickel spheres. In one series, nickel spheres which contained PuF_4 from previous PuF_6 decomposition experiments were used; in the other series, prefluorinated nickel spheres which had not been previously exposed to PuF_6 were used. In the first series, which consisted of six experiments in which from 21.8 to 35.3 mg of PuF_4 was present during the introduction of PuF_6 , the average value of the average rate of PuF_6 decomposition was 0.53% per day with a standard deviation of 0.12% per day. In the second series of experiments in which PuF_4 was initially absent, an average PuF_6 decomposition rate of 0.65% per day with a standard deviation of 0.06% per day was observed for four experiments.

At 80 to 83°C, the presence of PuF_4 at the beginning of the PuF_6 decomposition decreased the average PuF_6 decomposition rate from 0.65 ± 0.06 to $0.53 \pm 0.12\%$ per day. This trend was in general agreement with data ($0.19 \pm 0.03\%$ per day to $0.14 \pm 0.03\%$ per day in the presence of PuF_4) obtained in previous tests of similar duration at 26°C (ANL-6800, p. 340).

Table II-6

DECOMPOSITION OF PuF₆ BY ITS ALPHA RADIATION (77 Days)

Spherical Nickel Vessels: 125 to 129 cc
 Storage Temperature: 80 to 83°C, unless otherwise indicated
 Duration of Decomposition: 77 days
 Initial PuF₆ Pressure: 100 mm Hg
 Prefluorination Conditions: 1) 4 days at 26°C with F₂ at 400 mm Hg.
 2) 1/2 hr at 26°C with ClF₃ at 1200 mm Hg.
 1/2 hr at 40°C with F₂ at 500 mm Hg,
 and 24 hr at 100°C with F₂ at 100°C.

Prefluorination Conditions	Initial Weight of PuF ₆ (mg)	Initial PuF ₄ (mg)	PuF ₆ Decomposed (mg)	Average Rate of PuF ₆ Decomposition (% per day)
1	233.1 ^a	45.9	23.8	0.13
1	232.5 ^a	41.6	32.6	0.18
1	237.9	23.8	62.4	0.34
1	236.1	27.6	85.5	0.47
2	232.4	26.9	88.4	0.49
1	237.9	34.5	104.6	0.57
2	227.1	35.3	110.3	0.63
1	238.1	21.8	122.6	0.67
2	231.5	-	106.1	0.60
2	230.1	-	109.5	0.62
2	230.9	-	115.2	0.65
2	232.9	-	129.3	0.72

^a Storage temperature was 26 ± 2°C. These spheres contained nickel wool.

Previously, it was reported (ANL-6800, p. 339) that the decomposition rate of PuF₆ at 26°C increased from 0.19% per day to 0.30% per day in spheres packed with nickel wool. In the present series of tests, two experiments were carried out using spheres packed with nickel wool and also containing PuF₄. The spheres were refilled with 100 mm of PuF₆ and stored for 77 days at 26°C. Decomposition rates for the PuF₆ in these spheres were found to be 0.13 and 0.18% per day (Table II-6). These rates are nearly the same as those previously obtained in unpacked nickel spheres (0.19% per day) and in unpacked nickel spheres with initial PuF₄ (0.14% per day), but are much lower than the PuF₆ decomposition rate observed in packed nickel spheres with no PuF₄ initially present (0.30% per day). These data indicate that, for decomposition carried out for 75-77 days, the initial

presence of PuF_4 has a greater effect on the PuF_6 decomposition rate than does the increased nickel surface area. Consideration of the results of experiments carried out with nickel wool packing and with PuF_4 initially present along with the previous conclusion that there is no obvious correlation between the amount of initial PuF_4 and the PuF_6 decomposition rate suggest that PuF_6 reacts chemically with the nickel surface, and that once the nickel surface is deactivated, no major effect of surface on the rate of decomposition is apparent.

e. Effect of Surface-to-Volume Ratio

The effect of a decrease in the surface-to-volume ratio of the containers, which would allow more complete dissipation of the alpha energy in gaseous PuF_6 , was investigated in two experiments using spheres of large volumes, 5.96 liters and 22.55 liters. Purified PuF_6 was expanded into a prefluorinated, 5.96-liter nickel sphere, to a pressure of 100.0 mm at 26.7°C. The PuF_6 was stored at 26°C for 75 days. Fluorine resulting from the PuF_6 decomposition and undecomposed PuF_6 was evacuated from the sphere through three traps cooled to -80°C and then through a trap containing 61.7 g of activated alumina. The cold traps efficiently removed the PuF_6 from the mixture, since only 0.36 mg of PuF_6 was found in the activated alumina. Based on the weight of undecomposed PuF_6 retained in the traps, the PuF_6 decomposition rate for 75.0 days was found to be 0.11% per day. When this value is compared to the 0.19% per day obtained for 100 mm of PuF_6 in 127-cc nickel spheres for 75 days (ANL-6800, p. 218), it is seen that an increase in container volume results in a decrease in PuF_6 decomposition rate.

A decomposition experiment was carried out in a prefluorinated 22.55-liter Monel sphere wherein 42.54 g of PuF_6 was expanded into the sphere to a pressure of 100.2 mm Hg at 27.5°C and stored for 572 days. The average decomposition rate, based on the weight of PuF_6 collected in a series of cold traps at the termination of the test, was found to be 0.065% per day. Comparison of this value with the results obtained in tests of similar duration with 127-cc nickel spheres (0.044% per day, Table II-5) suggests that an increase in storage volume results in an increase in PuF_6 decomposition rate. This conclusion is the opposite of that obtained from the 77-day, 5.96-liter experiment described above, and gives further evidence that the decomposition rate of 0.044% per day may be unreliable.

f. Summary

In summary, the average rate of alpha decomposition of gaseous PuF_6 (100 mm at $26 \pm 2^\circ\text{C}$ in 127 ± 2 cc nickel spheres) decreases nonlinearly with increasing time; the change in the average rate is small from 327 days to 571 days.

Results of tests of long duration indicate that the PuF_6 decomposition rate is dependent on the initial pressure of the PuF_6 and that an increase in the initial PuF_6 pressure results in an increase in PuF_6 decomposition rate.

The effect of container volume appears to indicate that an increase in volume (decrease in surface-to-volume ratio) decreases the PuF_6 decomposition rate. This conclusion is substantiated in 75-day experiments in which the decomposition rate decreased from 0.19% per day to 0.11% per day when the container volume was increased by a factor of about 50.

When the surface-to-volume ratio was increased tenfold (by packing 127-cc spheres with nickel wool), the average rate of PuF_6 decomposition increased from 0.19% per day to 0.30% per day. However, when the packed spheres were re-used, with PuF_4 present in the spheres, the PuF_6 decomposition rates in two experiments decreased to 0.13 and 0.18% per day. These rates are similar to the rate (0.14% per day) found in experiments with 100 mm PuF_6 after 75 days of decomposition in unpacked 127-cc spheres which contained some PuF_4 from a previous PuF_6 decomposition. The results indicate that the effect of increased surface area is important only initially. The increased rate at the beginning of the decomposition period may be the result of a chemical reaction between the PuF_6 and the vessel walls. Since subsequent PuF_6 decomposition tests in the same vessel are relatively independent of the amount of PuF_4 present, the reaction of PuF_6 with the walls of the container must proceed at a rapidly diminishing rate.

The decomposition rate of gaseous PuF_6 at 80 to 83°C (0.65% per day) is higher than the decomposition rate under similar conditions at 26°C (0.19% per day). A lower PuF_6 decomposition rate (0.53% per day) was obtained at 80 to 83°C when some PuF_4 was present from a previous PuF_6 decomposition.

A series of experiments is in progress in which the short-term decomposition rate of PuF_6 will be measured over the intervals of 0.5, 1, 2, 5, 8, 12, and 16 days. All experiments in this series are being carried out with 100 mm of PuF_6 in prefluorinated 127-cc nickel spheres. No further experiments are planned on the alpha decomposition of gaseous PuF_6 after the completion of these tests.

4. Lattice Constants for UF_6 , NpF_6 and PuF_6 (R. Schablaske)

The crystal structure of PuF_6 has not been determined although the similarity in properties between UF_6 , NpF_6 and PuF_6 indicates similar structures. The only available X-ray diffraction data on PuF_6 are those of

Florin.¹ The uranium hexafluoride structure was solved by Hoard and Stroupe.² They found that uranium hexafluoride is orthorhombic with the D_{2h}^{16} -Pnma space group. On the basis that the structures of uranium hexafluoride, neptunium hexafluoride, and plutonium hexafluoride are isotopic, lattice constants for all three hexafluorides were calculated from the X-ray data (Table II-7) of Florin, Tannenbaum, and Lemons.¹ Miller indices accorded each reflection in the data of Florin et al. are also indicated in the table. Lattice parameters were calculated by means of a least squares analytical treatment that has been programmed for the IBM-704 computer.³

Table II-7

X-RAY DATA FOR URANIUM, NEPTUNIUM
AND PLUTONIUM HEXAFLUORIDES^a

(Copper K-alpha Radiation)

hkl	$\sin^2 \theta_{\text{UF}_6}$	$\sin^2 \theta_{\text{NpF}_6}$	$\sin^2 \theta_{\text{PuF}_6}$
020	0.0293	0.0290	0.0294
210	0.315	0.0319	0.0317
111	0.0352	0.0353	0.0354
121	0.0574	0.0575	0.0577
301	0.0757	0.0764	0.0760
311	0.0834	0.0838	0.0842
230	0.0908	0.0904	0.0912
420	0.1265	0.1261	0.1265

^a From A. E. Florin, I. R. Tannenbaum, and J. F. Lemons, J. Inorg. Nucl. Chem. 2, 368 (1956).

It is to be noted that the accuracy of a lattice parameter determination increases with increasing Bragg angle. Very accurate parameters are obtainable from 60°-90° Bragg angle data. The Bragg angles associated with the data of Florin range from 10°-40° and therefore the parameters reported herein should be treated accordingly. Effort was made to keep each computation for each hexafluoride comparable. Only reflections that appeared in all three X-ray patterns were used; also, only those reflections that were clearly assignable a single set of indices were used in the computation.

Lattice constants and unit cell volumes for uranium hexafluoride, neptunium hexafluoride, and plutonium hexafluoride appear in Table II-8. Probable errors (50% confidence limit) are given. Evidence for the actinide contraction is apparent from the values of the unit cell volumes, an observation that serves to add a certain measure of confidence to these calculations.

¹ A. E. Florin, I. R. Tannenbaum, and J. F. Lemons, J. Inorg. Nucl. Chem. 2, 368 (1956).

² J. L. Hoard and J. D. Stroupe, Cornell University Reports A-1242 and A-1296, 1944.

³ M. H. Mueller and L. Heaton, Argonne National Laboratory Report ANL-6176, 1961.

Table II-8

LATTICE CONSTANTS AND UNIT CELL VOLUMES FOR
URANIUM, NEPTUNIUM AND PLUTONIUM HEXAFLUORIDES

	a (Å)	b (Å)	c (Å)	Unit Cell Volume (Å ³)
UF ₆ *	9.95	9.02	5.26	472
UF ₆ *	9.900 ± 0.002	8.962 ± 0.002	5.207 ± 0.002	462.0
UF ₆ **	9.916 ± 0.003	8.960 ± 0.004	5.245 ± 0.004	466.0
NpF ₆ **	9.909 ± 0.003	8.997 ± 0.004	5.202 ± 0.004	463.8
PuF ₆ **	9.912 ± 0.004	8.942 ± 0.005	5.206 ± 0.006	461.4

* Taken from Ref. 2.

** Calculated as indicated in text.

B. Engineering-Scale Investigations of Fluid-Bed Fluoride Volatility Processes
(A. A. Jonke)

1. Development of Fluid-Bed Fluoride Volatility Processes for the Recovery of Uranium and Plutonium from Uranium Dioxide Fuels

- a. Design and Construction of an Engineering-Scale Alpha Facility
(N. Levitz, G. J. Vogel, E. L. Carls, L. J. Anastasia, W. Murphy, R. Kinzler, B. Kullen, A. Rashinskas, V. Lemke, J. Savage)

An engineering-scale alpha facility is being installed to study the main steps in the fluid-bed fluoride volatility process for recovery of fissionable values from spent nuclear reactor fuel of the UO₂-PuO₂ type. Process equipment for two of the basic steps is being installed in the facility which consists of two large alpha boxes, one containing the main processing equipment, the other containing auxiliary equipment such as scrubbers and gas distributor manifolds. Details of the facility have appeared in ANL-6569, p. 110 and ANL-6800, pp. 242-245. Equipment now being installed includes fluorination equipment for processing batches of UO₂-PuO₂ pellets to hexafluorides and a converter system for the preparation of dense mixed uranium-plutonium oxide particles from mixed hexafluorides. Consideration has also been given to the use of the converter equipment (basically, a 2-in. dia. fluid-bed unit) for demonstrating the thermal decomposition⁴ of PuF₆. With this step, separation of the plutonium from a mixed uranium-plutonium hexafluoride stream is achieved.

⁴Trevorrow, L. E., 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.

All of the equipment and process lines for the fluorination step have been installed and made leak tight; a helium mass spectrometer was used in final leak testing. In order to passivate equipment that will be exposed to fluorine during actual operation, a prefluorination run was carried out. In the final phase of the passivation step, the fluorination reactor was exposed to high (90%) concentrations of fluorine at a temperature of 500°C for about 6 hr; a lower temperature (300°C) was employed in pre-fluorination of the process lines.

Instrument calibration and final testing of the auxiliary equipment for the fluorinator system, such as the process gas scrubber (shown in Figure II-2), gas recycle pump,* fluorinator reactor, cooling water system, and gas analysis apparatus, remain to be done in preparation for the planned shakedown testing of the fluorination pilot plant with UO_2 pellets. Initial experiments with UO_2 pellets will be made without the windows installed in the main (larger) alpha glovebox and are intended to test the control systems and general operability of the fluorinator system. An operating manual will be prepared during this preliminary testing period. Following the shakedown tests, any necessary equipment and modifications will be made and the windows will then be installed. Additional experiments in the fluorinator system will then be conducted with UO_2 pellets for final testing of the equipment and operating procedure before proceeding with UO_2 - PuO_2 pellet feeds.

Figure II-2

VIEW OF THE SMALL GLOVEBOX
SHOWING THE PROCESS OFF-
GAS CLEANUP EQUIPMENT

108-7241-A

*An 18-in. dia. diaphragm compressor, model G-2, a product of the Lapp Co.

Detail work, such as establishing bagout procedures, installation of alpha-monitoring equipment, and establishing safety procedures for studies with plutonium, is being carried out and coordinated with the above program. It is expected that the two efforts will end concurrently and work with plutonium can commence, perhaps by the end of 1964.

Design of all equipment components for the converter system has been completed and fabrication of most items is in an advanced stage. In-box instruments (pressure transmitters, gauges, rotameters) and a major portion of the in-box pneumatic runouts have been installed. Electrical work is also proceeding. Final tie-in of both pneumatic and electrical lines to the control panel is in progress. After shakedown testing of the converter equipment with uranium hexafluoride feed, work with mixed uranium-plutonium hexafluorides will be initiated. An operating manual will be prepared as with the fluorinator system.

Refrigeration Unit. An important equipment item in the alpha facility is the refrigeration unit which will be used to supply coolant [trichloroethylene (C_2HCl_3)] at about $-75^\circ C$ to the uranium and plutonium hexafluoride condensers. Installation of this unit has been completed and performance tests carried out as described below. The required condenser temperature is obtained by split-stage compression, whereby a low-boiling refrigerant (Freon 13) rejects absorbed heat to a high-boiling refrigerant (Freon 502). The C_2HCl_3 is cooled by heat exchange with the Freon 13 and is then circulated through the process condensers.

In order to provide a realistic test load on the refrigeration unit, C_2HCl_3 was circulated through an electrically heated test loop. The actual load on the refrigeration unit was determined by measuring the temperature of the C_2HCl_3 at the inlet and outlet of the loop. With no electrical input to the test loop, heat losses through the process piping and test loop amounted to approximately one-third of the refrigeration design load of 1/2 ton (6000 Btu/hr); when the refrigeration load (combined heat losses and electrical heating) was increased to 6150 Btu/hr, the temperature of the inlet C_2HCl_3 was maintained at $-76^\circ C$ (within the design specification of -72 to $-83^\circ C$). In terms of UF_6 production rates, the peak rates are expected to correspond to about 100 lb/(hr) (sq ft reactor cross section). At this rate, a refrigeration capacity of only 500 Btu/hr is required. Therefore, the existing refrigeration unit should be of adequate capacity. Since the temperature attained under load satisfies the design specification (-72 to $-83^\circ C$), the performance of the unit was considered satisfactory for the intended use.

b. Cleanup of Cell Exhaust Air Contaminated with Plutonium Hexafluoride
(R. Kessie, B. Misek,* L. Marek)

Studies on the kinetics of the processes involved in the cleanup of air-borne PuF_6 are in progress. Under conditions of normal

* Co-op student from Northwestern University, Evanston, Illinois.

atmospheric moisture the air-borne PuF_6 is hydrolyzed by the moisture resulting in solid products which can be filtered. The overall reaction may be considered as $\text{PuF}_6(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{PuO}_2\text{F}_2(\text{s}) + 4\text{HF}(\text{g})$. Better understanding of the hydrolysis and filtration mechanisms is desirable in order to design efficient cleanup devices for the exhaust air from the facilities in which PuF_6 is handled. Extremely efficient removal of plutonium from the ventilation air is necessary due to the low permissible concentrations in air (3×10^{-8} mg of ^{239}Pu per cubic meter of air).⁵

A main objective of this investigation is the evaluation of the performance of high efficiency AEC-type filters under various conditions of PuF_6 release. For those cases where AEC-type filters alone prove to be inadequate, design and evaluation of additional cleanup methods will be attempted. During these evaluations the range of conditions (moisture concentration, flow rates, etc.) which are expected to occur in future facilities handling PuF_6 as well as those present in the currently operating facilities will be covered.

The initial experiments in this program, previously reported, were performed simulating the accidental release of pure PuF_6 . Small quantities (1 to 25 mg) of pure PuF_6 were released into flowing air containing amounts of moisture representative of the range normally present in the cell atmosphere. It was found that when there was an excess of water present the hydrolysis reaction went to completion rapidly; a fume which consisted of small particles (0.1μ) of plutonyl fluoride (PuO_2F_2) formed. The majority of the plutonium was carried by the air and collected on two filter disks (segments cut from an AEC filter) mounted in series. With an air velocity incident to the face of the filter of 1 cm/sec, two filters in series reduced the plutonium concentration to between 10^{-6} to 10^{-9} of the entering concentration. Investigation of the chemical nature of the reaction products by X-ray diffraction patterns indicated that the hydrolysis product is PuO_2F_2 , homologous to the compound formed by the hydrolysis of UF_6 .

Recently, experiments were performed to simulate leaks of dilute PuF_6 gas streams. The experiments were carried out with the similarly behaving UF_6 to facilitate the design of experiments with PuF_6 . The results of these experiments indicated that when the UF_6 is diluted to a concentration of less than 100 ppm in dry nitrogen and then mixed with moist nitrogen, the hydrolysis reaction proceeds by a mechanism different from the one described above. The reaction no longer takes place at a significant rate in the gas phase but occurs mainly on any solid material which is contacted by the gas. Under the actual test conditions with an air velocity incident to the filter face of 10 cm/sec (about 4 times the recommended velocity) over 10% of the uranium was found to pass through a single AEC filter. (For additional details see ANL-6596, p. 124, ANL-6725, p. 157, and ANL-6800, pp. 245-252.)

⁵ U. S. Department of Commerce National Bureau of Standards Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air and in Water for Occupational Exposure" Washington, D. C. (1959), p. 87.

In current work, experiments simulating leakage of diluted PuF_6 into glovebox atmospheres were continued. The objective of the current work was to determine the hydrolysis rates of the reactions which are catalyzed by solid surfaces. The information on the hydrolysis rates would be helpful in the estimation of the surface area needed for an optimum clean-up system. Since the overall hydrolysis reactions are similar for both UF_6 and PuF_6 , experiments were made in the current work with UF_6 to facilitate the design of proposed experiments with PuF_6 .

Apparatus and Procedure

Surface reaction kinetics of the hydrolysis reaction of dilute mixtures of UF_6 were measured in a packed bed of 3.2-mm glass spheres in the apparatus shown in Figure II-3. The bed was contained in a 1.5-in. ID acrylic (Plexiglas) tube, supported on stainless steel screen separators. The two entering nitrogen gas streams, one containing the UF_6 and the other

Figure II-3

URANIUM HEXAFLUORIDE HYDROLYSIS APPARATUS

containing the moisture, were rapidly mixed by a stirrer rotating at 500 rpm. Results of preliminary tests indicated that the reaction rates were independent of stirrer speeds between 500 and 1500 rpm.

An extremely dry source of gas was needed for this work, and nitrogen from a liquid nitrogen supply was found satisfactory as the carrier gas since its dew point was very low (-100°F corresponding to 3 ppm moisture). It was assumed that there would not be any difference in the experimental results if either nitrogen or air was used.

The UF_6 stream was generated by passing a small flow of dry nitrogen over a bed of 1/8-in. NaF pellets that had been saturated with UF_6 . Equilibrium of the gas with the bed was attained since this system was very similar to that used in the original measurement of the equilibrium pressure of UF_6 over the $\text{UF}_6\text{-3 NaF}$ complex as a function of temperature.⁶ The vapor pressure of UF_6 was given as:

$$\log p \text{ (mm Hg)} = 10.88 - \frac{5090}{T}$$

where T is the absolute temperature, $^{\circ}\text{K}$. The flow rate of nitrogen through the pellet bed was 83.7 ml/min in all runs and the temperature of the bed was adjusted from 134 to 212°C to give the desired pressure of UF_6 in the feed stream to the hydrolysis apparatus. The UF_6 -containing stream from the NaF bed was mixed with additional dry nitrogen to give a total feed rate of 3.3 liters/min.

The humidified nitrogen stream was produced by mixing dry nitrogen with moist nitrogen that had been saturated in a water bubbler. By changing the proportion of wet and dry stream flow rates the moisture content of the mixed stream could be adjusted. The moisture content was determined by passing a small part of this stream to an automatic dew point recorder while the bulk stream was fed to the packed-bed hydrolysis apparatus. The exit gas stream from the packed bed of glass spheres passed through three AEC filter media disks mounted in series.

A clean bed of glass beads and clean filters were used for each experiment. All the flow rates and temperatures were adjusted and allowed to stabilize before starting the UF_6 flow which was conveyed in the nitrogen stream from the NaF- UF_6 bed. The filters were inserted about 5 min after the UF_6 flow was started and were removed shortly before the UF_6 flow was stopped to eliminate the errors due to transient conditions. At the end of each run the separate bed segments and filters were each immersed in 100 ml of 10% nitric acid containing 0.01% Aerosol* (wetting agent). The solution was analyzed for uranium by the fluorophotometric method.

* Obtained from E. H. Sargents and Co.

⁶ Cathers, G. I., Bennett, M. R., and Jolley, R. L., $\text{UF}_6\text{-3 NaF}$ Complex Formation and Decomposition, Ind. Eng. Chem. 50, 1709 (1958).

Results and Discussion

Hydrolysis rates were calculated from the uranium deposited on the surfaces of glass spheres in each packed bed segment. The quantities of uranium found in the various packed-bed segments and also the quantity collected on each of the filter disks are reported in Table II-9. In all experiments there was a large excess of water over that required for complete reaction. The hydrolysis rates increased with increase in the partial pressure of either water or UF_6 . The rates ranged from 0.3×10^{-4} to $0.1 \text{ mg of U/(hr)(sq cm)}$. The highest reaction rate was less than the mass transfer rate⁷ calculated from known physical properties, indicating the reaction is not mass transfer limited.

Table II-9

SURFACE REACTION DATA FOR URANIUM HEXAFLUORIDE HYDROLYSIS KINETICS

Run	$p_{\text{UF}_6}^0$ (mm Hg)	$p_{\text{H}_2\text{O}}^0$ (mm Hg)	Feed Rate (mg U/hr)	t Bed ^a (min)	mg U per Bed Segment ^b			t Filter ^a (min)	mg U per Filter		
					0-1/2 in.	1/2-1 in.	1-2 in.		1st	2nd	3rd
UM-11	0.00310	0.050	15.9	55.2	1.7c		1.0	50.0	0.48	0.40	0.38
UM-12	0.00310	0.15	15.9	56.0	4.2c		1.6	50.0	0.35	0.099	0.035
UM-13	0.00310	0.27	15.9	55.0			1.3	50.0	0.063	0.0023	0.0017
UM-14	0.00310	0.42	15.9	58.4	3.2	1.6	0.7	50.0	0.040	0.005	0.0012
UM-15	0.00310	0.72	15.9	52.5	4.7	0.6	0.10	50.0	0.047	0.003	0.0011
UM-16	0.00310	1.3	15.9	56.8	5.2	0.3	0.04	50.0	0.070	0.006	0.0014
UM-18	0.00310	3.8	15.9	61.7	4.2	0.15	0.12	50.0	1.0	0.17	0.007
UM-19	0.00310	5.1	15.9	58.7	2.8	0.10	0.10	50.0	2.8	0.07	0.08
UM-20	0.000314	0.43	1.62	91.2	0.20	0.017	0.014	50.0	0.002	0.002	0.002
UM-22	0.00155	0.43	7.96	90.0	4.2	1.0	0.26	70.0	0.004	0.0004	0.0008
UM-14d	0.00310	0.42	15.9	58.4	4.3	1.3	0.7	50.0	0.040	0.005	0.0012
UM-23	0.0150	0.43	77.3	26.9	5.4	3.4	4.9	15.0	0.60	0.43	0.13
UM-21	0.0308	0.42	158.5	25.0	7.5	5.9	8.2	15.0	3.6	0.99	0.38

^a t Bed and t Filter represents the time during which the reactant flow was maintained through the bed and the filter, respectively.

^b Bed area = $332 \text{ cm}^2/\text{in.}$, wall area = $30.4 \text{ cm}^2/\text{in.}$, area of screen between beds = 20.7 cm^2 .

^c Beds in UM-11 and 12 were divided into 1-in. segments only.

^d Run UM-14 is tabulated twice to aid in comparison of data.

The ratios of the quantity of uranium collected on the first filter to that retained on the packed-bed segment immediately preceding the filter varied from about 0.1 to 250, the majority being less than one. The higher ratios indicate the presence of gas-phase reaction (fume formation) and low filtration efficiency of the packed bed for such a reaction product.

It is expected, from the results obtained with the earlier pure PuF_6 release experiments where the product was primarily of a particulate form, that particulate penetration of a single AEC filter would be much less than 1%. Since the lowest filter penetration recorded in the current work is larger than 5%, filter penetration appears to be a result of unreacted UF_6 (or a volatile intermediate product) passing through the filter.

⁷ Gupt, A. D., and Thodos, G., Transfer in the Flow of Fluids Through Fixed and Fluidized Beds of Spherical Particles, A.I.Ch.E. J. 8:608 (1962).

Since the hydrolysis reaction produces a solid reaction product (UO_2F_2), any surface at which the reaction takes place will be covered with the reaction product. This is true for all solid surfaces whether they be fixed solid parts of the equipment, or particles being carried in the gas as fume. The reaction rate measured on the surface of packed beds may be expected to be the same as at the surface of a particle suspended in the gas phase under the same conditions of gas composition and pressure at the reaction surfaces. Thus reaction rates measured in the packed beds may be used in predicting the growth rate and particle size distribution of the fume produced in the gas phase part of the reaction.

To more clearly define the effects of partial pressures of UF_6 , water and HF , the experimental data are being correlated using a semi-empirical rate equation proposed by Hougén and Watson⁸ for reaction catalyzed by solid surfaces. The following rate equation has been found to fit the experimental data

$$r = \frac{k \text{ } p_{\text{UF}_6} \text{ } p_{\text{H}_2\text{O}}}{1 + K_1 \text{ } p_{\text{UF}_6} + K_2 \text{ } p_{\text{HF}}}$$

where

r = reaction rate, mg $\text{U}/(\text{hr})(\text{sq cm})$

k = rate constant

p = partial pressure of subscripted component at the surface, mm Hg

K = adsorption constant

The rate equation and the following equations for describing mass transfer and material balance were programmed for a computer to estimate the constants in the rate equation by a least squares method.

Mass Transfer

$$r = k_D (p_{\text{UF}_6(g)} - p_{\text{UF}_6})$$

where

k_D = diffusion coefficient

$p_{\text{UF}_6(g)}$ = partial pressure of UF_6 in the gas phase, mm Hg

p_{UF_6} = pressure of UF_6 at the reacting surface, mm Hg

⁸Hougén, A.O., and Watson, K. M., Chemical Process Principles, Part Three, John Wiley and Sons, New York, 1947, p. 920.

Material Balance for Reaction

The fraction of UF_6 unreacted, x , is defined by the following reaction.

$$\text{PUF}_6(\text{g}) = x \text{ PUF}_6.$$

Material balance on the other reactants gives

$$\text{P}_{\text{H}_2\text{O}} = \text{P}_{\text{H}_2\text{O}}^0 - 2\text{P}_{\text{UF}_6}^0 (1 - x)$$

$$\text{P}_{\text{HF}} = 4\text{P}_{\text{UF}_6}^0 (1 - x)$$

$$r \, dS = -F \, dx$$

where

P^0 = partial pressure of subscripted component at the inlet, mm Hg

S = surface area of reaction bed

F = input rate of UF_6

The result from the computer calculation is

$$r = \frac{191.5 \text{ P}_{\text{UF}_6} \text{ P}_{\text{H}_2\text{O}}}{1 + 597 \text{ P}_{\text{UF}_6} + 95.5 \text{ P}_{\text{HF}}}.$$

Data from 37 bed segments correlated to a standard deviation of 26%. Data from eight bed segments were not used in the computation because of collection of gas-phase reaction products (fume).

Future Work

Data on the rates of hydrolysis of PuF_6 catalyzed by solid surfaces will be obtained in facilities that are nearing completion. Following this, some experiments will be designed to determine if the gas phase reaction (fume forming) is induced by an initial homogeneous reaction followed by spontaneous nucleation, or if it is dependent on nuclei present in the gas initially. It is expected that the surface reaction kinetics measured on the packed beds will also be useful in predicting the growth of particles in the gas phase.

c. Related Process Studies: Decladding Stainless Steel-Clad Fuel

(J. D. Gabor, D. Ramaswami, D. Raue)

The development of a decladding procedure for stainless-clad UO_2 fuels which would be applicable to the fluid-bed fluoride volatility process has been undertaken. One procedure which is being investigated involves removing the stainless steel cladding with aqueous hydrochloric acid in an air-fluidized bed.

A literature survey indicated that, in order to obtain practical corrosion rates of stainless steel by hydrochloric acid, an aqueous phase is necessary. Uhlig⁹ reported a corrosion rate for stainless steel of 4.3 mils/hr for 12 w/o hydrochloric acid at 90°C in the presence of a corrosion inhibitor (carbon monoxide); whereas Farber¹⁰ reported that the reaction of Type 18-8 stainless steel in pure gaseous HCl did not proceed at a measurable rate at temperatures approaching the melting point of stainless steel.

Although the aqueous phase is necessary for practical corrosion rates, the presence of a liquid in a gas-fluidized bed alters the fluidization characteristics of the bed. A greater tendency for channeling was reported by Parker and Stevens¹¹ for air-fluidized beds of glass beads in which the water content was greater than 0.5 w/o than for beds in which a lower or no liquid content was present. When the quantity of liquid present is large enough to fill completely the interparticle voids of a bed with liquid (void fraction for randomly packed spheres is 0.4), the particles no longer adhere to one another by surface tension forces. The bed at this point would be a slurry.

Experimental Equipment and Procedure

In the current work, tests were made with a 0.82-in. ID Monel column and a $1\frac{1}{2}$ -in. ID glass column. Both columns were $1\frac{1}{2}$ ft in length. Alumina grain (-30 +50 mesh) was the fluidized material, and air was the fluidizing gas for all the experiments.

In the experiments conducted in the Monel column, hydrochloric acid was injected into the bed through a $1/4$ -in. OD nickel tube. The bed consisted of approximately 150 g of alumina grain. The HCl concentration in the acid was about 30 w/o and the liquid content in the fluidized bed was estimated to be 10 w/o. A stainless steel (Type 304) thermowell ($1/2$ -in. OD) which extended from the top of the column to within 1.5 in. from the bottom of the bed served both as the corrosion specimen as well as the means for obtaining the temperature of the bed.

⁹ Uhlig, H. H., Ind. Eng. Chem. **32**, 1490 (1940).

¹⁰ Farber, M., Journal of Electrochemical Society, **106**, 4, 751 (1959).

¹¹ Parker, H. W., and W. F. Stevens, A.I.Ch.E. Journal, **5**, 3, 314 (1959).

In each of the tests conducted in the glass column, approximately 300 g of alumina (12-in. bed height) was charged to the column. The glass column provided a means for observing the quality of fluidization. A Type 304 stainless steel rod, 1/2 in. in diameter, was used as the test specimen. Corrosion rates were determined by weight loss and by dimensional changes. In runs in which the liquid content of the bed was low, the hydrochloric acid was transported to the fluidization column by bubbling the fluidizing gas through hydrochloric acid (37 w/o HCl in water) at a temperature of 90 to 100°C. The acid was carried into the fluidization column by vaporization and entrainment and then deposited in the fluidized bed by de-entrainment and condensation. The amount of liquid in the column was regulated by adjusting the temperature of the acid. The liquid content of the fluidized bed was determined at the end of each run by means of weighing three bed samples (each sample approximately 20 g) before and after drying in an oven. The HCl concentration in the liquid phase of the bed was about 20 w/o. In the test in which the liquid content of the fluidized bed was high (26 w/o), the hydrochloric acid was fed through a 1/4-in. OD polyethylene tube. The polyethylene tube entered the column at the top and extended downward to a point 6 in. above the gas distributor plate.

Results

Table II-10 summarizes the corrosion results. The runs are listed in order of increasing amounts of liquid present in the fluidized bed. The corrosion of the stainless steel specimens, in terms of weight loss, increased from 0.001 to 0.86 w/o per hour as the liquid content in the bed increased from 0.2 to 26 w/o.

Table II-10
CORROSION OF TYPE 304 STAINLESS STEEL WITH AQUEOUS HYDROCHLORIC ACID IN A FLUIDIZED BED

Run	Time (hr)	Bed Temp (°C)	Bed Weight (g)	Liquid Content in Bed (w/o) ^a	Air Velocity (ft/sec)	Specimen Weight Loss [(w/o)/(hr)]	Corrosion Rate (mils/hr)
Fluidizing Gas: Air							
Fluidized Bed Material: Sintered alumina grain, -30 +50 mesh							
Fluidized Bed Columns: 1-1/2-in. dia. glass column for Runs 24D, 24G, 24E, and 14							
0.82-in. dia. Monel column for Runs M1, M2, M3, and M4							
Corrosion Specimens: Type 304 SS rod, 1/2-in. dia. for tests with glass column							
Type 304 SS 1/2-in. OD thermowell for tests with Monel column							
HCl Content in Liquid Phase in Fluidized Bed: 20 w/o							
24D	6.5	93	300	0.2	4.2	0.001	b
24G	5.75	93	300	0.6	4.2	0.004	b
24E	1.75	100 to 75	300	2.7	4.2	0.052	0.5
M1	1.5	25	150	10	2.5	b	1.0
M2	1.5	60	150	10	2.5	b	8.5
14	6.75	75	300	26	1.0	0.86	8.7
M3	1.5	25	0	100	2.5	b	0.5
M4	1.5	60	0	100	2.5	b	1.0

^a Liquid content based on bed sample taken at end of run.

^b Not measured.

In the runs (glass column) that were conducted with the low liquid contents (< 2.7 w/o), the corrosion at temperatures of about 90°C was so slight that it was not possible to determine dimensional changes, but weight changes were noted. However, in the tests (Monel column) that were carried out with liquid contents of about 10 w/o, the corrosion rate increased an order of magnitude from 1.0 to 8.5 mils/hr as the temperature was increased from 25 to 60°C . In tests made with no alumina particles present in the Monel column, corrosion rates of 0.5 and 1.0 mils/hr at 25°C and 60°C , respectively, were obtained.

In the run (glass column) that was made with a high liquid content (26 w/o), the corrosion rate was 8.7 mils/hr at 75°C . At this high liquid content, the bed was a slurry through which the fluidizing air bubbled.

Discussion of Results

Tests performed in the Monel column without a fluid bed indicated that a significant increase in corrosion is attained with temperature increase. Also, there was an order of magnitude increase in corrosion at 60°C with the use of fluidized particles. The fluidized particles may have an abrasive effect which would remove films of corrosion products. Corrosion increases with increased liquid content in the fluidized bed. For liquid contents in the bed of less than 2.7 w/o, the corrosion rates were less than 0.5 mil/hr; higher rates are desirable. However, a liquid content of 2.7 w/o appeared to be about the upper limit for maintaining satisfactory fluidization of the bed.

Future Plans

Tests are planned in which corrosion rates for stainless steel specimens will be determined in fluid beds having liquid contents in the region of 5 to 10 w/o. A 3-in. dia. glass column is being constructed to carry out the tests. In work in which a comparison of the fluidization of coal particles in 2-in. and 3-in. diameter columns was made, Leva¹² reports data which show no channeling for the coal particles fluidized in the 3-in. column whereas channeling existed in the 2-in. column. Besides providing better fluidization characteristics, the 3-in. dia. column will allow simultaneous charging of several cladding specimens which will simulate more nearly actual processing conditions.

- d. Conversion of Uranium Hexafluoride to Uranium Dioxide:
Preparation of High-Density Particles
 (I. Knudsen, N. Levitz, T. Tamura, D. Raue)

A fluid-bed process for preparing high-density spheroidal particles of uranium dioxide (UO_2) from uranium hexafluoride (UF_6) has been under study. Concluding tests aimed at developing techniques suitable for

¹² Leva, Max, Fluidization, McGraw-Hill Book Co., New York, 1959, p. 24.

the preparation of dense $\text{PuO}_2\text{-UO}_2$ particles from mixed hexafluoride feeds were carried out this period.

The process involves reaction of the hexafluoride with a mixture of steam and hydrogen in a fluidized bed of oxide particles at elevated temperatures. Experimentally, periods of UF_6 feed are alternated with periods of fluoride cleanup when only steam and hydrogen are fed. Each period is usually of 30-min duration. The bed weight is maintained approximately constant by the removal of product at the end of each cleanup period.

Earlier process studies carried out at temperatures of 650°C and 700°C in a 3-in. dia. Monel reactor studied the effects of process variables on particle density. Improved particle density was obtained with:

1. a steam rate equivalent to about twice the UF_6 rate (in moles),
2. lower UF_6 rates within the range 17 to 50 g/min,
3. a bed depth of 18 in. rather than 9 in., and
4. the higher temperature.

The most pronounced effect was that of the steam rate; the product density was lower at steam inputs both lower and higher than the value noted above. No apparent effect of the hydrogen rate on particle density was noted. Material in the size range 16 to 170 mesh was produced. The highest density achieved was 9.8 g/cc, nearly 90% of theoretical density.

Current Work

In this process, the gas-to-solid hexafluoride conversion reaction occurs preferentially on the surface of the bed particles with resultant particle growth. The addition of seed material to the bed is required to offset this growth pattern and allow the average size of the bed material to be maintained at a uniform value. A part of the seed requirements is provided as a normal consequence of the production of small particles from that portion (~5 to 10%) of the UF_6 which reacts in the gas phase (in the bed zone) rather than on the surface of bed particles. However, material produced in the gas phase may have only limited utility as seeds, since the individual particles are probably very small ($<< 325$ mesh) and are readily elutriated from the reaction zone.

The bulk of the seed has been provided by grinding a portion of the product and recycling this material. Since future work will involve the handling of plutonium oxides, an alternative procedure that minimizes solids handling was developed. Current studies were therefore devoted to

the testing and evaluation of an in-situ seed-preparation method that employs an oxidation step to achieve particle breakup (size reduction) followed by hydrogen reduction of the material back to UO_2 before use.

In practice, either a portion of a bed might be treated in a separate unit and then returned as seed or the entire bed which has "grown" through the UF_6 conversion process to a practical limit may be re-sized in place. Both schemes were demonstrated following a study of the effect of oxidation on the extent of size reduction.

Studies of Size Reduction by Oxidation-Reduction

A series of seed preparation tests were carried out in the 3-in. dia. fluid-bed reactor system with relatively small amounts of material, 1.0 and 1.5 kg beds of +80 mesh particles of UO_2 . (In one test, a bed of -20 +40 mesh particles was used.) Oxidation was conducted at either 400°C or 650°C, with either 10% or 20% air in nitrogen. The quantity of air used ranged from 0.65 to 1.20 times the stoichiometric amount required for conversion of UO_2 to U_3O_8 . Oxidation periods ranged from 29 to 58 min. The reduction of the oxidized particles was conducted at 650°C with essentially 100% hydrogen (some nitrogen purge dilution). The reactor was purged with nitrogen before and after the reduction step. An overall evaluation of these experiments was based on the amount of material found in the final bed in a size range smaller than the starting material (extent of breakup). Of importance, also, was the amount of fines (<325 mesh) produced, since fluid-bed systems are sometimes difficult to control when excessive amounts of fines are present.

These preliminary tests established that (a) particle breakup was extensive when as little as 0.65 stoichiometric equivalents of oxygen were used, (b) fines (-325 mesh) production was a function of extent of oxidation, (c) the higher oxidation temperature promoted the formation of fines, and (d) the higher air concentration gave greater breakup and a slightly better (lower) proportion of fines in the final material. Other effects noted were that material which was oxidized under conditions of higher temperature and higher air concentration had a higher particle density (after reduction). Finally, sieve analyses taken at intervals during the reaction sequence showed that particle breakup continued if the bed was maintained fluidized after the oxidation step; for example, breakup continued during the reduction step as well as during the intermediate and final purge periods.

Material prepared in these oxidation-reduction studies was evaluated as seeds in UO_2 production runs. The runs were of 12- and 17-hr duration, and were made under normal operating conditions (see Table II-11).

Seed material (sieve analysis given in Table II-12) was added in 170- to 200-g increments as needed on the basis of sieve analyses carried out during the run on hourly products.

Table II-11

OPERATING CONDITIONS FOR THE
CONVERSION OF UF₆ TO UO₂

Temperature:	650°C
Superficial Gas Velocity:	1.0 ft/sec
UF ₆ Feed Rate:	50 g/min
Steam/UF ₆ Mole Ratio:	2.6/1
H ₂ /UF ₆ Mole Ratio:	6.7/1
UF ₆ Feed Period Duration (per cycle):	30 min
Cleanup Period Duration (per cycle):	30 min
Steam/H ₂ Mole Ratio during Cleanup:	1/1

Table II-12

PARTICLE SIZE DISTRIBUTION
OF SEED PARTICLES USED
IN UO₂ PRODUCTION RUNS

<u>Mesh Size</u>	<u>w/o</u>
+120	0.6
-120 +140	8.2
-140 +170	21.6
-170 +230	17.6
-230 +270	16.3
-270 +325	12.4
-325	23.3
	<u>100.0</u>

The first experiment was, for the most part, satisfactory except that the major portion of the -325 mesh material fed with the seed stream apparently accumulated in the reactor (mainly on the filters). Seven additions of seed material were made in the 12-hr period. Rapping on the column, initiated during the second experiment, effected the return of these fines to the bed, and the fines concentration in the bed was maintained at 20 to 30% of the bed weight. After 17 hr of a 24-hr planned run, the UF₆ nozzle plugged, probably because of the high fines content of the bed and the resulting poor quality of fluidization. These experiments did indicate that seed material prepared by the oxidation-reduction method could be used satisfactorily; however, consideration must be given to the size distribution of the seed stream. The proportion of -325 material in the seed stream should be minimal.

In-Place Particle Size Reduction of Whole Beds

A test of the use of the oxidation-reduction technique for in-place particle size reduction of an entire bed was carried through three complete cycles of particle size reduction (oxidation-reduction) and particle growth (hexafluoride-to-oxide conversion). A fourth oxidation-reduction treatment was given the final bed. To shorten the amount of time needed to carry out the growth portions of the test, the bed weight was held to 6 kg. For one period the bed was permitted to increase to about 12 kg before any product was drawn. This latter period illustrated a procedure in which hourly product take-off would not occur.

Oxidation was conducted at 400°C with 20% air diluted with nitrogen. The quantity of air used ranged from 0.25 to 0.52 times the stoichiometric amount required for conversion of UO_2 to U_3O_8 . The oxidized particles were reduced for 1 hr at 650°C with hydrogen with a small amount of purge nitrogen dilution. Operating conditions for the hexafluoride conversion portions of the test were nominal conditions used in previous tests, Table II-11.

Size reduction and particle growth was successfully carried through three cycles. The process steps and particle size behavior are summarized in Table II-13. Normal solids deposition occurred during the hexafluoride-to-oxide conversion periods, which ranged from 10 to 17 hr. An average of 2.7 bed equivalents of UO_2 were produced per cycle. A flattening of the particle size distribution of the bed was noted, and no accumulation of coarse particles occurred during the run. Particle density varied in the range 8.0 to 8.4 g/cc.

Table II-13

SUMMARY OF HEXAFLUORIDE CONVERSION AND OXIDATION-REDUCTION CYCLES

Equipment: 3-in. dia. Monel reactor

Process Step	Duration (hr)	Average Bed Particle Diameter ^a (μ)	
		Initial	Final
1. Oxidation-Reduction UF_6 -to- UO_2	3	360	154
	16	185 ^b	386
2. Oxidation-Reduction UF_6 -to- UO_2	3	386	(180) ^c
	17	(180) ^c	379
3. Oxidation-Reduction UF_6 -to- UO_2	3	379	171
	10	202 ^b	402

^a D_v/s , the mean volume-surface particle diameter, $\frac{\sum nd^3}{\sum nd^2}$, as defined by Dallavalle, J. M., Micromeritics, 2nd Ed., Pitman Publishing Corp., New York, 1948, p. 47.

^b After particle-size adjustment by removing a portion of the -120 mesh particles.

^c Estimated value.

In all four oxidation-reduction treatments, somewhat greater particle breakup occurred than that expected on the basis of the data obtained in the earlier tests with 1.0 to 1.5 kg beds. In one of these earlier tests with shallow beds, the -80 mesh fraction increased to about 42% when 0.70 stoichiometric equivalent of oxygen were fed; in the current test, breakup was almost as extensive (30% minus 80 mesh) when only about one-half as much oxygen (0.37 equivalents) was used. This difference is attributed to two factors, increased utilization of the oxygen in the deeper beds and additional particle breakup occurring when fluidization was continued with nitrogen after the completion of the oxidation-reduction treatment. To avoid the use of excessive amounts of fines in the starting beds for the hexafluoride conversion periods, a portion of the -120 mesh fraction was removed after the first and third reduction treatments. The adjusted average particle diameters are shown in Table II-13. In the second cycle, sieve analyses of bed samples after oxidation-reduction did not indicate that excessive fines were present and the hexafluoride conversion period was started without removing any bed material. (The average particle diameter shown in Table II-13 for this test is actually an estimate based on subsequent analyses.) Later samples, however, showed the presence of excessive amounts of fines and the bed was withdrawn for partial sieving. The screened bed was recharged and the cycle completed.

The fourth oxidation-reduction treatment was carried out on the final bed to determine the extent of particle breakup during subsequent periods of fluidization. The amount of oxygen fed was equal to 0.25 equivalents; other operating conditions were the same as above. Particle breakup, expressed as cumulative values for the -80 mesh fraction, was as follows:

After oxidation:	0.4%
After reduction:	2.5%
After 8 hr of fluidization:	12.5%
After 16 hr of fluidization:	16.6%
After 24 hr of fluidization including heating to 650°C and treating with steam and hydrogen for 1 hr:	21.3%

All size fractions, including the coarse (+45 mesh) material, exhibited this continuing breakup phenomenon. This breakup phenomenon must be taken into consideration in setting conditions for particle breakup by the oxidation-reduction method.

Conclusions

A convenient in situ oxidation-reduction method has been developed for the preparation of seed material needed for regulating overall particle growth in the conversion of UF_6 to UO_2 . Using, as starting material, a wide size spectrum of dense UO_2 particles prepared by the fluid-bed method,

appreciable breakup can be achieved by oxidation at 400°C with as little as 0.25 times the amount of oxygen (fed as 20% air in nitrogen) required to oxidize the UO_2 to U_3O_8 . Reduction of the oxidized material back to UO_2 can be achieved in 1 hr at 650°C with hydrogen. Oxidizing conditions may be tailored to fit a particular need for seed material; generally, conditions that minimize fines (-325 mesh) production are desirable.

This work on the development and testing of the oxidation-reduction method for preparing seed material is the final phase of the current (uranium only) hexafluoride conversion program. A summary report of these studies has been issued, ANL-6902. Application of the results of this work to the preparation of mixed uranium-plutonium oxide particles from mixed hexafluoride feeds is planned as part of the volatility reprocessing studies on low-enriched ceramic oxide reactor fuels.

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

a. Fluidization of Fine Particles (Manfred Baerns, D. Ramaswami)

A basic study has been started of the fluidization of fine particles in the size range of less than 50 μ . Fluidization of fine particles is of interest in processes such as the fluorination of U_3O_8 fines, the preparation of uranium monocarbide and the coating of reactor fuel particles. Such small particles are, in general, difficult to fluidize and it is the goal of this investigation to elucidate the reasons for these difficulties.

The difficulty in fluidizing fine particles is due to the effect of interparticle forces^{13,14} of an adhesive and frictional nature. The adhesive forces are caused by intermolecular interactions¹⁵⁻¹⁷ between the particles while the frictional forces depend mainly upon the surface geometry of the particles. To fluidize a particulate material both the adhesive and the frictional forces have to be overcome in addition to the gravitational force. The interparticle forces are generally negligible for larger particle sizes ($>100 \mu$) and the larger particles are readily fluidizable. If, however, the particle size is small ($<50 \mu$), the effect of interparticle forces becomes significant and fluidization is not easily achieved. The relationship between these interparticle forces, the fluidizability and the quality of fluidization is being investigated in the current work.

The fluidizability is quantitatively expressed in the form of a fluidizability index which is the ratio of the theoretical gas velocity,

¹³ Morse, R. D., Ind. Eng. Chem. **47**, 1170 (1955).

¹⁴ Parker, H. W., and Stevens, W. F., A.I.Ch.E. J. **5**, 314 (1959).

¹⁵ Boehme G., Krupp, H., Rabenhorst, H., and Sandstedt G., Trans. Inst. Chem. Engrs. (London) **40**, 252 (1962).

¹⁶ Haase, H., and Hardtke, B. H., Chem. Ing. Tech. **29**, 814 (1957).

¹⁷ Jordan, D. W., Brit. J. Appl. Phys. **5**, Supplement No. 3, 194 (1954).

$\mu_{\min}$, calc., at which fluidization of the solid particles begins if interparticle forces are not present to the experimentally observed minimum gas velocity, $\mu_{\min}$, obs., at which particle movement first takes place (incipient fluidization). The theoretical gas velocity can be calculated.¹⁸ When interparticle forces have to be overcome, the actual gas velocity for incipient fluidization is higher than the calculated one, i.e., the defined index is smaller than 1.

The quality of fluidization concerns the comparative behavior of fluidized beds chiefly with respect to the achievement of good solids mixing and consequently high rates of heat transfer.

Apparatus and Procedure

The apparatus being used for the fluidization experiments is shown in Figure II-4. The experiments were performed in two Lucite

Figure II-4

SCHEMATIC DIAGRAM OF APPARATUS USED FOR FLUIDIZATION EXPERIMENTS

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columns of 8.2- and 14-cm dia. A porous metal plate was used as the fluidizing gas (nitrogen) distributor. Two pressure probes, connected to a water manometer, were located in the column to determine the pressure drop across the bed. An electrically heated plate (6.8 by 5.0 by 0.95 cm) was immersed in the bed for heat transfer measurements; the surface temperature of the plate was measured with four thermocouples. These temperatures and the bed temperature were registered on a recorder. When the temperature difference between the heated plate and the bed was small ($<1^{\circ}\text{C}$) the difference was directly measured with a potentiometer to increase accuracy.

The incipient fluidization velocity was derived from the measurements of the pressure drop of the gas across the bed and the heat transfer coefficients. The latter were also used as a measure of the quality of fluidization.

To determine the interparticle adhesion and friction an apparatus was used similar to that described by Pecht.¹⁹ In principle, a plate is inclined and the angle of inclination is measured. The plate is uniformly covered with the particulate material; then the angle of inclination (angle of slide) at which the bulk of the particles slides from the plate owing to the force of gravity is determined. This apparatus was located in a glovebox which was continually purged with nitrogen to establish constant and reproducible ambient conditions. To measure the friction and adhesion between particles and to avoid interaction between the particles and the substrate, a multilayer of particles was first glued upon the surface of the plate.

The following equation expresses the relationship²⁰ between the angle of slide, ϕ , the adhesive force per unit area, F_a , and the friction coefficient between the particles and the plate, μ :

$$mg \sin \phi = \mu mg \cos \phi + F_a A$$

where m is the weight of the particles on the substrate, g is the gravitational constant, and A the surface area of the substrate. By repeating the measurements for different amounts of material and plotting ($mg \sin \phi$) versus ($mg \cos \phi$) on Cartesian coordinates, the friction coefficient, μ , is obtained from the slope of the line and the total adhesive force from the intercept on the ordinate. To obtain the adhesive force, F_p , exerted by a single particle in contact with the plate, F_a is divided by the number of particles per unit area. The number is assumed to be $1/d_p^2$ for spherical particles, where d_p is the particle diameter in length units. (It should be noted that Boehme *et al.*¹⁵ expressed some doubt whether the true adhesive force of an individual particle is correctly determined by this method. They pointed out that the adhesive force of a single particle surrounded by a group of particles is actually being measured; this, however, meets exactly the condition which is of interest in a bed of particles.)

¹⁹ Pecht, H., Chem. Ing. Tech. 33, 691 (1961).

²⁰ Cremer, E., Conrad, F., and Kraus, Th., Ang. Chem. 64, 11 (1952).

Experimental Conditions

A series of experiments with various material (iron, nickel, alumina) ranging from approximately 2 to 150 μ in diameter has been performed. The experimental conditions are summarized in Table II-14 together with the results for the experimentally observed incipient fluidization velocity, the adhesive force of the particles, and the interparticle friction coefficient. (The heat transfer data are not included since their evaluation as a measure of the quality of fluidization has not been completed as yet. Their variation with increasing gas velocity, however, was used along with the pressure drop measurements to determine the incipient fluidization velocity.)

Table II-14
FLUIDIZATION OF FINE PARTICLES.
EXPERIMENTAL CONDITIONS AND DATA ON PARTICLE AND BED PROPERTIES^a

Material	Average Particle Size ^b $\bar{d}_p$ (μ)	Density (g/cm^3)	Amount of Material Charged (g)	Bed Height (Static Condition) (cm)	Adhesive Force F_p (dyne)	Friction Coefficient, μ	Minimum Fluidization Velocity, Observed (cm/sec)
Nickel ^d	137	8.9	3315	16.5	1.8×10^{-2}	0.53	5.8
	18	8.9	740	3.6	1.5×10^{-3}	0.66	0.5
			1480	7.2			0.6
			2220	10.5			0.5
Iron ^e	3.3	7.3	1100	7.2	5.5×10^{-5}	1.15	2.4
			1500	10.3			2.6
			2950	19.8			2.3
	1.6	7.3	7240	15.0	2.5×10^{-5}	0.79	1.5 ^c
Alumina ^f	27	3.9	2300	17.0			2 ^c
	11	3.9	710	9.0	3.1×10^{-3}	0.77	0.5 to 0.7
			520	9.5	7.7×10^{-4}	0.61	3.5 ^c
			280	5.4			3.5 ^c
{ Alumina + Glass Spheres	11 200	3.9 ca. 2.5	500 220	{ 16.5			{ 4

^a The fluid bed diameter was 8.2 cm with the exception of the experiment with 1.6 μ iron particle (charge 7240 g) where the diameter was 14 cm.

^b The average particle size, $\bar{d}_p$, is calculated as $1/\bar{d}_p = \sum x/d_p \cdot x$, where x = weight fraction, dimensionless, of particle diameter d_p . The size distribution was obtained by Coulter Counter analysis.

^c No fluidization was achieved; the velocity at which the formation of channels occurred is listed.

^d Product of Federal Mogul Bower Bearings.

^e Product of Antara Chemicals, Division of Aniline and Film Corporation.

^f Product of Aluminum Company of America.

Results and Discussion

For all materials, Δp increased initially with increasing gas velocity in a fashion similar to that for a packed bed. After the Δp exceeded the value Δp_{fb} (the characteristic pressure drop for incipient fluidization; Δp_{fb} = weight of bed/cross section of bed), it decreased to a value which was about 15% smaller than Δp_{fb} . (The pressure drop Δp remained constant and was equal to Δp_{fb} after fluidization had begun only in the case of 137 μ nickel particles.) The decrease in Δp was an indication that channels (regions of low gas resistance) has formed in the bed. With a further increase in gas velocity, the pressure drop began to increase again in the

case of nickel particles ($\bar{d}_p^* = 18 \mu$), alumina particles ($\bar{d}_p = 27 \mu$), a mixture of 70 w/o alumina particles ($\bar{d}_p = 11 \mu$) and 30 w/o glass spheres ($\bar{d}_p = 200 \mu$), and iron particles ($\bar{d}_p = 3.3 \mu$); also, the heat transfer coefficient increased sharply in these instances indicating that fluidization started. In tests with alumina particles with a $\bar{d}_p$ of 11μ and iron particles with a $\bar{d}_p$ of 1.6μ , the pressure drop did not increase again and no change in the heat transfer coefficient occurred; however, very stable gas channels could be visually observed even at gas velocities up to approximately 50 cm/sec. A typical plot of both the pressure drop in the form of $\Delta p / \Delta p_{fb}$ and the heat transfer coefficient as a function of the gas velocity in those cases where fluidization was achieved is shown in Figure II-5.

Figure II-5

FLUIDIZATION OF FINE IRON PARTICLES

Effect of Gas Velocity Pressure Drop
and Heat-transfer Coefficient

($\bar{d}_p = 3.3 \mu$; bed diameter = 8.2 cm;
static bed height = 10.3 cm)

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The incipient fluidization velocities, obtained by means of the pressure drop and heat transfer measurements, were used to determine the fluidizability indices (see Table II-15) as defined previously. In those instances where fluidization was not obtained at all, the velocity at which the formation of channels was observed is substituted in the index.

The fluidization index appears to be related to a force ratio which is defined as the ratio of the gravitational force, G_p , of a particle and

* For the definition of the average particle diameter, $\bar{d}_p$, see footnote b in Table II-14.

the sum of G_p and the adhesive force, F_p [Fluidization index = $\sqrt{G_p/(G_p + F_p)}$]. Comparing the fluidization index to the force ratio is appropriate since the calculated incipient fluidization velocity is related to the weight of a particle while the observed incipient fluidization velocity is related to the sum of gravitational and adhesive forces. The frictional force, which can be shown to be relatively small, is neglected.

Table II-15

**FLUIDIZATION OF FINE PARTICLES.
RESULTS OF THE FLUIDIZATION EXPERIMENTS**

Material	Average Particle Diameter $\bar{d}_p$ (μ)	Force Ratio, $G_p/(G_p + F_p)$	Fluidizability Index	
			$\mu_{\min. \text{ calc.}}$	$\mu_{\min. \text{ obs.}}$
Nickel	137	0.4		1.1
Nickel	18	1.8×10^{-2}		2.5×10^{-1}
Alumina	27	1×10^{-2}		2×10^{-1}
Alumina	11	2.6×10^{-3}		5 to 7×10^{-3} ^a
Alumina + Glass Spheres	11 200	b		5×10^{-3} ^c
Iron	3.3	2.5×10^{-3}		1.5×10^{-3}
Iron	1.6	6.1×10^{-4}		$\sim 5 \times 10^{-4}$ ^a

^aNo fluidization was achieved, the velocity at which channeling occurred was substituted for $\mu_{\min. \text{ obs.}}$ to calculate the index.

^bNo data available

^c $\mu_{\min. \text{ calc.}}$ for 11 μ alumina particles was used to calculate the index.

The results obtained thus far show that the fluidizability index decreases with diminishing force ratio, which means, as F_p becomes large in comparison with G_p , the material becomes more difficult to fluidize. Fluidization was achieved with spherical particles (18 μ nickel, 3.3 μ iron) as long as $G_p/(G_p + F_p)$ was not smaller than approximately 1×10^{-3} and for irregular shaped material (27 μ alumina) when $G_p/(G_p + F_p)$ was larger than about 3×10^{-3} .

A preliminary and tentative explanation of the above results may be formulated as follows: The difficulties associated with the fluidization of small particles are believed to be due to the interparticle adhesive force which in turn results in the formation of channels. The channels are unstable as long as the force ratio is in the range of about 1 to 1×10^{-1} ; i.e., the adhesive forces between particles are relatively small and due to the relatively free movement of particles into the channels, the channels disappear immediately after formation with the production of gas bubbles in

the bed. The presence of bubbles results in better quality of fluidization. However, the smaller the force ratio becomes, (i.e., when the particle adhesive force is large compared to the weight of the particle), the more stable are the channels. When the force ratio is less than about 10^{-3} , gas channels become stable and hence, no particle movement into the channel occurs; this was shown for 1.6μ iron particles and 11μ alumina particles. In these instances provisions must be made to disturb the stability of these channels in order to fluidize the particles. Such a channel disturbance was achieved by the addition of 200μ glass spheres to a bed of 11μ alumina particles. (The adhesive force of the glass spheres was negligible compared with their weight.)

Summarizing, the work to date shows the fluidizability of a material may be predicted from measurement of interparticle adhesive force. The fluidization of fine particles may be improved by the addition of relatively large particles.

Future Work

Future work will be directed toward three objectives: (1) to establish a relationship between the fluidizability and interparticle adhesion and friction, (2) to investigate the effect of the fluidizability index on the quality of fluidization, the quality being expressed by the heat transfer properties of the bed, and (3) to evaluate means of achieving fluidization in systems where stable gas channels prevail.

3. Process Studies on the Recovery of Uranium from Highly Enriched Uranium Alloy Fuels

Development studies were continued on a fluid-bed volatility process for recovering highly enriched uranium from uranium-alloy fuels. The overall objectives of these studies are to develop and demonstrate an economical, high-decontamination, and high (99%) uranium recovery process that is applicable to a variety of fuels. Presently, tests are being conducted with uranium-aluminum and uranium-Zircaloy alloy fuels.

The process involves hydrochlorination of the fuel subassemblies to separate the bulk of the alloying material as a volatile chloride followed by a fluorination step to recover the uranium as the hexafluoride; both reactions are conducted in the same vessel. These reactions are highly exothermic and by conducting them in a fluid bed of granular alumina advantage is taken of the excellent heat transfer characteristics of fluid bed systems and near isothermal conditions are obtained. The progress of the reactions can be followed continuously by measuring the concentration of key components in the off-gas stream by the use of in-line thermal conductivity cells.

Hydrochlorination is carried out at temperatures greater than the sublimation point of the chloride of the alloying element (sublimation points at 1 atm for ZrCl_4 and AlCl_3 are 331°C and 180°C , respectively), thereby providing a means of separating the main fuel constituents. During hydrochlorination, uranium is converted to solid uranium trichloride. The uranium chloride remains, for the most part, associated with the fluid-bed material; however, a portion of the uranium chloride is entrained in the gas stream and is collected on a packed bed of alumina which serves as a high-temperature filter. After the fuel charge has been completely reacted, the bulk of the solid chlorides are converted to fluorides by reaction with hydrogen fluoride at 350°C . This step was adopted for use in process studies to avoid the production of gaseous chlorine and chlorine fluorides in the direct fluorination of uranium trichloride. However, it may not be necessary to prescribe this processing step in the commercial application of the process. The system is then fluorinated with elemental fluorine and the uranium is recovered as the volatile hexafluoride (sublimation point for UF_6 at 1 atm is 56.6°C).

Currently experimental work is being carried out in two facilities: a bench-scale unit with a $1\frac{1}{2}$ -in. dia. reactor and a pilot scale facility with a 6-in. dia. reactor. The objectives of the studies in the bench-scale reactor are to establish suitable conditions for each of the steps in the reaction sequence and to evaluate the suitability of packed beds as high temperature filters. The goal of the investigation in the pilot-scale reactor is to demonstrate the process on a practical engineering level. These studies are being conducted with the nonirradiated fuel material. Studies involving highly irradiated material are planned for another bench-scale ($1\frac{1}{2}$ -in. dia.) unit now being assembled for operation. Corrosion studies in support of the fluid-bed volatility program on both high-enriched and low-enriched fuel are also in progress. The developments to date in the various phases of this program are outlined in the following.

a. Bench-Scale Hydrochlorination and Fluorination Reaction Studies on Enriched Uranium-Alloy Fuels and Evaluation of Packed-Bed Filters
(D. Ramaswami and J. Strand)

Process development studies on the hydrochlorination and fluorination steps of a fluid-bed volatility process for the recovery of enriched uranium from uranium-alloy fuels were continued in a $1\frac{1}{2}$ -in. dia. fluid-bed reactor (nickel-200) system. The apparatus and experimental procedure have been described in detail in an earlier report (ANL-6569, pp. 114-118). Presently, tests are being conducted with normal uranium-Zircaloy-2 and normal uranium-aluminum alloy fuels.

In recent studies (ANL-6800, pp. 271-282), operating conditions which gave the desired (99%) recoveries of uranium were reported for processing both types of alloys. Considerable flexibility in the choice

of operating conditions of temperature and reactant concentration was found to exist. The operating conditions were similar for both types of alloys except that a lower temperature can be used during hydrochlorination of aluminum fuels. Recommended temperatures for the hydrochlorination of uranium-zirconium alloy subassemblies were 350 to 450°C for the fluid bed and 330 to 350°C for the packed-bed filter. For the hydrochlorination of uranium-aluminum alloy subassemblies, temperatures of 200 to 400°C for the fluid bed and 180 to 200°C for the packed-bed filter proved satisfactory. The concentration of HCl in the feed was varied from 5 to 75 v/o to maintain high reaction rates. The hydrochlorination rates averaged ~30 to 40 g of alloy per hour. Alumina in 6 to 12-in. deep static beds was found to satisfactorily retain the particulate uranium chlorides entrained from the fluid-bed reactor during hydrochlorination. Nearly complete conversion of residual chlorides to fluorides was accomplished by hydrofluorination for 2 hr at temperatures of 275 to 350°C. Fluorination, initiated at a low temperature (250°C) and with a low fluorine concentration, and completed at a high temperature (500°C) and high fluorine concentration resulted in very low retention of uranium by alumina at the end of fluorination.

Three additional runs were made in the current work to

(1) test an improved fluorination procedure which requires very low fluorine flow rates and obviates the recycle of fluorine. (Runs Zr-42, Al-5); (2) determine whether the previously established operating conditions would be applicable to the processing of a fuel in which fission product elements were alloyed with uranium-Zircaloy-2 (Run Zr-42); (3) confirm the reproducibility of the distributions reported previously (ANL-6800, p. 277) for the minor elements of Zircaloy-2 (Run Zr-41); (4) determine the distribution of fission products added to the reactor as an alloy with the fuel (Run Zr-42) and compare the results with those obtained previously (ANL-6800, pp. 274 to 277) from tests in which simulated fission products were added separately to the fluid-bed material; and (5) test the suitability of using sintered alumina rather than a fused form for both the fluid and filter beds while processing uranium-zirconium alloy subassemblies (Runs Zr-41 and Zr-42).

Process Conditions

Miniature, multiplate fuel element subassemblies (5 to $8\frac{1}{2}$ -in. long), similar to those used in the previous work, were processed in the current runs. Four 5.2 w/o uranium-aluminum alloy subassemblies weighing 46 g each were used in Run Al-5. Two 1.9 w/o uranium-Zircaloy-2 subassemblies (137 g each) and 13.7 g of 11 simulated fission products were added separately to the reactor and reacted in Run Zr-41. The eleven fission product elements used in Run Zr-41 were strontium, yttrium, niobium, molybdenum, ruthenium, rhodium, antimony, tellurium, cesium, barium, and cerium. The composition of the fission product mixture was similar to that used previously and was based on the calculation by Burris and Dillon (ANL-5742, pp. 29-30) for ^{235}U with a 150-day irradiation, 30-day cooling. In Run Zr-42,

two subassemblies (205.5 g each) made of 4.0 w/o uranium-Zircaloy-2 alloyed with fission product elements were processed. The alloy containing fission product elements and uranium-Zircaloy-2 was prepared at Battelle Memorial Institute utilizing consumable electrode arc-melting techniques. The weight percents of inactive fission products in the alloy ingot were determined to be: cerium, 0.7, niobium, 0.005, ruthenium, 0.1, molybdenum, 0.03 to 0.07, barium, <0.003, and tellurium, 0.04. The ingot was rolled to 0.069 in. thick²¹ plates and the subassemblies were fabricated from these plates.

Sintered alumina* was used as bed material in the fluid-bed reactor and also as a packed-bed filter in all cases except for the packed bed in the aluminum run (Al-5). In this instance, fused alumina** (534 g, 10-in. depth) from a previous run with uranium-aluminum elements was reused. The current experiment with aluminum alloy employed a fluid bed consisting of 320 g of -40 +120 mesh sintered material from a previous run, whereas in the zirconium alloy runs, the fluid-bed charge was 320 g of -30 +60 mesh fresh alumina. A coarser material, -14 +20 mesh, was used for the filter beds (6-in. depth). The reused fluid bed and filter bed contained 0.004 w/o and 0.003 w/o residual uranium, respectively.

The complete reaction cycle, hydrochlorination, hydrofluorination and fluorination was used in all three runs. The hydrochlorination of the uranium-aluminum alloy was carried out while maintaining the fluid bed at a temperature of 250°C and the filter bed at 200°C in a period of 7 hr. The corresponding temperatures during the hydrochlorination of uranium-zirconium alloys were ~400 and ~350°C. The hydrochlorination time was 8 hr for Run Zr-41 and 11 hr for Run Zr-42. Almost similar quantities of HCl (2.3 to 2.9 stoichiometric amounts) were used in the three runs.

The operating conditions during hydrofluorination were similar for all the runs. This step was conducted with 25 to 50 v/o HF in the feed gas for a period of 1 to 2 hr at an average temperature of 350°C for both the fluid bed and packed-bed filter.

Two different fluorination procedures were used, the main difference between the two being the state of the alumina bed in the fluid-bed reactor during the final part of fluorination. The alumina in the fluid-bed reactor was operated in a static-bed (nonfluidized) condition during the final parts of the two most recent runs (Al-5 and Zr-42). In Run Zr-41, the bed was maintained fluidized throughout the entire fluorination period. In the aluminum run, the following 3-part fluorination of the fluid bed was carried out: (1) gradual heating from 250°C to 500°C in a period of 1½ hr while the

* Type T-61 manufactured by Aluminum Company of America.

** Type 38 Alundum manufactured by Norton Company.

²¹ The Shippingport Pressurized Water Reactor, Addison-Wesley Publishing Company, Reading, Massachusetts, 1958, p. 586.

alumina was fluidized with 5 v/o fluorine, (2) gradual reduction of the diluent nitrogen feed to a negligible amount during the next 1/2 hr resulting in a static condition for the alumina (the fluorine feed rate and the temperature were not changed), and (3) maintaining the alumina at 500°C as a static bed for the next 2 hr under 95 v/o fluorine. The same temperature sequence was used in the packed-bed filter. For Run Zr-42 a modified fluorination procedure was employed to determine the effects of temperature and time on the removal of uranium from the static alumina bed. The modified procedure involved four separate steps: (1) heating the fluid bed from 250°C to 400°C in a period of $1\frac{1}{2}$ hr, while the alumina bed material was fluidized with 5 v/o fluorine in nitrogen; (2) reducing, during the next $1\frac{1}{2}$ hr, the nitrogen concentration in the reacting gas to nearly zero (~ 95 v/o fluorine), thereby producing a static-bed condition within the reactor; (3) maintaining the static bed at 400°C for 2 hr; (4) concluding the fluorination at 500°C for 11 hr under static-bed conditions. During Run Zr-42 the three-step fluorination technique was used for the packed-bed filter. Of particular advantage, with the static-bed procedure, the fluorine feed rates were low and constant during the entire fluorination period, 0.15 and 0.4 liter/min at 70°F and 1 atm during the aluminum and zirconium runs, respectively.

In the other run with zirconium, Run Zr-41, the fluorination was conducted for 2 hr at each of two temperature levels, 250°C, followed by 500°C. At each temperature level, the concentration of fluorine was gradually increased from 5 to 90 v/o during the first $1\frac{1}{2}$ hr, and then left at the high value for the remaining period.

Results and Discussion

Effectiveness of the New Static-Bed Fluorination Procedure. The uranium retained by alumina at the end of fluorination during Run Al-5 was very low. The final concentrations of uranium in alumina were 0.009 and 0.007 w/o for the sintered alumina in the fluid bed and for the fused alumina in the packed-bed filter, respectively. These values correspond to a uranium removal of 99.6%. The material remained free-flowing and was readily removed after the experiment. These levels of uranium are similar to those retained at the end of previous runs in which the bed had been maintained in a fluidized state continuously, indicating that the current static-bed fluorination procedure is as effective for removal of uranium. The fluorine required in the current run was less than 1/10 of that in previous runs, suggesting fluorine recycle (by pumping) may not be required.

Effect of Fluorination Temperature Sequence on the Recovery of Uranium from Alumina. Results now show the 250-500°C fluorination sequence results in lower uranium retention than the 250-400°C sequence under static-bed conditions as well as under all-fluid bed conditions (ANL-6648, p. 164). The concentration of uranium was 0.066 w/o at the end

of the 400°C fluorination (Run Zr-42) while the corresponding value for the run (Al-5) with the higher final temperature was 0.005 w/o. Although a comparison is made here of an aluminum experiment with one involving zirconium, the comparison is considered valid.

Subsequent fluorination at 500°C for 5 hr of the bed treated at 400°C resulted in additional recovery of uranium; the residual concentration of uranium in alumina decreased from 0.066 w/o to 0.009 w/o. No further reduction in the concentration of uranium was achieved by continuing the fluorination at 500°C for an additional 6 hr. The concentration of uranium appears to reach an equilibrium value for each level of temperature and fluorine concentration.

Processing of Uranium-Zircaloy Alloyed with Fission Product Elements. Results were comparable for the processing of fuel charges in which fission product elements were alloyed with uranium-Zircaloy-2 and those obtained from experiments in which fission products were added separately to the bed material. The average alloy reaction rates were 37 and 34 g/hr and the HCl used was 2.9 and 2.6 times the stoichiometric amounts, respectively, for Runs Zr-42 and Zr-41, the former with the alloyed fission products. The concentrations of uranium in alumina at the end of fluorination were also similar, 0.009 and 0.008 w/o uranium. High recovery of uranium was achieved, over 99% of that accounted for. These results indicate, in addition to the applicability of similar reaction conditions to various kinds of charges, the effectiveness of the new static-bed fluorination technique for processing uranium-Zircaloy alloys.

The uranium material balances in these two runs were highly satisfactory. Typically, the uranium accounted for in the experiment with the prepared fission product alloy was 100.8% of that in the charge. This agreement between the quantity of uranium charged and that accounted for indicates the reliability of the earlier material balances which were based only on the uranium accounted for in the product and waste streams since the concentration of uranium in the charge in the earlier runs was nonuniform.

The overall distributions for minor elements of Zircaloy-2 and fission products in the current runs were consistent with those reported previously (ANL-6800, p. 277). The relative distributions of most of the elements were in conformity with those which might be estimated from the volatilities of their higher valent chlorides and fluorides.

Behavior of Sintered Alumina. Current zirconium runs were the first in which uranium-Zircaloy-2 alloy was processed in beds of sintered alumina. On the basis of these tests it appears that sintered alumina is a satisfactory inert bed material for use in both the fluid-bed and packed-bed filter.

Recommended Operating Conditions for Achieving High Recoveries of Uranium from Uranium-Alloy Fuels. The operating conditions used in the two most recent runs, Zr-42 and Al-5, were found to be the best, to date, and are recommended for processing both uranium-Zircaloy-2 alloy and uranium-aluminum alloy fuels. The conditions for processing both fuels are similar except that possibly lower temperature can be used during hydrochlorination and deeper packed-bed filters are needed while processing the aluminum-alloy fuels. The recommended operating conditions for processing uranium-Zircaloy alloy fuels are:

Bed Material:

High-fired alumina (fused or sintered).
 Fluid Bed: Sufficient quantity of nominal 40 mesh alumina to cover the element (a multiplate assembly).
 Packed-bed Filter: -14 +20 mesh alumina, 6 in. deep.

Hydrochlorination: Temperature of fluid bed: 350 to 450°C.
 Temperature of packed-bed filter: 330 to 350°C.

Time: ~8 hr per charge.

Gas Velocity: 0.5 to 0.7 foot per second in the fluid-bed and packed-bed filter (down flow of gases).

Quantity of HCl: ~2.5 times stoichiometric amounts.

Concentration of HCl: 5 to 75 v/o as required to maintain high reaction rates.

Fluorination:

Gradual increase in temperature from 250°C to 500°C while fluidizing with 5 to 10 v/o fluorine in nitrogen, then gradual increase in fluorine concentration to 90 v/o.

Total time about 4 to 8 hr depending on the quantity of uranium charge.

For processing uranium-aluminum alloys, packed-bed filter depths of 8 to 12 in. and filter-bed temperatures of 180 to 200°C are desirable; the temperature of the fluid bed may be maintained in the range of 200 to 400°C.

Future Work

Since the objectives of the current investigation in the bench-scale reactor were achieved, the experimental work is being suspended. A statistical correlation of the existing data will be attempted in order to define the effects of specific operating conditions on uranium retention by alumina and on the uranium loss through a packed-bed filter during hydrochlorination. These correlations are expected to facilitate process scaleup.

- b. Pilot Plant Demonstration of the Fluid-Bed Volatility Process for Enriched Uranium-Alloy Fuels
(J. Holmes, J. Barghusen, H. Stethers, C. Schoffstoll, W. Kreamsner)

The first pilot plant demonstration of the fluid-bed volatility process for recovering uranium from enriched uranium-alloy fuels was successfully completed using a uranium-Zircaloy-2 fuel charge. Prior to the run with uranium-containing assemblies, six shakedown experiments were conducted, the final three experiments being performed during this report period and the initial three experiments having been reported in ANL-6800, p. 282. The pilot-scale facility consists of a 6-in. dia. halogenation reactor, a 9-in. dia. packed-bed filter for retaining particulate uranium chlorides, a 6-in. dia. fluid-bed reactor for converting the volatile alloy chlorides to solid oxide waste with steam, and UF₆ product collection traps. The facility is being operated with fuel charges which simulate Shippingport PWR Core I seed assemblies (Zircaloy-2-uranium alloy) and MTR and ETR assemblies (aluminum-uranium alloy). The processing capacity of the pilot plant is about 30 kg per batch of Zircaloy fuel and 14 kg per batch of aluminum fuel.

The objectives of the shakedown experiments (Runs 1 through 6) were (1) to gain operating experience with the equipment and instrumentation, (2) to determine the effect of HCl feed rate and concentration on alloy reaction rate, (3) to demonstrate the operation of the hydrolysis reactor for zirconium-based and aluminum-based fuels, and (4) to demonstrate the operability of a pilot-scale packed-bed filter. The objective of the initial uranium-Zircaloy-2 run (Run 7) was to demonstrate good uranium removal from the beds using a two-step fluorination procedure established during bench-scale investigations (see Section II-B-3-a of this report).

Equipment Modifications

Prior to the final shakedown experiment, two modifications were made to the pyrohydrolysis reactor which have significantly improved its operation. A bubble-cap gas distributor has been replaced with a 60° cone bottom which has a ball check valve for retaining solids. This modification was made because of accumulation of bed particles in the chamber below the distributor plate and subsequent plugging of the holes in the plate; the new inlet cone has completely corrected the problem.

A continuous product take-off system, shown schematically in Figure II-6, has eliminated a troublesome electrically operated solids valve. The fluidized bed height is now held constant at about 31 in. The product receiver is vented into the column disengaging section. The entire product take-off system is heated to prevent condensation of steam.

Figure II-6

FLUID-BED PYROHYDROLYSIS REACTOR

108-7981

difference being the fluid-bed temperatures employed during hydrochlorination. The bed temperatures are approximately 100°C higher for hydrochlorination of Zircaloy fuels; typical bed temperatures are 350°C for aluminum and 450°C for Zircaloy. The difference in the hydrochlorination temperature for the two fuels is dictated by the relative volatility of zirconium and aluminum chlorides. (The sublimation points at 1 atm are 331°C for ZrCl_4 and 180°C for AlCl_3 .) A summary of the processing conditions used in current tests is presented in Table II-16.

During the fluorination step of the pilot plant runs with uranium alloy assemblies, two sodium fluoride (NaF) traps in series are being used to collect the UF_6 product. The NaF traps are easy to operate and offer a simple means for obtaining analytical samples. In preparation for a run, each of the traps is charged with 9 kg (6-in. bed diameter) of 1/8-in. pellets of sodium bifluoride ($\text{NaF}\cdot\text{HF}$).^{*} The pellets are activated

^{*} Obtained from Harshaw Chemical Company.

Experimental Procedure and Conditions

Details of the equipment and the operating procedure were reported previously in ANL-6800, pp. 282-290. The fuel charges in the current shake-down runs consisted of welded multi-plate assemblies of aluminum which weighed 12.1 kg (Run 4) and 12.3 kg (Run 5) and of zirconium which weighed 19.15 kg (Run 6). In the first run with an unirradiated uranium alloy charge (Run 7), the welded, multiplate uranium-Zircaloy-2 assembly weighed 19.6 kg. Each run involved complete hydrochlorination of the fuel assembly followed by a hydrofluorination reaction step. The fluorination reaction step was carried out only in the experiment (Run 7) with the uranium alloy charge. The pyrohydrolysis column was operated in series with the main reactor in each of the runs in order to convert the volatile wastes (either zirconium or aluminum chlorides) to solids (oxides).

The conditions for processing aluminum and zirconium alloy fuels are nearly identical, with the major difference being the fluid-bed temperatures employed during hydrochlorination. The bed temperatures are approximately 100°C higher for hydrochlorination of Zircaloy fuels; typical bed temperatures are 350°C for aluminum and 450°C for Zircaloy. The difference in the hydrochlorination temperature for the two fuels is dictated by the relative volatility of zirconium and aluminum chlorides. (The sublimation points at 1 atm are 331°C for ZrCl_4 and 180°C for AlCl_3 .) A summary of the processing conditions used in current tests is presented in Table II-16.

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^{*} Obtained from Harshaw Chemical Company.

for UF_6 absorption by desorbing the hydrogen fluoride at $300^\circ C$ in a stream of nitrogen. Uranium hexafluoride is absorbed with a temperature of $100^\circ C$ at the inlet to the first trap and $30^\circ C$ at the outlet of the second trap. At the end of the run, the entire bed is ground and sampled for analyses. Results from preliminary tests showed that of the uranium retained by the two NaF beds in series, over 99.8% is collected in the first bed. The efficiency of the absorption has been shown to be over 99%.

Table II-16

TYPICAL PROCESSING CONDITIONS AND RESULTS FOR PILOT PLANT EXPERIMENTS

I. Hydrochlorination		Zircaloy Fuel PWR Type	Aluminum Fuel MTR and ETR Type	II. Hydrofluorination		Zircaloy Fuel PWR Type	Aluminum Fuel MTR and ETR Type
A. Typical Charge				A. HF Concentration (v/o)			
Weight (kg)		20	7	B. Superficial Gas Velocity (ft/sec)			10-20
No. Plates		14	19	C. Process Temperatures ($^\circ C$)			0.5
Length (in.)		48	36	Reactor Bed			350
Uranium (g)		180	280	Packed-Bed Filter			350
B. Average Inlet HCl Concentration (v/o)		70	80	D. Reaction Time (hr)			2.0
C. Superficial Gas Velocity (ft/sec)		0.6	0.6				
D. Process Temperatures ($^\circ C$)				III. Fluorination			
Reactor Bed		450	350	A. F ₂ Concentration (v/o)			<5
Reactor Wall		350	300	0 to 2.0 hr			80-100
Packed-Bed Filter		350	200	2.0 to 4.0 hr			
Pyrohydrolyzer Bed		350	300-350				
E. Processing Rates				B. Superficial Gas Velocity (ft/sec)			
Average HCl Utilization (%)		50	60	0 to 2.0 hr			0.5 (fluidized bed)
Reaction Rate (kg/hr)		2.0-3.0	1.0-2.0	2.0 to 4.0 hr			0.03 (settled bed)
Reaction Time (hr)		7-10	4-5				
F. Inert-Bed Material				C. Process Temperatures ($^\circ C$)			
Reactor Bed		Alcoa T 61 Alumina, 28-100 mesh		Reactor Bed and Packed-Bed Filter			
Packed-Bed Filter		Alcoa T 61 Alumina, 14-28 mesh		0 to 2.0 hr			250 increasing to 500
Pyrohydrolyzer Bed		Final oxide bed from previous run		2.0 to 4.0 hr			500
				D. Reaction Time (hr)			4.0

The hydrochlorination periods were 7.9, 6.5, 8.6 and 10.9 hr for Runs 4, 5, 6, and 7, respectively. The average temperatures of the fluid bed during hydrochlorination were $380^\circ C$ and $365^\circ C$ when zirconium was being reacted (Runs 6 and 7) and were about $370^\circ C$ and $290^\circ C$ when the aluminum was being reacted (Runs 4 and 5). The respective hydrofluorinations were of 1- to 2-hr duration at bed temperatures of $260^\circ C$ to $350^\circ C$. The fluorination step in the run with the uranium alloy (Run 7) was conducted with a low (5.7%) inlet fluorine concentration for the first 2 hr. During this period, the reactor bed and filter bed were heated from 250 to $500^\circ C$. The final 2 hr of fluorination were conducted at $500^\circ C$ with 80 v/o fluorine during which time the reactor bed was in a settled (nonfluidized) state.

Results and Discussion

A summary of representative processing conditions and results based on data obtained from pilot plant runs made to date is shown in Table II-16. These conditions are not considered optimum, but represent the processing conditions which resulted in satisfactory operation of the pilot plant facility.

Hydrochlorination. The overall HCl utilization was high, 50% to 60%, for typical batch charges of either aluminum or zirconium fuel and was over 70% during the initial two-thirds of a typical hydrochlorination reaction period. During the intervals where the HCl utilization was very high, the utilization as well as the reaction rate was essentially independent of bed temperature indicating that the major factor which limits the reaction rate is the feed rate of the HCl. The observed average reaction rates for typical batch charges were from 2.0 to 3.0 kg/hr for the zirconium fuel and about 1.0 to 2.0 kg/hr for the aluminum fuel. Maximum rates of 4.2 and 3.2 kg/hr were recorded during early parts of the hydrochlorination step for the zirconium and aluminum fuels, respectively.

Bed temperatures were well controlled to desired operating levels by the reactor cooling system even in tests in which greater than 90% HCl was fed to the reactor, as in Run 5 (aluminum) and Run 7 (Zircaloy-uranium). The maximum temperatures in the channels between the fuel plates were 710°C for the zirconium fuels and 465°C for the aluminum fuels. In both cases the temperatures are well below the melting points of the zirconium and aluminum alloys.

The results of the seven runs show that the average hydrochlorination reaction rate increases with increasing HCl inlet concentration but at the expense of overall HCl utilization. The HCl utilization and reaction rates can probably be improved by optimizing the input rate and concentration of HCl and by arranging the charge in the reactor to utilize more effectively the cross-sectional area of the column. Only about 20% of the column cross-sectional area was occupied by the plate assemblies in the current series of runs. The overall HCl utilization can also be improved by hydrochlorinating the first fuel charge to the point where the rate starts to diminish (about 60 to 80% completion), and then charge a second, third, fourth, etc. element after the previous charge is reacted to this point. With such a procedure, the period of low HCl utilization which occurs near the end of a single batch hydrochlorination is minimized. The hydrofluorination and fluorination step would be conducted after a number of fuel charges had been hydrochlorinated. The total processing time for typical batch charges of Zircaloy fuel should be less than 20 hr and less than 16 hr for the aluminum alloy fuels; these times include purge periods between process steps.

Pyrohydrolysis. Chemical analyses of products from the pyrohydrolysis reactor indicated that the conversion of chloride to oxide by the reaction with steam has not been complete. In the zirconium runs, the residual chloride in the oxide product ranged from 3.2 to 0.3 w/o. The chloride content of the aluminum oxide products has been about 10 to 4 w/o. The presence of this quantity of chloride in the waste oxide is not expected to be harmful to the storage properties of the solid. The oxide product from the pyrohydrolysis reactor for both fuels was, primarily, in the form of

fine particles (-200 mesh) and there was little or no indication of any oxide coating on the starting bed material. The large proportion of fines did not appear to affect the operation of the reactor; bed temperatures remained uniform and no significant increase in pressure drop across the sintered metal filters was noted.

Packed-Bed Filter. The packed-bed filter operated smoothly in the aluminum runs (Runs 4 and 5); however, an increase in pressure drop across the filter occurred during the hydrochlorination step in both Runs 6 and 7 and blowback of the filter was required. The blowback procedure involves momentarily turning off the main fluidizing gas stream (the beds are static during this short time) and applying a reverse-flow pulse of nitrogen through the filter. This procedure proved to be quite effective.

The increased pressure drop is believed to be caused by deposition of alumina fines from the reactor bed, uranium chlorides, and nonvolatile alloy and corrosion product chlorides, all of which are carried over from the reactor to the filter by the fluidizing gas. Operation with lower reaction wall temperatures (below 350°C) throughout the equipment appears to minimize plugging of the filter.

Uranium-Material Balance. The uranium material balance for Run 7 is presented on Table II-17. The reactor bed after fluorination contained 1.3 g of uranium (0.0036 w/o of the alumina) and the packed-bed filter contained 0.8 g of uranium (0.0083 w/o of the alumina). These uranium concentrations are nearly equal to those obtained in bench-scale work in which uranium removals of greater than 99.5% were demonstrated. The sum of these values represent 1.15% of the uranium charges. Although the loss of uranium to the pyrohydrolysis reactor in Run 7 was high (2.6% of the uranium in the charge), this value can be significantly reduced by adjusting the operating conditions of the packed-bed filter:

1. Lower the operating temperature of the packed-bed filter from 400°C to 350°C thereby reducing the loss of uranium as volatile UCl_4 .
2. Increase height of the filter bed from 5 to 12 in. to increase filtration efficiency.
3. Decrease the frequency of filter blowback which allows uranium particulate material to pass directly to the pyrohydrolysis reactor.

Future Work

In general, the operation of the equipment and instrumentation of the pilot plant installation has been satisfactory for the seven runs made to date. Minor problems have been successfully corrected and the last four runs have been especially smooth.

Table II-17

URANIUM BALANCE (Run 7)

	<u>Weight (g)</u>	<u>Percent</u>
Charge as 0.93% U-Zircaloy (13 g per plate)	182 ± 4	100
<u>Uranium Recovered (g)</u>	179.7	98.7
1) In NaF Traps	176.4	
2) In Activated Alumina	1.4	
3) In Samples	1.9	
<u>U Lost Nonrecoverable (g)</u>	7.1	3.9
1) To Pyrohydrolyser	4.7	
2) To Reactor Bed	1.4	
3) To Filter Bed	0.9	
4) To Scrub System	0.1	
<u>U Accounted for</u>	186.8	102.6

The future program for the pilot plant will include the following:

1. Determine the effects of scale-up from the bench-scale unit (1.5 in.) to the pilot plant apparatus (6.0 in.) on:
 - a. uranium recovery,
 - b. optimum process conditions,
 - c. the fate of the minor constituents of the aluminum and Zircaloy fuels, and
 - d. the reuse of the reactor- and filter-bed material from the standpoint of uranium loss, attrition, etc.
2. Demonstration of:
 - a. fluorine recycle,
 - b. satisfactory pyrohydrolysis of the metal chlorides to disposable oxide waste,

- c. the effects of various fuel loading procedures, including:
 - (1) loading two fuel assemblies one above the other and
 - (2) loading a second assembly before the first is completely reacted,
- d. equipment corrosion life.
- c. High-activity-level Studies on Enriched Uranium Alloy Fuels
(A. Chilenskaskas, K. S. Turner,* J. Kincinas, W. Gottwald**)

Work is proceeding on the installation of a bench-scale facility (see ANL-6800, p. 290) for the study, at high radiation levels, of the fluid-bed volatility process for highly enriched uranium alloy fuels. Irradiated specimens of both uranium-Zircaloy and uranium-aluminum fuels will be used as fuel charges to investigate (1) the distribution of fission products, (2) extent of decontamination and (3) the effects, if any, of irradiation and fission products on uranium recovery and alloy reaction rates. The equipment is similar to that previously described (see ANL-6569, pp. 114-118) for inactive studies, but, in addition, will include a series of sodium fluoride (NaF) traps together with cold traps for UF₆ collection and purification. The re-action cycle will also be similar to that used for the inactive studies (see Section II-B-3-a of this report) except that the hydrofluorination step may not be included. The unit will be installed in the Senior Cave facility of the Chemical Engineering Division.

All of the process equipment components have been fabricated. To carry out preliminary testing of the complete unit, the equipment components were assembled in the cave service area. A preliminary check-out of the anticipated operating procedure was made using Model 8 (mechanical) manipulators installed in the service area. Although not all of the steps in the procedure could be conducted with these manipulators, no difficulties are expected to arise in the cave where the more flexible electronic manipulators are installed. The preliminary testing revealed the need for the following changes to improve the remote operations of the facility: (1) minor modifications in process equipment items to facilitate satisfactory remote operation with the manipulators, and (2) redesign of some of the devices for remote handling of process materials and of assembly and disassembly tools. These changes are now in progress.

The equipment has been moved to an isolation room which is adjacent to the cave and connected temporarily to a previously installed flow control panel (located in the isolation room) and instrument panel (located in the cave operating area). Cold runs will commence after insulation of the

* Guest scientist from the Australian Atomic Energy Commission.

** On special assignment from ANL Central Shops.

equipment and check-out of the instruments. Following these runs, a final check-out of the remote operation of the facility will be made, after which the facility will be installed in the Senior Cave. Experiments in the cave with irradiated materials are expected to be initiated in the fall of 1964.

d. Corrosion Studies
(A. A. Chilenskas, G. Gunderson)

A corrosion program in support of the Fluoride Volatility Program is in progress. Two types of tests have been used for this program, small-scale laboratory tests in tube furnaces and in-plant exposure tests. The laboratory tests were designed to examine the effect of short-term and long-term exposures of nickel to selected gaseous environments which were representative of gaseous environments found in Fluoride Volatility processing. The in-plant tests consist of exposing specimens within various pieces of pilot-plant equipment and evaluating the corrosion rates after the completion of one or more process cycles.

The first series of laboratory tests in which welded and nonwelded specimens of nickel-200 were exposed to selected gaseous environments was completed. Specimen description, test conditions, and results are summarized in Table II-18. Each value shown represents an average value for four specimens. The environment described in footnote e, Table II-18 is representative of the gaseous environment found in the processing of high-enriched uranium alloy; environment (3) Table II-18 is representative of the gaseous environment found in low-enriched oxide fuel processing while environment (1) Table II-18 serves as a base-line test.

Table II-18

THE LONG-TERM CORROSION OF NICKEL-200 PLATE AND WELDED NICKEL-200 PLATE IN GASEOUS ENVIRONMENTS

Environment	Nickel-200 plate ^a			Corrosion Rate (mils/yr)			Nickel-200 welds ^c		
	240 hr	480 hr	960 hr	240 hr	480 hr	960 hr	240 hr	480 hr	960 hr
(1) F ₂ at 475°C ^d	0.9	0.9	0.9	1315	763	695	2.0	3.4	0.6
(2) F ₂ /HCl at 450°C ^e	2.1	1.5	0.9	67	76	70	3.3	2.2	1.1
(3) F ₂ /O ₂ at 500°C ^f	1.9	3.8	4.1	382	673	707	5.0	4.4	2.2

^a Nickel-200 plate, thicknesses 1/16 and 1/8 in., manufactured by the International Nickel Co., Inc., having a nominal composition in percent: Ni 99.5, C 0.06, Mn 0.25, Fe 0.15, S 0.005, Si 0.05, and Cu 0.05. The corrosion rate was calculated by obtaining the weight loss of the specimen after defiling and assuming that the film had formed uniformly on all exposed surfaces of the specimen.

^b These specimens were made of two pieces of nickel-200 plate, 3/16-in. thick welded together using nickel filler metal 61 and the Inert Gas Tungsten Arc (TIG) process. The filler metal is manufactured by the International Nickel Co., Inc., and has the following nominal composition in percent: Ni 93.0, C 0.15, Mn 1.0, Fe 1.0, S 0.001, Si 0.75, Cu 0.25, Al 1.50, Ti 2.0-3.5, other 0.50. The corrosion rate was calculated by determining the weight loss after defiling and assuming this was lost uniformly from the original weld area.

^c These specimens were made of two pieces of nickel-200 plate, 3/16-in. thick, TIG welded together using nickel-200 filler metal. The corrosion rate was calculated by determining the weight loss of the specimen after defiling and assuming this was lost uniformly from the total specimen area.

^d Environment (1). Specimens held at 475 ± 35°C in an atmosphere of 50 v/o fluorine in nitrogen at about 1000 mm Hg absolute. Gas velocity past coupons about 0.002 ft/sec.

^e Environment (2). Specimens held at 450 ± 10°C in an atmosphere of 50 v/o fluorine in nitrogen alternated with an atmosphere of 50 v/o HCl in nitrogen every 24 hr. System pressure and gas velocity similar to those listed in footnote ^d above.

^f Environment (3). Specimens held at 500 ± 25°C in an atmosphere of 50 v/o fluorine in nitrogen alternated with an atmosphere of 50 v/o oxygen in nitrogen every 24 hr. Flow conditions similar to those listed in footnote ^d above.

The corrosion rate of nickel-200 plate was found to be 0.9 mils/yr for an atmosphere of 50 v/o fluorine in nitrogen with the specimens held at about 475°C. The corrosion rates for the fluorine-hydrogen

chloride environment and fluorine-oxygen environment were found to be somewhat higher than the 50 v/o fluorine environment but the range of values (0.9 to 4.1 mils/yr) indicates that only a small change in the corrosion rate occurs by alternating a fluorine environment with either hydrogen chloride or oxygen. Metallographic examination of the specimens after exposure disclosed no evidence of intergranular penetration.

A comparison of the values for the corrosion rate of nickel-200 welded with weld filler metal 61 and nickel-200 welded with nickel-200 filler shows clearly that the welds made with nickel-200 filler have superior corrosion resistance in every instance. The reason for the high corrosion rates exhibited by the 61 filler metal welds is believed due to the presence of titanium in the filler metal. That is, the titanium present in the weld forms volatile compounds under the film of nickel fluoride which ordinarily forms a protective layer on the nickel. The pressure buildup under the film and subsequent release of pressure results in a rupture and loss of integrity of the film. An analysis by X-ray diffraction has shown TiOF_2 to be the major constituent of a material condensed from the gas stream exhausting from one of the test furnaces in which the specimens were exposed to environment (2), Table II-18.

A comparison of the corrosion rates for nickel-200 plate with nickel-200 welded with nickel-200 shows that the welded specimens exhibit slightly higher corrosion rates than the plate specimens. Both welded and nonwelded specimens were examined metallographically for evidence of intergranular penetration or localized attack in areas where high-stress concentration would be expected. No such evidence was found.

III. HIGH TEMPERATURE REACTOR MATERIALS DEVELOPMENT*

(R. K. Edwards)

A program for the study of high temperature nuclear reactor materials is under way. The objective is to build up a reservoir of basic data which may be used for screening and evaluation. The study will be concerned with the chemical stability of potential high temperature fuels, i.e., oxides, phosphides, sulfides, arsenides, and nitrides of uranium and their solid solutions, and their reactions with hydrogen and its contaminants, and with supporting structural materials, such as tungsten, rhenium, molybdenum, tantalum, and certain alloys. These studies will be done in a quantitative manner to yield thermodynamic and phase diagram information. Each selected fuel-refractory metal-gas system is to be studied in an integrated way, using several methods of investigation that are mutually supporting.

The emphasis of current experimentation is on the determination of the phase diagram of the condensed state of the uranium-uranium dioxide system and on the equilibria between the vapor phase and condensed state of this system. Equipment is being constructed for studies in the hydrogen-uranium-uranium dioxide system. Experimental work to determine the tungsten-uranium-uranium dioxide phase diagram is projected. A previous report (ANL-6800, pp. 297-304) gives a discussion of the estimated relationships in these systems.

A. Effusion Vapor Pressure Studies

(M. S. Chandrasekharaiah, R. K. Edwards, P. M. Danielson)

Vapor pressure measurements are being carried out by the effusion method for the two-phase system, U (liquid, saturated with UO_2) in equilibrium with UO_2 (solid, saturated with U). (This system corresponds to the c-d-e plateau in Figures III-1 and III-2 of the preceding summary report, ANL-6800.) The work is being conducted in collaboration with R. J. Thorn and R. J. Ackermann of the Chemistry Division.

The effusion apparatus that is being used has been described elsewhere¹ and is shown in Figure III-1. Tungsten effusion cells such as that shown in Figure III-2 were used. Each cell consisted of two parts, which were tightly fitted together by means of a tapered joint. The effusion cells were heated by means of an induction coil. A Leeds and Northrup optical pyrometer was used to observe temperatures in the "black body" cavity in the base of the cell. The pyrometer was calibrated by using the melting

*A summary of this section is given on pages 34 and 35.

¹Ackermann, R. J., Gilles, P. W., and Thorn, R. J., J. Chem. Phys. 25, 1089 (1956).

species was determined by uranium alpha particle counting. In the course of a run, a metallic film began to build up on the fused silica condenser opposite the cell and symmetric

Figure III-2

TUNGSTEN EFFUSION CELL

108-7982

The vapor pressure was calculated by means of the equation,

$$P = \frac{W}{a} \left(\frac{2\pi RT}{M} \right)^{1/2} \left(\frac{d^2 + r^2}{r^2} \right),$$

where W is the weight of the effusing vapor per unit time, a is the area of the effusion orifice, r is the radius of the target disc, d is the distance between the orifice and the target, M is the molecular weight of the effusing species, R is the gas constant, and T is the temperature in $^{\circ}\text{K}$. The effusion orifice approximated a "knife edge" and no correction for non-ideality of the orifice was considered necessary.

The data are presented in Table III-1. Vapor pressures calculated on the assumption that the total effusate was uranium monoxide only are also given in the table and are shown in Figure III-3. For measurement series B and D, the uranium dioxide crucibles were fabricated from powder by pressing to shape and sintering at 2250°C in vacuum. These crucibles had densities of about 80% theoretical. For series C, a uranium dioxide crucible of 95% theoretical density was used. All crucibles were outgassed for an hour at high temperatures (2100°C) in vacuum prior to the introduction of uranium metal. In an attempt to reduce the creep problem, the crucible for series D was set on a small tungsten ring; however, some uranium escaped from the tungsten effusion cell after the seventh measurement in this series. Subsequent examination showed that the uranium dioxide crucible had shifted in position and was leaning against the tungsten cell.

Table III-1

VAPOR PRESSURE DATA^a FOR THE SYSTEMU (liquid saturated with UO_2) + UO_2 (solid saturated with liquid U)

Temp. (°C)	Orifice Radius (mm)	Distance d between Orifice and Target ^b (mm)	Weight of Effusate Collected on the Target ($\mu\text{g}/\text{sec}$)	P^c (atm)
Series B				
1983	0.589	94.4	8.27×10^{-2}	2.8×10^{-5}
1984			8.30×10^{-2}	2.8×10^{-5}
1812			8.12×10^{-3}	2.6×10^{-6}
Series C				
1756	0.617	91.05	6.20×10^{-3}	1.6×10^{-6}
2048			1.60	6.3×10^{-5}
1819			5.30×10^{-2}	5.4×10^{-6}
2058			1.80	1.15×10^{-4}
1943			4.60×10^{-2}	2.95×10^{-5}
Series D				
1770	0.564	91.40	3.16×10^{-3}	9.3×10^{-7}
1848			1.54×10^{-2}	4.6×10^{-6}
1918			1.04×10^{-2}	3.2×10^{-6}
1994			2.21×10^{-2}	6.9×10^{-6}
1915			8.73×10^{-3}	2.7×10^{-6}
1769			4.17×10^{-3}	1.2×10^{-6}
1659			6.80×10^{-4}	1.95×10^{-7}

^aThe data are listed in the order of the experiments.^bTarget radius: 9.58 mm.^cCalculated vapor pressures based on the assumption that the effusate consisted of uranium monoxide only. Figure III-3
VAPOR PRESSURE OF URANIUM-
BEARING SPECIES OVER THE
URANIUM-URANIUM DIOXIDE
TWO-PHASE SYSTEM

It is evident from Figure III-3 that Series C shows higher vapor pressures than Series B or D. No explanation is available at this time for the apparent discrepancy. Additional measurements will be made to establish the vapor pressure curve more firmly. Also, the data will be re-evaluated in the light of new mass spectrometric data (see next section of this report), which indicate that the uranium dioxide species may constitute about one-third and one-tenth of the total effusing gas at the highest and lowest temperatures, respectively. A curve for the vapor pressure indicated by the reaction,

has been calculated from the data tabulated by Ackermann and Thorn² and is included in Figure III-3 for comparison. Also given in the figure is a calculated curve for the reaction,

based on data in the same tabulation.² The total pressure over the condensed two-phase region is substantially higher than over pure solid uranium dioxide. This is in agreement with estimates made previously (see Figures III-1 and III-2, ANL-6800). Also, the apparent pressure of the uranium monoxide species in these experiments is lower than that which would be calculated from the data of Ackermann *et al.*² for liquid uranium and solid uranium dioxide, each present at unit activity. This is the expected result if these have decreased activities due to some mutual solubility. As noted in ANL-6800, pp. 297-300, the compositions at the phase boundaries are not known; however, there is evidence of mutual solubility. Some measurements are planned which may establish the compositions at the phase boundaries.

B. Mass Spectrometric Effusion Studies (J. W. Reishus, R. K. Edwards, P. M. Danielson)

Measurements of the relative concentrations of the gaseous species in equilibrium with condensed phases of the uranium-uranium dioxide system are being undertaken. In this study, a mass spectrometer is being used to determine the concentrations of the various species in the vapor effusing from a Knudsen effusion cell. Some measurements have been made; however, the values obtained must be considered tentative until a more complete evaluation of the data is made.

² Thermodynamics of Nuclear Materials, Proceedings of the Symposium on Thermodynamics of Nuclear Materials, International Atomic Energy Agency, Vienna, May 1962, pp. 445-464.

1. Measurement of the Gaseous Species in Equilibrium with Solid Uranium Dioxide and the Heat of Sublimation of Uranium Dioxide

In preparation for the study of the uranium-uranium dioxide system, the operation of the Bendix-T-O-F mass spectrometer was tested by measuring the species effusing from solid uranium dioxide. In order to establish the ionizing potentials for the various species in the effusing vapor, appearance potentials were determined. These determinations were made only for UO_2 and UO_3 since during the course of this work, values for the ionization potentials of the species of interest were published by Mann.³ Table III-2 gives the ionization potentials and energies obtained in this work and from the literature.^{1,3,4} One may estimate from the data listed in the table that voltages which are high enough to ionize UO_3 are likely to cause some electron impact fragmentation of UO_3 , UO_2 , and UO . Each of the respective dissociation products, UO_2 , UO , and U , will contribute to the ion current of these species. The contribution by fragmentation to the ion current for the U and UO species was demonstrated by observing an increase in the ion current ratios, $I_{\text{U}}/I_{\text{UO}_2}$ and $I_{\text{UO}}/I_{\text{UO}_2}$, as the ionization voltage was increased. The UO_2 fragmentation contribution to UO is also evident from the data in Table III-3, in which are listed the ion intensities

Table III-2

IONIZATION POTENTIALS AND DISSOCIATION ENERGIES OF GASEOUS URANIUM-OXYGEN SPECIES

Specie	Ionization Potentials (ev)			Dissociation Energies		
	This Work	Literature Values	Ref.	(to the gaseous elements)(ev)		
U	-	6.11 ± 0.05	(3)			
UO	-	5.72 ± 0.06	(3)	$D_0^0(\text{UO}) = 7.55$		(4)
UO_2	5.8 ± 0.8	5.5 ± 0.1	(3)	$D_0^0(\text{UO}_2) = 14.4$		(1)
UO_3	9.4 ± 0.5	$9.8 \pm <0.5$	(4)	$D_0^0(\text{UO}_3) = 21.0$		(4)

Table III-3

ION INTENSITIES^a OF VAPOR SPECIES OVER STOICHIOMETRIC UO_2 AS A FUNCTION OF TEMPERATURE AND IONIZING ENERGY

Energy (ev)	Temp. (°K)	Order of Measurement	I_{U}	I_{UO}	$I_{\text{UO}_2}/I_{\text{UO}}$	I_{UO_2}	$I_{\text{UO}_2}/I_{\text{UO}_3}$	I_{UO_3}
11	2413	1	1	174	15.2	2650	106	25
11	2375	3	1	126	12.7	1596	145	11
11	2316	5	-	71	11.9	847	165	5
11	2254	7	-	37	10.5	388	194	2
11	2196	6	-	15	11.0	163	163	1
11	2116	4	-	4	13.0	51	-	-
11	2060	2	-	2	13.0	24	-	-
9	2411	1	-	24	41.6	998	-	-
9	2254	2	-	3	51.0	153	-	-
9	2195	4	-	1	62.0	62	-	-
9	2100	3	-	-	-	18	-	-

^aAll ion intensities are reported in amperes multiplied by 10^{11} .

³Mann, J. B., J. Chem. Phys. 40, 1632 (1964).

⁴Berkowitz, J., Chupka, W. A., and Inghram, M. G., Physics Division Summary Report, July-September, 1957, ANL-5786, p. 73.

measured as a function of temperature for two ionizing voltages, 11 and 9 ev. The ionization energy of 9 ev was chosen as the minimum which would permit observation of the UO species. For the series of measurements at 9 ev, the ratio $I_{\text{UO}_2}/I_{\text{UO}}$ is seen to vary with temperature; however, the ratio is nearly constant with temperature for the measurements at 11 ev. This constancy indicates that, at an ionization energy of 11 ev, I_{UO} is more dependent on the UO_2 concentration than on the true UO concentration, and thus I_{UO} contains a dominant contribution from fragmentation of the UO_2 species. Some contribution of this type may also be involved at an ionization energy of 9 ev, and this point will be checked by additional measurements at lower ionization energies, if it proves possible to increase the sensitivity of the mass spectrometer.

The work of Ackermann, Gilles, and Thorn¹ and subsequent measurements by Ackermann and Thorn⁵ established that the nonstoichiometric solid uranium dioxide will, on vaporizing under Knudsen effusion conditions, shift in composition and finally vaporize congruently at the composition $\text{UO}_{2.00}$. The uranium dioxide vaporizing in the mass spectrometric measurements is assumed to have had the stoichiometric composition since all of the measurements were made after the concentrations of each gaseous species had reached steady-state values at the selected temperatures.

It is of interest to compare measured ion current ratios with values which can be calculated by using congruency and thermodynamic relationships. For congruent vaporization of stoichiometric solid uranium dioxide, the total rate of transport of oxygen out of the effusion cell is twice the total rate of transport of uranium out of the cell. Letting R be the effusion rate of the species denoted by the subscripts, we may write,

$$\frac{3 R_{(\text{UO}_3)} + 2 R_{(\text{UO}_2)} + R_{(\text{UO})} + 2 R_{(\text{O}_2)} + R_{(\text{O})}}{R_{(\text{UO}_3)} + R_{(\text{UO}_2)} + R_{(\text{UO})} + R_{(\text{U})}} = 2.$$

The thermodynamic data listed by Ackermann and Thorn² may be used to show that $R_{(\text{U})}$, $R_{(\text{O}_2)}$ and $R_{(\text{O})}$ may be neglected in the above expression and, therefore, the equation

$$R_{(\text{UO})} = R_{(\text{UO}_3)}$$

should be substantially correct. Other thermodynamic relations listed by Ackermann and Thorn² may be used to give the equilibrium constant for the reaction,

⁵Ackermann, R. J., and Thorn, R. J., Argonne National Laboratory, private communications, November 1963.

The equation for the equilibrium constant in terms of partial pressures,

$$K_T = \frac{P_{(\text{UO}_2)}}{P_{(\text{UO})}} \times \frac{P_{(\text{UO}_2)}}{P_{(\text{UO}_3)}},$$

yields the values

$$K_{T=2412^\circ\text{K}} = 4.25 \times 10^2 \text{ and}$$

$$K_{T=2254^\circ\text{K}} = 6.37 \times 10^2.$$

The rate of effusion of a given species is related to its partial pressure by

$$R_i \propto \frac{P_i}{\sqrt{M_i}},$$

where M is the molecular weight of the species. Thus the equilibrium expression may be written,

$$K_T = \frac{R_{(\text{UO}_2)}}{R_{(\text{UO})}} \times \frac{R_{(\text{UO}_2)}}{R_{(\text{UO}_3)}} \div \sqrt{\frac{M_{(\text{UO}_2)} M_{(\text{UO}_2)}}{M_{(\text{UO})} M_{(\text{UO}_3)}}}.$$

Since the divisor is essentially unity,

$$K_T = \frac{R_{(\text{UO}_2)}}{R_{(\text{UO})}} \times \frac{R_{(\text{UO}_2)}}{R_{(\text{UO}_3)}}.$$

Then, if the congruency condition is imposed,

$$\frac{R_{(\text{UO}_2)}}{R_{(\text{UO})}} = \frac{R_{(\text{UO}_2)}}{R_{(\text{UO}_3)}} = \sqrt{K_T}.$$

Calculated values at the two temperatures are,

$$\frac{R_{(\text{UO}_2)}}{R_{(\text{UO})}} = \frac{R_{(\text{UO}_2)}}{R_{(\text{UO}_3)}} = 20.6 \text{ at } 2412^\circ\text{K},$$

and

$$\frac{R_{(\text{UO}_2)}}{R_{(\text{UO})}} = \frac{R_{(\text{UO}_2)}}{R_{(\text{UO}_3)}} = 25.2 \text{ at } 2254^\circ\text{K}.$$

The calculated ratios should be equal to ion current ratios within 3% based on simplified theories of ionization cross sections^{6,7} and detector efficiencies,^{8,9} except for the interference from fragmentation. However, in Table III-3, the $I_{(\text{UO}_2)}/I_{(\text{UO})}$ values for the 9 ev series of measurements are seen to be a factor of two higher than the above calculated values. Correction for the fragmentation contribution to UO from UO_2 would result in even higher observed ratios. Thus the true ratio is not less than a factor of two greater than that derived above from the thermodynamic data used. The values of $I_{(\text{UO}_2)}/I_{(\text{UO}_3)}$ obtained at 11 ev, when compared to the $I_{\text{UO}_2}/I_{\text{UO}}$ values obtained at 9 ev, indicate that UO_3 suffered fragmentation of from 50 to 75%. That is, if $R_{(\text{UO}_3)} = R_{(\text{UO})}$ and the $I_{(\text{UO}_2)}/I_{(\text{UO})}$ ratios obtained for the measurements at 9 ev are assumed to be valid, the value of $I_{(\text{UO}_2)}/I_{(\text{UO}_3)}$ at 2413°K should be essentially the same as the $I_{\text{UO}_2}/I_{(\text{UO})} = 41.6$ value at 2411°K (series at 9 ev). Since the observed ratio $I_{(\text{UO}_2)}/I_{(\text{UO}_3)}$ (series at 11 ev) is 106, it would appear that over half of the UO_3 species was fragmented by ionizing electrons of 11 ev energy.

For the species, UO_2 , and fixed mass spectrometer operating conditions,¹⁰

$$P_{(\text{UO}_2)} \propto I_{(\text{UO}_2)}^+ T.$$

Therefore the expression,

$$\frac{d \ln [I_{(\text{UO}_2)}^+ T]}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R_*}$$

where R_* is the gas constant, may be used to obtain ΔH° , the heat of sublimation of uranium dioxide solid to form UO_2 gas. A plot of $\log [I_{(\text{UO}_2)}^+ T A]$ versus $1/T$ is given in Figure III-4. The term, A , is a constant factor used to convert the $[I_{(\text{UO}_2)}^+ T]$ values to pressures in atmospheres. It was derived from relating our data to the pressure measurements of Ackermann, Gilles and Thorn.¹ The least squares value obtained for ΔH° , 137.1 kcal/mole, is possibly subject to an error of about 0.6 kcal

⁶Bethe, H., Ann. Physik. 5, 352 (1930).

⁷Otvos, J. W., and Stevenson, D. P., J. Am. Chem. Soc. 78, 546 (1956).

⁸Stanton, H. E., Chupka, W. K., and Inghram, M. G., Rev. Sci. Instr. 27, 109 (1956).

⁹Ploch, W., and Walcher, W., Rev. Sci. Instr. 22, 1028 (1951).

¹⁰Honig, R. E., J. Chem. Phys. 22, 126 (1954).

pending more definitive calibration of the optical pyrometer used to measure temperatures. However, it is in good agreement with the value for ΔH° of 137.4 kcal/mole obtained by Ackermann, Gilles and Thorn¹ who assumed negligible contributions from gaseous species other than UO_2 in their measurements of total Knudsen effusion rates. This assumption is well substantiated by the ion intensity data which disclosed only small amounts of species other than UO_2 .

Figure III-4

$[\text{LOG } (I_{\text{UO}_2} T A)] \text{ VS } 1/T$
FOR STOICHIOMETRIC UO_2

The constant factor, A, was used to convert the $(I_{\text{UO}_2} T)$ values to pressures in atmospheres. It was derived from relating our data to the pressure measurements of Ackermann, Gilles and Thorn.¹

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2. Measurement of the Species in Equilibrium with a Two-Phase System of Uranium Dioxide Solid and Uranium Liquid

The uranium dioxide crucible used in the Series D determination of vapor pressures by the Knudsen effusion method (see above) was placed in the tungsten effusion cell assembly and mass spectrometric observations were carried out. Ionizing electrons of 8 ev were used. Although the uranium pellet was removed prior to the introduction of the crucible into the cell, microscopic examination of this crucible showed it to contain a considerable quantity of the uranium phase distributed in the pores of the uranium dioxide crucible.

The results of the study are listed in Table III-4. It is presumed that the liquid uranium phase was present during the measurements. The last measurement, No. 8, was performed at the same temperature as No. 3, but was carried out one hour later. In both experiments the same ratio of $I(\text{UO})/I(\text{UO}_2)$ was obtained. The agreement of these two values is evidence that the two condensed phases still coexisted at the time of the

last measurement or that the change in composition of the substoichiometric solid during the measurements was so small that no significant change in the oxygen partial pressure occurred. The overall oxygen-to-uranium ratio of the residue in the cell was measured and found to be 1.910.

Table III-4

ION INTENSITIES^a OF VAPOR SPECIES OVER U-UO₂ MIXTURES
AS A FUNCTION OF TEMPERATURE

Temp. (°K)	Order of Measurement	IU	IUO	IUO ₂	IUO/IU	IUO/IUO ₂
2333	5	39	1970	735	51	2.7
2297	1	29	1304	393	45	3.3
2251	3	28	1189	319	42	3.7
2195	4	22	710	143	32	5.0
2152	7	17	536	87	32	6.2
2115	2	14	314	41	22	7.6
2034	6	6	124	10	21	12.4
2252 ^b	8	28	1278	348	46	3.7

^aIon intensities are reported in amperes multiplied by 10¹¹.

^bThese observations were made 1 hr after those of "measurement No. 3." The initial weight of the sample was 0.4986 g. The final residue had an oxygen/uranium ratio of 1.91₀. The total time at high temperatures was approximately 2 hr. The total weight loss calculated from the effusion equation was approximately 0.090 g.

Further measurements of the relative concentrations of the gaseous species in equilibrium with the two-phase system, uranium dioxide solid and uranium liquid, will be carried out.

3. Some Tentative Calculations of Oxygen Partial Pressure Relations over UO₂ Solid Relative to UO₂-x Solid

The data from Tables III-3 and III-4 may be combined in such a manner that the oxygen activity of uranium dioxide solid saturated with liquid uranium may be compared with the oxygen activity of the stoichiometric solid. The data for the temperatures 2195°K and 2251°K for the two-phase system and the data for the temperatures 2196°K and 2254°K for stoichiometric UO₂ seem consistent, and they are used in the following calculation.

Consider the following gaseous equilibrium and its mass action expression,

and

$$K_T \times \frac{P_{(UO_2)}}{P_{(UO)}} = P_{(O)}.$$

The relative activity of oxygen is given by,

$$a = \frac{P''_O}{P'_O} = \frac{P''_{(UO_2)}}{P'_{(UO)}} \times \frac{P'_{(UO)}}{P'_{(UO_2)}}$$

where the P'' and P' refer respectively to pressures over the stoichiometric UO_2 solid and over the two-phase system. Ion-current ratios are substituted for pressure ratios and the relative activities obtained are:

$$2195^\circ K, \quad a \approx 54$$

$$2253^\circ K, \quad a \approx 39$$

The possible fragmentation errors are such that these relative activities are probably minimum values.

C. Transpiration Studies of Vaporization (M. Tetenbaum, C. Clifton)

Extension of the vapor pressure measurements to higher temperatures than those possible in the effusion measurements is to be carried out by means of the transpiration method (ANL-6800, p. 302). The vaporization from uranium dioxide will be measured in the temperature range 2000-3000°C with hydrogen and hydrogen-water mixtures as reactive carrier gases and also with inert carrier gases.

Figure III-5

TRANSPIRATION APPARATUS

A schematic diagram of the transpiration apparatus is shown in Figure III-5. The tungsten sample holder and condenser tubes and the rhenium outer tube required for the transpiration apparatus have been received from the vendors. Final assembly of the transpiration apparatus awaits tube modifications that are now being made.

An alternative assembly has been constructed from tungsten-molybdenum alloy and will serve as a backup apparatus. A Brew Model 1064 vacuum resistance furnace capable of reaching a temperature of approximately 3000°C is operational.

D. Phase Diagram Studies, the Uranium-Uranium Dioxide System (A. E. Martin, F. C. Mrazek)

1. Discussion of the Literature

Two studies^{11,12} of the liquidus of this system at high uranium compositions have been reported. Although the techniques employed were similar, i.e., the saturation of liquid uranium with solid uranium dioxide at a given temperature followed by rapid cooling or casting of the product and chemical analysis of the ingot produced, the results of the two studies are in wide disagreement. These two sets of data are given in Table III-5. The liquidus curve from the earlier study¹¹ does not extrapolate reasonably to the composition and melting temperature, about 2870°C, of uranium dioxide. Accordingly, these data suggest a two-liquid immiscibility gap at elevated temperatures. The data of the more recent study¹² extrapolate quite well to the uranium dioxide composition at 2870°C and must be taken as evidence against the existence of an immiscibility gap.

Table III-5

LIQUIDUS DATA ON THE URANIUM-URANIUM DIOXIDE SYSTEM

Reference	Literature Data			Derived Data	
	Temp., °C	a/o O	w/o UO ₂	a/o UO ₂	O/U Ratio
11	1400	0.079	-	0.0395	0.0008
	1600	0.156	-	0.078	0.0016
	1800	0.280	-	0.140	0.0028
	2000	0.432	-	0.216	0.0043
12	1530	-	17.5	15.7	0.315
	1680	-	25	22.7	0.454
	1960	-	42	39	0.779
	2290	-	62	59	1.18

Some data have also been reported on the solidus in this system at elevated temperatures. Gray and Thompson¹¹ reported on the oxygen solubility in solid uranium. A number of studies¹³ have yielded evidence that "uranium dioxide" can exist over variable composition range, possibly considerably¹⁴ deficient in oxygen, at elevated temperatures. It has also been reported¹⁵ that uranium dioxide substoichiometric in oxygen

¹¹ A. G. Gray and J. G. Thompson, CT-2618 (1944).

¹² P. L. Blum, P. Guinet and H. Vaugoyeau, Compt. Rend. 257, 3401 (1963).

¹³ J. Belle, Uranium Dioxide, USAEC, Naval Reactors, Division of Reactor Development, Washington.

¹⁴ E. A. Aitken, H. C. Brassfield and J. A. McGurty, Trans. A.N.S. 6, 153 (1963).

¹⁵ R. N. Duncan and H. M. Ferrari, Trans. A.N.S. 6, 154 (1963).

has a higher melting point than the stoichiometric compound, i.e., that the maximum melting point is at a substoichiometric composition. The formation of solid uranium monoxide has been reported^{13,16} but there appears to be disagreement as to whether it is a stable phase in the binary system uncontaminated with nitrogen or carbon.

There is a need to clarify the qualitative and quantitative relations in the uranium-uranium dioxide phase diagram.

2. Experimental Work

As a preliminary check on the existence of an immiscibility gap in the system, pressed pellets of high purity uranium dioxide, oxygen-to-uranium ratio of 2.02, were arc melted with chunks of high purity uranium on a water-cooled copper hearth. The prepared compositions of the charges corresponded to oxygen-to-uranium ratios of 0.50, 0.75, and 1.00. It was observed in each case that the liquid metal and liquid oxide phases would not fuse together at the temperature of the arc, even after prolonged treatment. The products in each case consisted of metal buttons within oxide buttons.

These observations in themselves indicated that a two-liquid immiscibility gap existed in the system at the temperature of the preparations. Polished specimens of the quenched products of the tests were examined under the microscope. The oxide portions from each test had the same characteristic structure, that of a fine dispersion of elongated uranium particles in a uranium dioxide matrix. The structure obviously corresponded to that of a monotectic composition. The metal portions from each test also had a common appearance, that of a metal phase with a relatively small amount of precipitated oxide. Figure III-6 is a photograph of the $\text{UO}_{0.50}$ product. The oxide monotectic structure and the metal structure are shown on the left and right, respectively.

Experiments of a more quantitative nature are being planned to define the extent of the immiscibility gap and to establish the monotectic temperature. However, some approximate values were obtained from the above experiments as follows:

- (1) The metal and oxide buttons from the three tests were separated crudely and weighed. Material balance calculations made from these weights indicated that the compositions of the metal and oxide buttons at the preparation temperatures, expressed as oxygen-to-uranium ratios, were approximately 0.094 and 1.31 respectively. These numbers are very approximate as the separation of the finer buttons of metal from the oxide phase was incomplete and no correction could be applied for unknown selective vaporization losses.

¹⁶Williams, J., and K. H. Westmacott, Rev. Met. 53, 189-204 (1956).

Figure III-6

PHOTOMICROGRAPH OF THE PRODUCT FROM
ARC MELTING A MIXTURE OF URANIUM AND
URANIUM DIOXIDE AT THE
OVERALL COMPOSITION $\text{UO}_{0.50}$

The quenched monotectic liquid structure, consisting of elongated uranium particles within a uranium dioxide matrix, is seen on the left. On the right is seen the quenched uranium liquid, consisting of precipitated uranium dioxide particles within a uranium matrix.

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(2) The largest metal button from the $\text{UO}_{0.50}$ product was analysed. The oxygen-to-uranium ratio was 0.174. This is only an approximate value for the metal composition at the arc temperature for the same reasons as given under (1).

(3) An areal analysis of the monotectic structure from a photomicrograph was made which indicated that its composition corresponded to an oxygen-to-uranium ratio of 1.15.

Failure of the two liquids to fuse together does not appear to be due to inadequate equilibration conditions. In an earlier series of tests, pressed pellets of mixed powders of uranium and uranium dioxide (reactor grade purity for both) were similarly melted. Even with the more intimate conditions for reaction, a mixture with an oxygen-to-uranium ratio of 1.14 showed the presence of small buttons of the metal phase within the main button which had the monotectic structure. Two other preparations at oxygen-to-uranium ratios of 1.35 and 1.56 yielded no excess metal phase in the form of buttons. Instead, they contained substantial amounts of the monotectic structure and also areas of higher uranium dioxide content. In the latter areas uranium metal, formed by precipitation, was present as a coating around the uranium dioxide grains and also as a deposit within the grains. It is apparent that the compositions of these two preparations lie between the monotectic composition and the composition for uranium dioxide in the phase diagram.

Only a very approximate value for the monotectic temperature, below 2465°C , is available as yet. This value was obtained by remelting portions of the monotectic material.

Thus the combined data indicate rather conclusively the existence of a wide immiscibility gap in the system at temperatures above about 2465°C . The approximate form of the phase diagram is shown in Figure III-7.

Figure III-7
APPROXIMATE FORM OF
URANIUM-URANIUM DIOXIDE
PHASE DIAGRAM

E. Interdiffusion Studies, the Uranium-Uranium Monosulfide System (L. N. Yannopoulos)

Studies of interdiffusion between nuclear fuels of interest and refractory metals that are being considered for use as containers or cladding are important to the program for the development of high temperature reactor materials. Preliminary evidence indicated that solid US can diffuse through a tungsten encapsulation at a considerable rate. Assessment of the magnitude of possible bulk diffusion of US through tungsten was considered of importance in order that an evaluation could be made of the potential use of tungsten as a cladding.

A number of experiments, in which US was sealed inside tungsten containers and subjected to different heat treatments, were carried out. The tungsten crucibles were sealed (in vacuo) by electron-beam welding. During the heat treatments, some of the crucibles developed microcracks in the vicinity of the welds; however, the cracks could be avoided by annealing the crucibles for two hours at 1200°C after the welding operation. The procedure which was found satisfactory was to heat the crucibles slowly to the annealing temperature, and then to cool the crucibles slowly. After this treatment, the crucibles were examined for integrity.

The results of the several experiments are presented in Table III-6. Tungsten crucibles formed by powder metallurgical techniques (Kulite brand) were used in experiments LY-40-a and LY-40-b. These crucibles are porous to a small degree and appreciable penetration of US along the pore structure was observed. However, the lids for these crucibles had been fabricated by a swaging process and were not porous. Penetration of the lids by US did not occur, although the penetration of the crucible was uniform and not limited to regions of direct contact between the US and tungsten. The next two experiments, LY-43 and 44 were carried out in crucibles which were machined by the Elox process from swaged Kulite rod. Penetration by the US was exclusively along tungsten grain boundaries and extended only as far as the first grain diameter. Again, no penetration of the crucible lids took place. A possible explanation, offered by Dr. A. E. Martin, for the difference in behavior of the crucibles and lids was that the Elox process had led to mechanically loosened grains on the surface of the tungsten. For the next two experiments, LY-45 and 46, interiors of the crucibles (swaged tungsten, Elox fabrication) were polished in order to remove any loosened grains. The heat treatment conditions for these experiments were more severe both with regard to time and temperature than those in the previous experiments. The US was molten (m.p. 2460°C) during most of the time. However, no attack on the tungsten grain boundaries was observed. Neither in these experiments nor in any of the previous experiments was any precipitation of US within tungsten grains observed. Further examination to determine whether US dissolves in tungsten will be carried out by use of the electron beam microprobe analyzer when scheduling permits.

Table III-6

EXPERIMENTS ON THE ATTACK OF US ON W CONTAINERS

Experiment No.	Type of W Crucible Used	Initial US Material			Conditions of Heat Treatment	Weight Loss of US during Treatment (w/o)	Microscopic Observations of Cross Sections of W Crucible Wall after Treatment	Micrographic Observations on Polished Cross Sections of Crucible and Contents
		Oxygen Contamination (w/o)	Micrographic Observation	S/U Atom Ratio				
LY-40-a	Sintered pressed powder "Kulite" (wall thickness = 1.5 mm).	0.214	Contaminant UOS phase present.	0.99	Slow heating; hold 2 hr at 1950°C; slow cooling.	~0	No cracks	-
LY-40-b	Sintered pressed powder "Kulite" (wall thickness = 1.5 mm). (Same crucible as LY-40-a.)	0.214	Contaminant UOS phase present.	0.99	Slow heating; hold 1 hr at 2460-2445°C; sudden cooling.	12.6	Considerable number of cracks in the vicinity of the weld.	US had been molten. ^a Penetration of crucible by US to a depth of 0.3 mm. No penetration of crucible top. UOS phase observed in the US.
LY-43	Swaged "Kulite" rod machined into a crucible by the Elox process (wall thickness = 3.1 mm).	0.214	Contaminant UOS phase present.	0.99	Slow heating; anneal 2 hr at 1218°C; slow heating; hold 2 hr at 2372-2351°C; slow cooling.	~0	No cracks	Penetration of crucible only along grain boundaries and only to the extent of 1 grain diameter (~100 μ). UOS phase observed in the US. No penetration of the crucible top.
LY-44	Swaged "Kulite" rod machined into a crucible by the Elox process (wall thickness = 3.1 mm).	0.095	No UOS phase observable.	1.00	Slow heating; anneal 2 hr at 1200°C; slow cooling; slow heating; hold at 2180°C for 3 hr; slow cooling.	~0	No cracks	Penetration of crucible only along grain boundaries and only to the extent of 1 grain diameter (~100 μ). No penetration of crucible top. No UOS phase was observed in the US.
LY-45	Swaged "Kulite" rod machined into a crucible by the Elox process (wall thickness = 3.1 mm). ^b	0.095	No UOS phase observable.	1.00	Slow heating; anneal at 1200°C for 2 hr; slow cooling; slow heating; hold at 2550-2440°C for 4 hr; slow cooling.	~0	No cracks	US had been molten. ^a No penetration of crucible top or of submerged single crystal of W. No UOS phase observable in the US.
LY-46	Swaged "Kulite" rod machined into a crucible by the Elox process (wall thickness = 3.1 mm). ^b	0.095	No UOS phase observable.	1.00	Moderately rapid heating; hold at 2467-2482°C for 64 hr; sudden cooling.	~0.068	A few micro-cracks in the vicinity of the weld.	US had been molten. ^a No penetration of crucible, except in the micro-cracks, or of top. No UOS phase observable in the US.

^aFor the tests in which US melted, small amounts of W precipitated within the US were observed.^bThe interior of the crucible was polished after fabrication.

The data indicate that dense tungsten is suitable for containing US if proper attention is given to fabrication procedures. However, small amounts of tungsten dissolve in the molten US (precipitated spherical tungsten particles are observed in cooled ingots).

IV. CALORIMETRY* (W. N. Hubbard, H. M. Feder)

For many compounds of interest in high temperature chemistry thermochemical data of acceptable accuracy are completely lacking. For some of these compounds this lack is due to experimental difficulties in making the necessary measurements. For others it is due to the difficulty of obtaining a well-characterized sample. A program has been undertaken here to determine some of the needed data. Emphasis has been placed equally on the procurement of well-characterized samples and the development of adequate experimental techniques.

The basic data needed are enthalpies of formation at 25°C. Part of the program of the group consists of determinations of these enthalpies by oxygen bomb calorimetry. However, many of the compounds of interest are difficult to burn in oxygen and, consequently, cannot be studied by this method. To study the compounds that are not amenable to oxygen bomb calorimetry, the techniques of the bomb calorimetric method, which has been developed to a high degree of precision and accuracy, have been modified so that fluorine can be used as the oxidant.

The accumulation of enthalpy of formation data for fluorides is both a necessary preliminary to the general use of fluorine bomb calorimetry for compounds and a valuable program on its own merit. To date, enthalpy of formation values have been determined for the following fluorides: the difluorides of cadmium, magnesium, and zinc; the trifluorides of boron and aluminum; the tetrafluorides of titanium, zirconium, hafnium, and silicon; the pentafluorides of niobium, tantalum, and ruthenium; and the hexafluorides of molybdenum and uranium. The enthalpies of formation of several compounds, boron nitride, silicon dioxide, and the diborides of zirconium and niobium, have also been determined by fluorine bomb calorimetry.

To determine thermodynamic properties at high temperatures one combines values of enthalpies of formation at 25°C with values of the enthalpy of substances at high temperatures. A drop calorimeter system for making enthalpy increment measurements up to 1500°C has been assembled and is being tested. Testing has shown where various improvements could be made. Testing of design concepts for a drop calorimeter for making enthalpy increment measurements up to 2500°C is also in progress. The use of electron bombardment heating for the furnace has been demonstrated. The components of the electron guns are on hand and a design of the complete calorimeter has been drawn.

A. Combustion of Hafnium Diboride in Fluorine (G. K. Johnson, E. Greenberg)

The combustion of hafnium diboride in fluorine is a part of the continuing program to determine the enthalpies of formation of transition metal

* A summary of this section is given on page 35 and 36.

diborides by fluorine bomb calorimetry. The experimental work on this phase of the program has been completed.

The results of six combustions by the technique previously described for zirconium diboride (ANL-6596, p. 173) are presented in Table IV-1. The entries in the table are:

m , the mass of sample burned, as obtained by subtraction of the mass of unburned hafnium diboride from the mass initially charged to the bomb;

Δt_c , the observed increase in the calorimeter temperature, corrected for heat exchanged between the calorimeter and its surroundings;

$\epsilon(\text{calor})(-\Delta t_c)$, the energy equivalent of the calorimetric system minus the contents of the bomb, multiplied by the negative of the corrected temperature rise;

$\Delta E_{\text{contents}}$, the difference between the energy equivalents of the initial and final contents of the bomb, corrected to the hypothetical isothermal process at 25°;

ΔE_{sulfur} , the energy supplied by combustion of the sulfur used to promote combustion;

ΔE_{gas} , the net correction for reducing the pressure of the bomb gas to standard state conditions;

ΔE_{blank} , the combined thermal correction for expansion of fluorine into the evacuated combustion bomb and reaction with the bomb walls;

$\Delta E_{\text{impurities}}$, the net correction for fluorination of the impurities in the sample; and,

$\Delta E_c^0/M$, the energy evolved per gram of hafnium diboride burned.

Table IV-1

RESULTS OF HAFNIUM DIBORIDE COMBUSTIONS

Combustion No.	1	2	3	4	5	6
m , g	1.15307	1.16536	0.59478	0.59348	0.59120	0.59036
Δt_c , deg	1.71368	1.73641	0.94799	0.94223	0.94087	0.94656
$\epsilon(\text{calor})(-\Delta t_c)$, cal	-5757.37	-5833.73	-3184.91	-3165.56	-3160.99	-3180.99
$\Delta E_{\text{contents}}$, cal	-11.12	-11.41	-6.12	-6.16	-5.99	-6.03
ΔE_{sulfur} , cal	422.62	450.96	430.72	419.38	426.85	449.79
ΔE_{gas} , cal	-2.32	-2.32	-2.21	-2.21	-1.41	-1.41
ΔE_{blank} , cal	12.04	12.04	12.04	12.04	12.13	12.13
$\Delta E_{\text{impurities}}$, cal	-18.03	-18.23	-9.30	-9.28	-9.25	-9.23
$\Delta E_c^0/M$, cal g ⁻¹	-4643.41	-4636.07	-4640.00	-4636.70	-4632.37	-4632.50

Mean $\Delta E_c^0/M = -4636.8$ cal g⁻¹

Std. Dev. of Mean = ± 1.8 cal g⁻¹

The boron, oxygen, carbon, nitrogen and hydrogen contents of the sample were determined analytically. The hafnium content of the sample was obtained by difference because of a suspected low bias in its analytical determination. After correction for the amount of hafnium combined with impurities, the boron/hafnium ratio in the diboride phase was determined to be 2.01.

Combination of the value $-4636.8 \text{ cal g}^{-1}$ for the energy of combustion and 200.220 for the molecular weight of $\text{HfB}_{2.01}$ with $-461.40 \text{ kcal mole}^{-1}$ and $-269.88 \text{ kcal mole}^{-1}$, the enthalpies of formation of HfF_4 and BF_3 , leads to a preliminary value of $-73.7 \text{ kcal mole}^{-1}$ for the enthalpy of formation of $\text{HfB}_{2.01}$.

B. Combustion of Tantalum Diboride in Fluorine (G. K. Johnson, E. Greenberg)

A series of combustions of tantalum diboride in fluorine has been completed. The technique used was similar to the one previously described. The results indicate that the precision of the series is excellent. Calculation of the enthalpy of formation of tantalum diboride is in progress.

C. Combustion of Silicon Carbide and Graphite in Fluorine (E. Greenberg, C. A. Natke)

Discrepancies^{1,2} among various literature values for the heat of formation of silicon carbide may be resolved by determining the heat of combustion of silicon carbide and of graphite in fluorine. The heat of formation of silicon tetrafluoride has already been determined.³

The experimental technique developed for the combustion of silicon carbide in fluorine was described in a previous report (ANL-6800, p. 313). Fifteen calorimetric combustions have been completed. Preliminary results are presented in Tables IV-2 and IV-3. Several more calorimetric combustions with varying sample sizes are in progress.

The entries in the tables are similar to those described for Table IV-1 with the following additions:

$\Delta E_{\text{ignition}}$, the electrical energy input for ignition of the fuse, measured with an integrating circuit;

¹Chipman, J., J. Am. Chem. Soc. 83, 1762 (1961).

²d'Entremont, J. C., and Chipman, J., J. Phys. Chem. 67, 499 (1963).

³Wise, S. S., Margrave, J. L., Feder, H. M., and Hubbard, W. N., J. Phys. Chem. 67, 815 (1963).

$\Delta E_{\text{Mo fuse}}$, the correction for the energy supplied by combustion of the molybdenum fuse wire;

$\Delta E_{\text{C}_2\text{F}_6}$ and $\Delta E_{\text{C}_3\text{F}_8}$, the respective corrections for the quantities of fluorocarbon side products formed during combustion.

Table IV-2

PRELIMINARY RESULTS OF SILICON CARBIDE COMBUSTIONS

Combustion No.	Alpha Crystalline Modification									
	1a°	2a°	3a°	1°*	2°	6°	7°*	10°*	12°	
m, g	0.49153	0.47841	0.47179	0.48120	0.48435	0.50894	0.50310	0.49608	0.49657	
Δt_c , deg	2.04395	1.99203	1.95598	1.99999	2.00687	2.11012	2.08182	2.04678	2.05975	
$\epsilon(\text{calor})/(-\Delta t_c)$, cal	-7238.04	-7054.18	-6926.52	-7081.56	-7105.93	-7471.51	-7371.31	-7247.24	-7293.16	
$\Delta E_{\text{ignition}}$, cal	0.29	0.41	0.31	0.81	0.12	0.43	0.07	0.17	0.22	
$\Delta E_{\text{Mo fuse}}$, cal	18.65	26.46	18.72	27.66	9.48	14.55	6.89	15.78	10.44	
$\Delta E_{\text{C}_2\text{F}_6}$, cal	-6.57	-3.69	-14.43	-7.72	-10.79	-15.11	-12.41	-19.15	-27.72	
$\Delta E_{\text{C}_3\text{F}_8}$, cal	-4.17	-0.58	-1.23	-4.65	-6.45	-10.76	-9.74	-16.80	-16.20	
$\Delta E_{\text{impurities}}$, cal	-1.76	-1.72	-1.69	-3.73	-1.74	-1.83	-3.90	-3.84	-1.78	
$\Delta E_c^0/M$, cal g ⁻¹	-14712.43	-14701.41	-14677.80	-14690.75	-14690.43	-14705.53	-14689.72	-14657.07	-14757.64	

Mean $\Delta E_c^0/M$ = 14,698.1 cal g⁻¹

Std. Dev. of Mean = ± 9.2 cal g⁻¹ or 0.06%

*Sample No. 1

**Sample No. 2

Table IV-3

PRELIMINARY RESULTS OF SILICON CARBIDE COMBUSTIONS

Combustion No.	Beta Crystalline Modifications						
	3°	4°*	5°	8°*	9°*	11°	
m, g	0.49780	0.50111	0.49791	0.50609	0.49499	0.49944	
Δt_c , deg	2.06471	2.07864	2.06623	2.10061	2.05564	2.07376	
$\epsilon(\text{calor})/(-\Delta t_c)$, cal	-7310.73	-7360.05	-7316.11	-7437.84	-7278.61	-7342.77	
$\Delta E_{\text{ignition}}$, cal	0.12	0.24	0.07	0.17	0.19	0.17	
$\Delta E_{\text{Mo fuse}}$, cal	18.72	12.42	10.83	12.57	8.36	12.88	
$\Delta E_{\text{C}_2\text{F}_6}$, cal	-4.44	-4.17	-4.88	-5.72	-3.53	-1.93	
$\Delta E_{\text{C}_3\text{F}_8}$, cal	-3.61	-3.03	-3.01	-3.66	-1.79	± 0.00	
$\Delta E_{\text{impurities}}$, cal	-11.85	-5.59	-11.85	-5.64	-5.52	-11.89	
$\Delta E_c^0/M$, cal g ⁻¹	-14688.21	-14687.75	-14711.39	-14701.18	-14709.19	-14703.55	

Mean $\Delta E_c^0/M$ = -14,700.2 cal g⁻¹

Std. Dev. of Mean = ± 4.2 cal g⁻¹ or 0.03%

*Sample No. 3

**Sample No. 4

Four different samples of silicon carbide were studied in order to see if any difference in the heat of combustion of alpha and beta modifications could be detected, and also to check the accuracy of the impurity corrections. The variation of the experimental results is such that no significant difference in the results for alpha and beta or for different samples of each

can be discerned. However, the beta samples are more finely powdered, burn more completely (>99%), and show less scatter in the results than the alpha samples. Additional investigation of these points may be necessary before the significance of the difference (if any) can be established.

Literature values for the enthalpy of formation of tetrafluoromethane vary over a range of several kilocalories. An accurate redetermination by our direct method would be appropriate at this time.

The experimental problem of carrying out calorimetric combustions of graphite in fluorine was discussed in ANL-6800, p. 490. The use of a double-chamber bomb for this combustion is still under investigation. A different approach to this and similar problems is the use of a flow calorimetric system in place of a bomb calorimetric system. This is discussed in the following section.

D. Fluorine Flow Calorimetric System (J. Settle, P. O'Hare, R. Terry)

The rate of reaction of a sample with fluorine in a sealed bomb is largely determined by the rate of diffusion of the gas to the reaction surface. The rate may be varied to some extent by changing the fluorine pressure and/or by diluting the fluorine with an inert gas. The total amount of sample that reacts may be controlled by limiting the quantity of the combustible material or by limiting the fluorine pressure in the bomb. However, the experimenter frequently finds that he must tolerate some unwanted side reaction in order to obtain the optimum yield of the reaction being studied. It was thought that a flow reactor might have some advantages over a sealed bomb reactor, particularly when some of the products of reaction are volatile. Fluorine-sensitive compounds could be kept in an inert atmosphere until it was desired to introduce fluorine and start the reaction. The rate of reaction could be varied simply by varying the rate of flow of fluorine into the reactor. If a jet were used to direct the incoming stream of fluorine directly onto the surface of the combustion sample, the volatile products would be swept away and not impede the diffusion of fluorine to the reaction surface.

A very simple, model, flow reactor has been built. It consists of an inlet line in series with a flowmeter for introducing gases, a Pyrex reaction vessel of about one-liter volume, and an exit line in series with traps and a vacuum system. This flow reactor has been used to study the combustion of graphite, uranium monosulfide, sulfur, silicon, selenium, and boron nitride.

The experiments with sulfur, silicon, selenium, and boron nitride were performed to evaluate their use as ignition aids. It was found that the first three substances and powdered boron nitride ignited spontaneously at fluorine pressures between 0.1 and 1 atm; sintered rods of boron nitride did

not ignite even at 2-atm pressure. The combustion of sulfur and selenium gave very hot flames of short duration; they could be used to ignite uranium monosulfide and sintered boron nitride, which have low ignition temperatures, but they could not be used to ignite graphite, which has a higher ignition temperature. Silicon ignited spontaneously in fluorine, but even at fluorine pressures above 1 atm the reaction rate was rather slow and did not supply heat rapidly enough to heat graphite to its ignition temperature. When silicon was doped with sulfur, the initial combustion of the sulfur heated the silicon enough to create the conditions necessary for a rapid, sustained reaction to occur; the combination was effective for bringing graphite to its ignition temperature.

1. Graphite

The graphite samples burned in the flow reactor were in the form of 1/8-in. or 1/4-in. diameter rods, cut to suitable lengths. A small hole was drilled in the upper end of a rod for insertion of the igniter. The rod was kept in a vertical position during combustion by an appropriate fastening of its lower end to a nickel sample holder. The reaction vessel was evacuated and charged to 800 mm Hg absolute pressure with argon. The flow of fluorine, at about 1000 ml/min, was started into the reaction vessel. During combustion, the pressure in the reaction vessel was maintained at 800 mm Hg by adjusting the flow of gases in the exit line. The combustion proceeded smoothly and consumed the rod from the top down to its level of good thermal contact with the nickel sample holder. The gaseous products of combustion were collected and analyzed by infrared spectrometry.

Observations on nine combustions are given in Table IV-4. The boron nitride and silicon ignition aids reacted to form BF_3 + N_2 and SiF_4 , respectively. The sulfur, however, formed detectable amounts of SF_4 and S_2F_{10} in addition to SF_6 . The complication of determining the relative amounts of sulfur fluorides analytically is undesirable. A possible solution is to ignite the silicon electrically.

Table IV-4

OBSERVATIONS ON THE COMBUSTION OF GRAPHITE RODS IN FLUORINE

No.	Ignition Aid	Graphite Sample Mass (g)	Length of Combustion Period (min)	Solid Residue (mg)	% Fluorocarbon Products		
					CF_4	C_2F_6	C_3F_8
1	BN	0.41	4	30	>99.6		0.3
2	Si-S	0.41	7.5	25	>98		0.1
3	Si-S	0.41	7	30	98.9	1	0.1
4	Si-S	0.41	8	18	>95	<5	0.1
5	Si-S	0.41	7	4.1	~99	1	~0.1
6	Si-S	0.52	6.5	6.5	98.5	1.2	0.2
8	BN	1.13	13	21.0	~99	~1	~0.1
9	Si-S	0.54	8.5	0.8	98	2	<0.1
11	Si-S	1.25	20	0.5	94.9	5.0	0.07

The gaseous products listed in Table IV-4 refer only to the relative amounts of fluorocarbons formed. An error estimate, based upon these analytical data, indicates that the enthalpy of formation of CF_4 could be determined with a precision of $\pm 0.2\%$, assuming that no further improvements in combustion or analytical techniques were made.

These trial combustions demonstrated that a fluorine flow reactor may be a preferred alternative to a bomb reactor for certain substances. A fluorine flow calorimeter is being designed and will be built as soon as possible in order to assess problems of precision and reproducibility.

2. Uranium Monosulfide

Uranium monosulfide was selected for study because it was assumed to be representative in its combustion characteristics of certain other uranium compounds, such as the selenides, the tellurides, and the phosphides. The strong tendency of uranium monosulfide and fluorine to react made uranium monosulfide a candidate for the flow reactor method. Preliminary combustion observations were made in the flow reactor. The samples were contained in fused silica crucibles, and sulfur was added as an ignition aid. The experiments were performed at fluorine pressures of 100 mm Hg absolute and flow rates ranging from 500 to 1500 ml per minute. The results indicated that the rate of reaction could be varied over wide limits and that the volatile products of combustion were swept away from the reaction zone. Some of the silica of the crucible reacted with fluorine during these combustions; the amounts were, however, considerably smaller than in comparable experiments in a bomb reactor. Further combustion studies of uranium compounds in the flow reactor will be done using nickel or some other inert substance for the sample container.

E. Combustion Methods for Metals Forming Nonvolatile Fluorides (E. Rudzitis)

Progress in fluorine bomb calorimetry depends to a large extent on the development of suitable combustion techniques. Physically and chemically similar substances often exhibit markedly different burning characteristics; in the early stages of development it seemed as if a special technique would have to be determined by trial-and-error for each new substance. Now that a certain amount of experience has been gained, some common patterns of behavior are beginning to emerge. In the following, an attempt will be made to review and assess combustion techniques for metals on the basis of the volatility of the metals and of their fluorides.

- i) For high-melting metals which form sufficiently volatile fluorides the volatilization of the combustion product and consequent exposure of underlying metal to fluorine can be balanced by utilization of proper

geometry to provide cooling via conduction and convection. By use of a supported "pin" or suspended sheet technique, controlled combustion can be achieved without melting of the metal. In this laboratory this technique has been used successfully for metals (titanium, zirconium, hafnium, niobium, tantalum, molybdenum, ruthenium, uranium) which melt at a temperature which exceeds the normal boiling or sublimation temperature of their highest fluoride by more than 1000°C.

ii) At the other extreme end of the scale are the metals which melt more than 1000°C below the boiling points of their highest fluorides. The requirement for their combustion emphasizes the necessity for supporting the burning, liquefied metal and for providing a large surface-to-mass ratio because of the quenching effect of the accumulation of combustion products. For this purpose the fluoride "dish" technique was developed; in this technique, the metal, in the form of filings, is contained in a pressed and sintered dish of its fluoride. With varying degrees of success, this technique was used for combustion of zinc, cadmium, magnesium, and aluminum.

iii) Subsequent investigations have centered around finding appropriate combustion conditions for relatively high-melting metals with non-volatile fluorides. Extensive experimentation indicated that the "pin" technique was not applicable because the accumulation of solidified fluoride on the unburned portion of the sample severely limited the extent of combustion. This suggested a return to the use of metal fluoride dishes as supports. Despite some limited success of the "dish" technique, three problems prevented its general acceptance: a) side reaction of oxide impurity in the fluorides with fluorine under combustion conditions; b) interaction of sputtered, liquefied metal with the bomb walls; and c) ignition difficulties due to the large heat capacity of the "dish." These deficiencies were eventually corrected as follows: a) treatment of the metal fluoride with a mixture of HF-ClF₃ at 250°C and 100-200 atm was effective for removing the oxide impurity; b) the bomb walls were lined with the metal fluoride; and c) the sample was ignited in the form of a sheet suspended by a thin wire.

Experimental evidence accumulated so far suggests the following sequence of events during combustion: Electrical energy ignites the fuse wire which in turn ignites a fuse foil. The burning of the foil (which constitutes approximately one-tenth of the mass) raises the temperature of the sample causing it to melt. Once the metal is liquefied, hot spots in the fluoride film cause local, and ultimately massive, evaporation. During this period the sample drops onto the fluoride dish, but its temperature is still sufficiently high to counteract the cooling effect of its surroundings. The combustion thereafter extends into the gas phase and the rate of metal evaporation becomes the rate-determining step. The combustion terminates when the temperature of the burning metal droplet falls below the level required to maintain the intense evaporation needed for its buoyancy on the

locally liquefied fluoride. According to this analysis the combustion yield should depend on the volatility of the metal at the melting point of its fluoride. The observations are generally in accord. This technique is now being used for combustions of yttrium and gadolinium, and to recheck the results for aluminum. Future plans include combustion of lanthanum, holmium and thorium.

F. High-Temperature Enthalpy Calorimetry

(J. E. Brugger, D. R. Fredrickson, A. T. Hu, R. Kleb, and R. L. Nuttall)

1. 1500°C Drop Calorimeter

A test version of the high precision, vacuum calorimetric system (ANL-6800, p. 321ff) for measuring changes in enthalpy up to 1500°C by the drop method has been assembled and is undergoing evaluation. A number of test drops with a copper sample have been made.

The copper block calorimeter (ANL-6800, Fig. IV-1, p. 322), circulating water thermostat, resistance thermometer reading and recording equipment, and electrical calibration circuitry are complete and operating. A value of $\epsilon_{\text{calor}} = 4418.9 \pm 0.9$ joules/deg C was obtained by electrical calibration of the calorimeter. This value was determined with air in the calorimeter well. Slightly different values are expected under normal operating conditions, i.e., for an evacuated well or with a low pressure of inert gas present.

The energy equivalent, ϵ_{calor} , of the calorimeter was determined by observing the temperature rise produced by the dissipation of a measured quantity of electrical energy (resistance heaters) in the calorimeter. The heater wells are concentrically located around the sample well. The total resistance of the "Evenohm" heater elements is 48 ohms. Electrical energy is provided by a precision d-c supply and is measured with a conventional electrical calibration circuit that provides for dissipation of the energy in a dummy heater when current is not being passed through the calorimeter heaters. Careful attention has been given to the problem of thermally isolating the copper block from the calorimeter shell and to the so-called "heater lead problem," which requires that one properly distribute the heat dissipated in the heater leads between the calorimeter block and the jacket. The electrical energy input to the calorimeter is given by the relation: $P = E \times I \times t$, where P = joules, E = volts, I = amp, and t = sec. The energy equivalent, ϵ_{calor} , of the system is the quotient of the power input, P , divided by the corrected temperature rise, ΔT , of the calorimeter.

Calculation of the corrected temperature rise from the raw data of either electrical calibration or actual sample drop has been set up for the IBM 704 computer. Additions will be made to the computer program later to handle calorimetric data completely.

The drop mechanism has been described in previous reports (ANL-6477, p. 164 and ANL-6800, p. 324). A NJE Model SY-60-10 regulated-d-c power supply has been installed to provide current for the eddy current brake magnet which decelerates the drop weight and sample-containing capsule near the bottom of the drop. The electronic circuitry is functioning satisfactorily. Attempts have been made to determine acceleration and deceleration curves for the fall of the drop weight as functions of the trickle current and of the full braking current. Multiple-image photographs of the falling drop weight were made with a Polaroid camera and a GR "Strobotac" flash lamp. Although some useful information was obtained, the results left much to be desired. The present plan is to develop a method for obtaining a recorder trace of the position of the drop weight vs time for each drop.

A number of drop wire materials are being tested. These include: tantalum, NRC "SGS" tantalum, tantalum-10% tungsten, molybdenum, tungsten-3% rhenium, and tungsten-25% rhenium. Tantalum-10% tungsten and some samples of tantalum purchased several years ago, which embrittled markedly, have been eliminated from further testing.

Following the evaluation of various thermocouple assemblies and of dust shield filler materials, the furnace was reassembled using the full complement of radiation shields, specifically, eleven stainless steel shields, three molybdenum shields, and the dust shield. The dust shield consists of a tantalum can within a second tantalum can, the annular space (2 cm) being filled with "Morganite" 100-mesh alumina grain. Silicon carbide grains (80, 150, 320, and 1000 mesh) were tested as dust shield filler. One thousand mesh silicon carbide grain was slightly more efficient than 100-mesh Morganite, but because of the added difficulty in handling it, its use was not justified. The inner can, which buckled inwards in previous heatups, was replaced with one fabricated of heavier tantalum.

A tantalum wire wound, high purity alumina core is being used. The use of tantalum-sheathed platinum-10% rhodium vs platinum and tungsten-3% rhenium vs tungsten-25% rhenium thermocouples has eliminated most of the electrical noise problem which had been encountered in the temperature control circuit with unsheathed thermocouples. The four-piece molybdenum core (see ANL-6477, p. 165, and ANL-6648, p. 184) is being slightly redesigned and reworked and will be installed next.

Whether the dust shield will also be used, or will be replaced by a radiation shield formed from rolled up, closely spaced turns of thin (0.003 in.) molybdenum foil, remains to be determined. The measured emissivity for the dust shield is about 0.01. The value for the molybdenum radiation shields was about 0.1. As a radiation shield, the dust shield is equivalent to about 10 molybdenum shields.

The gate mechanism (see ANL-6477, pp. 165-166) has been operating satisfactorily. An auxiliary high vacuum system has been installed to pump out the space below the gate, including the calorimeter proper. An optical determination of the temperature of the test sample in the furnace can be made by removing the copper block calorimeter and installing a glass viewing-plate below the gate. The furnace vacuum does not deteriorate sensibly when the bottom of the gate is at atmospheric pressure. When the volume between the viewing-plate and the gate is pumped out, the gate can be opened for direct viewing of the sample. An optical viewing device, which consists essentially of a right-angle prism that can be moved into position below the gate, is in Central Shops for design. The correction to the temperature observed by viewing through the prism and glass plate will be determined separately by measuring the temperature of the ribbon filament of a standard lamp with and without the optics in place. Measurements will be made with a Model 8622-C L and N portable optical pyrometer.

2. 2500°C Drop Calorimeter

A drop calorimetric system for determining enthalpies of materials of interest to 2500°C has been designed and certain components have been constructed in Central Shops.

The complete calorimeter consists of the adiabatic calorimeter proper, the electron-beam-heated furnace system, a support stand, vacuum systems, and control circuits. The furnace system includes the furnace proper and the drop mechanism. The drop mechanism consists of a chamber assembly, a plunger control section, and a motorized target assembly.

At this time, all parts of the furnace system proper, including the electron beam guns and power supply, have been fabricated or are on hand. The support stand and an adapter plate (to allow substitution of the copper block calorimeter for the adiabatic calorimeter) have also been constructed. Because of the press of work on the 1500°C calorimeter, effort on the 2500°C calorimeter has been temporarily suspended.

V. REACTOR SAFETY*

The program on reactor safety currently comprises three areas of research: (1) study of metal-water reactions, (2) studies of transient heat transfer, and (3) study of the oxidation and ignition processes of substances used in reactor technology.

In water-cooled reactors, coolant failure or a severe nuclear excursion could cause the reactor core metals to melt and disperse rapidly in the water. Chemical reactions between the metals and water could result in the release of energy approaching or exceeding the energy released by the fission process during a nuclear excursion. Studies of these reactions are being carried out so that realistic estimates can be made of the rates and extents of reaction during hypothetical reactor accidents.

The reactions of the metals of interest with water are being studied in several ways. Experimental methods include isothermal reaction rate determinations, nonisothermal studies of the reactions with fine metal particles, and meltdown experiments with specimens of typical reactor fuel materials in the Transient Reactor Test Facility (TREAT).

Isothermal studies of the aluminum-steam reaction by the levitation method have been extended to include studies with an aluminum-uranium-nickel-iron alloy and 6061 aluminum alloy. Isothermal studies of the stainless steel-steam reaction were carried out by the volumetric method. A high-temperature, high-pressure furnace is being constructed for future isothermal studies with aluminum and stainless steel. The furnace will also be used to simulate the environment following a loss-of-coolant accident in a power reactor. A brief study was completed of the thermal decomposition of steam over inductively heated surfaces.

Laboratory-scale studies of the nonisothermal reaction of small metal particles by the laser method were continued; studies of the water reaction and heat transfer rate were carried out with individual particles of aluminum and zirconium by the laser beam heating technique. Studies were performed of the aluminum-water reaction as a function of pressure with a modified condenser discharge method. Studies of metal-water reactions initiated by a nuclear transient in TREAT were concentrated on oxide core, Zircaloy-clad and stainless steel-clad fuel specimens. The program of studies with preirradiated fuel by the TREAT method has continued; metallic uranium alloy fuel pins and aluminum-uranium alloy fuel salvaged from the SL-1 reactor have been subjected to TREAT transients.

Investigations of transient heat transfer were initiated to study the role of rapid steam formation as a pressure-producing mechanism in reactor meltdown accidents. These studies should complement the metal-water

*A summary of this section is given on pages 36 to 40.

chemical reaction program. Initial efforts were directed toward a mathematical analysis of the violent pressure surge produced during the meltdown of the SPERT-1D reactor core. Future studies will include the testing of mathematical heat transfer models by comparison with observed bubble growth rates obtained in the laser heating experiment.

Studies of the oxidation and ignition behavior of metals used in reactor technology are providing information needed to minimize the hazards associated with the handling of these materials. Studies were continued of the ignition behavior of ternary alloys containing uranium, plutonium, and a small quantity of a third element for possible use in zero power critical experiments. A brief study was completed of the oxidation characteristics of uranium-10 w/o molybdenum alloy, which is frequently used in nuclear facilities. Studies of the thermal conductivity of metal powders were carried out in order to achieve a better understanding of powder ignition phenomena. Uranium and zirconium powders were used in the research, in which the effects of particle size, gas pressure, temperature, and extent of prior oxidation of the particles were determined.

Studies of the aluminum- U_3O_8 thermite reaction were continued.

The studies were designed to determine the rate and energy of the reaction induced by rapid heating. Studies have been made of the effect of particle size, cermet composition, and pretreatment.

A. Metal-Water Reactions (L. Baker)

1. Studies of the Aluminum-Steam Reaction by the Levitation Melting Method
(R. E. Wilson, C. Barnes, L. Baker)

The levitation method was developed to study the kinetics of reactions of molten metals with water vapor at high temperatures. This method, in which the sample is supported and heated by means of a radio-frequency field and is surrounded by a steam atmosphere, appears to be suitable for determining the nature of the reaction rate laws in the absence of contamination from crucibles or other supports.

The reaction of molten aluminum with water or steam is of particular interest because of the large number of reactors which use aluminum-base alloys as the fuel or cladding material.

The reaction of pure aluminum and aluminum-5 w/o uranium alloy was studied by the pressure pulse method over the range 800 to 1200°C (see ANL-6413, p. 178). The method was not satisfactory at temperatures greater than 1200°C because of the volatility of aluminum, which produced a reactive aluminum mirror during the initial heating

period. In the levitation method, however, small metal pellets are heated rapidly in flowing steam so that the immediate formation of an oxide film prevents the loss of aluminum by volatilization. Kinetic results with pure aluminum by the levitation method were reported previously (see ANL-6648, p. 196). The results of studies of the reaction of an aluminum-17 w/o uranium-2 w/o nickel-0.5 w/o iron alloy (SL-1 composition) and a commercial aluminum alloy, 6061, which contains 1.0 w/o magnesium, 0.6 w/o silicon, 0.25 w/o copper, and 0.25 w/o chromium (SPERT-1D cladding metal) are reported in the following paragraphs. In addition, previous results with pure aluminum are given for purposes of comparison and analysis.

a. Experimental Procedure

The levitation melting method was described in detail in ANL-6648, p. 196. Samples were initially etched with heated NaOH solution to produce a uniform surface and to adjust the initial sample weight. The original specimens, which were short lengths of rods, were washed, dried, and weighed, before they were suspended in flowing steam by means of a radiofrequency induction field. As the specimens were heated to the desired temperature (1200 to 1600°C), they melted, becoming approximately spherical and having a nominal diameter of 8 mm. Pellet temperature was measured and controlled by a two-color optical pyrometer. After exposure to steam at atmospheric pressure at the desired temperature for a fixed period of time, specimens were rapidly quenched to room temperature. The amount of unreacted metal remaining was determined by weighing the oxide-coated metal and then weighing the oxide after selective dissolution

of the unreacted aluminum. The quantity of metal reacted was then divided by the initial surface area exposed to steam on the assumption that the specimen was spherical.

Table V-1

EFFECT OF TEMPERATURE ON THE REACTION OF SL-1 ALUMINUM ALLOY^a WITH STEAM

(8-mm spheres in levitation)

Reaction Time (min)	1200°C	1300°C	1400°C	1500°C	1600°C
5	1.88 ± 0.37	2.09 ± 0.19	1.09 ± 0.29	2.55 ± 0.14	4.6 ± 1.1
10	1.21 ± 0.19	1.80 ± 0.05	1.78 ± 0.16	3.4 ± 1.1	6.8 ± 1.1
20	1.42 ± 0.22	1.71 ± 0.17	2.26 ± 0.40	4.48 ± 0.40	8.2 ± 2.0
30	1.12 ± 0.04	1.96 ± 0.12	3.03 ± 0.88	4.9 ± 1.3	10.3 ± 1.2
60	1.49 ± 0.21	2.52 ± 0.07	5.27 ± 0.56	-	-
100	1.68 ± 0.05	2.83 ± 0.29	6.0 ± 1.0	-	-

^aNominal composition: 17 w/o uranium, 2 w/o nickel, 0.5 w/o iron, remainder aluminum.

^bRoot mean square.

b. Isothermal Oxidation Rates

The results of experiments with SL-1 alloy specimens are given in Table V-1 and plotted as points in Figure V-1. The results with 6061 alloy are given in

Table V-2 and Figure V-2. Previous results with pure aluminum are plotted in Figure V-3. The root-mean-square errors are given in the tables and indicated as vertical lines in the figures.

Figure V-1
REACTION OF ALUMINUM-
17 w/o URANIUM-2 w/o NICKEL-
0.5 w/o IRON WITH STEAM

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Table V-2

EFFECT OF TEMPERATURE ON THE REACTION
OF 6061 ALUMINUM ALLOY^a WITH STEAM
(8-mm spheres in levitation)

Reaction Time (min)	Metal Reacted (mg/sq cm $\pm$ RMS ^b Error) at Indicated Temperatures				
	1200°C	1300°C	1400°C	1500°C	1600°C
10	1.06 $\pm$ 0.40	1.80 $\pm$ 0.20	2.68 $\pm$ 0.20	15.94 $\pm$ 0.05	18.15 $\pm$ 0.45
20	-	-	8.7 $\pm$ 2.9	17.7 $\pm$ 1.3	22.9 $\pm$ 1.2
30	1.12 $\pm$ 0.01	1.85 $\pm$ 0.28	32.6 $\pm$ 7.7	-	23.8 $\pm$ 2.0
60	1.84 $\pm$ 0.44	3.53 $\pm$ 0.34	-	-	-
100	-	-	-	28.3 $\pm$ 1.6	-

^aNominal composition: 1.0 w/o magnesium, 0.6 w/o silicon,
0.25 w/o copper, 0.25 w/o chromium, remainder aluminum.
^bRoot mean square.

Figure V-2
REACTION OF 6061 ALUMINUM
ALLOY (1% Mg) WITH STEAM

108-7460-T

Figure V-3

REACTION OF PURE ALUMINUM WITH STEAM

Data points obtained by levitation melting method, solid lines computed from cubic-linear rate equation, dashed lines obtained by pressure pulse method (see ANL-6413, p. 179).

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The pressure pulse results (ANL-6413, p. 178) with pure aluminum, shown as dashed lines in Figure V-3, followed a cubic rate law, i.e., the lines on a log reaction vs log time plot had a slope of approximately one-third. The cubic nature of the pressure pulse data was well established because the reaction was studied over a time period covering four decades (1, 10, 100, and 1000 sec). Such a wide range could not be achieved in the levitation studies because of the time required to heat the specimens, which was of the order of 1 to 2 min. The levitation results at 1200 and 1300°C, although somewhat scattered, appeared generally to have a cubic slope for pure aluminum and the two aluminum alloys studied (see Figures V-1, V-2, and V-3).

The quantity of reaction obtained during pressure pulse studies at 1200°C of the aluminum-steam reaction (see Figure V-3) was approximately twice that obtained in the levitation studies although both sets of data had a cubic slope. The greater reaction obtained in pressure pulse studies is now believed to be due to the diffusion of steam through the slightly porous alumina crucibles used to contain the molten metal. This diffusion apparently provided an effectively greater surface area for reaction. The following cubic rate law equation was therefore formulated for pure aluminum and both alloys which was based on the levitation results at 1200 and 1300°C:

$$w^3 = 4.0 \times 10^9 t \left[\exp \left(-\frac{73,500}{RT} \right) \right] \quad (1)$$

where

w = weight of metal reacted, mg Al/sq cm,

t = time, min,

R = gas constant, 1.987 cal/(mole)(°K), and

T = temperature, °K.

Equation 1 is plotted as solid lines in Figures V-1, V-2, and V-3 at 1200 and 1300°C. The activation energy used in the equation was taken to be 73.5 kcal/mole since this value was found for the linear reaction of pure aluminum with steam at 1400, 1500, and 1600°C (ANL-6648, p. 200) and it was not greatly different from the value of 65.1* kcal/mole derived from the cubic reaction of pure aluminum with steam over the range 800 to 1200°C in the pressure pulse studies (ANL-6413, p. 178).

The activation energy of 73.5 kcal/mole is very similar to reported values of the heat of vaporization of aluminum at the boiling point, i.e., 70.7 kcal/mole at 2467°C.¹ A similar coincidence between the energy of activation for magnesium-steam reaction, 33.7 kcal/mole, in the 500 to 575°C range and the heat of sublimation of magnesium, 34.4 kcal/mole, was reported.²

The reaction of steam with pure aluminum and with the two alloys studied differed from one another at 1400, 1500, and 1600°C. The reaction of the SL-1 alloy samples, shown in Figure V-1, appeared to be cubic at 1400, 1500, and 1600°C and agreed well with lines computed from Equation 1 at 1400 and 1500°C. At 1600°C, the experimental values of quantity of reaction were about 50% greater than the values calculated from Equation 1.

The reaction with pure aluminum at 1400, 1500, and 1600°C was approximately linear and was described by a linear rate equation (see ANL-6648, p. 200). It seemed reasonable, in view of the cubic nature of the pure aluminum reaction at lower temperatures and the cubic nature of the SL-1 alloy at all temperatures, that the linear reaction with pure aluminum was a second stage following an initially cubic reaction. It was then assumed that the transition from a cubic to a linear reaction occurred smoothly, i.e., that there was no discontinuity. It was then possible to equate reaction rates given by a cubic rate law

*The value of activation energy reported was 21.7 kcal/mole; however this referred to a cubic expression of the form: reaction $\propto$ (time)^{1/3} whereas in the levitation studies and in the present context, the cubic form: (reaction)³ $\propto$ time, is implied. The numerical value of the activation energy in the latter form is three times that in the former.

¹JANAF Thermochemical Data, Compiled and Calculated by the Dow Chemical Co., Thermal Laboratory, Aluminum Interim Table, Dec. 31, 1960.

²Gibbs, D. S., and Svec, H. J., Kinetics of the Reaction Between Magnesium and Water Vapor, ISC-779, Iowa State College, 1956.

(Equation 1) and a linear law and to obtain an expression involving two unknowns: the extent of reaction corresponding to the transition and the linear rate constant. This procedure led to the following linear equation which applied only after 2.3 mg Al/sq cm have reacted:

$$w = 2.5 \times 10^8 t \left[\exp \left(-\frac{73,500}{RT} \right) \right] \quad (2)$$

where

$$w > 2.3 \text{ mg Al/sq cm.}$$

The combined cubic-linear rate law (Equations 1 and 2) was used to calculate the solid lines in Figures V-2 and V-3 at 1400, 1500, and 1600°C. The experimental results for pure aluminum showed reasonable agreement with the computed lines.

Results with the 6061 alloy indicated anomalous behavior in the range 1400 to 1600°C. The curves calculated from the cubic-linear rate law derived for pure aluminum are included in Figure V-2; however, it is evident that the experimental points are generally above the lines. At 1400°C, the reaction rate after 10 min is increasing rapidly. At 1500 and 1600°C, the extent of reaction is between 15 and 30 mg aluminum reacted per square centimeter, nearly independent of both temperature and time. A possible explanation for the anomalous behavior with the 6061 alloy lies in the volatility of the magnesium used in the alloy. The magnesium is contained in the alloy at low temperatures as the compound, Mg_2Si , which decomposes at 1100°C. Magnesium itself boils at 1110°C and although it is greatly diluted by the aluminum, it may have an appreciable vapor pressure at 1500°C. Magnesium vaporization might cause disruption of the protective oxide film which would account for the increased reaction at 1500 and 1600°C. The increased reaction presumably would cease when magnesium no longer vaporized and hence the oxide coating was no longer disrupted. This would account for the apparent leveling out of the reaction at 1500 and 1600°C. One-third of the total magnesium content leaving as vapor would account for the observed reaction.

c. Ignitions

Oxidation studies at 1600°C could not be extended to times longer than 30 min because the specimens ignited. The nature of the delayed ignitions with pure aluminum was described previously (see ANL-6648, p. 200). Ignition occurred at 1600°C after 18 min, while ignition was immediate at 1750°C. Both of the alloys ignited at temperatures above 1600°C in the same manner as aluminum. The 6061 alloy was more readily ignitable, whereas the SL-1 material was more resistant to ignition; however, no quantitative differences were determined.

A possible explanation for the delayed ignition may be related to the formation of a volatile suboxide Al_2O . It has been shown that Al_2O is the primary vapor species present when aluminum and Al_2O_3 are present together at high temperature.³ The vapor pressure of aluminum at 1750°C, the temperature of immediate ignition, is 7 mm. The vapor pressure of Al_2O , however, reaches 7 mm at about 1600°C based on calculations from the thermodynamic data reported by Brewer and Searcy.³ The production of Al_2O , however, depends upon the presence of Al_2O_3 which forms as an oxide film at 1600°C. The ignition delay might then be identified with the time required to build up a quantity of Al_2O_3 to form suboxide vapor in sufficient quantity to ignite.

2. Isothermal Studies of the Stainless Steel-Steam Reaction by the Volumetric Method (R. E. Wilson, C. Barnes)

A knowledge of the rates of reaction of metals with steam under isothermal conditions is necessary for the prediction of metal-water reactions which might occur in the event of a reactor accident. A volumetric experiment (see ANL-6543, p. 184 and ANL-6800, p. 330) was designed to study metal-steam reactions. When the metal surface is above the critical temperature (374°C) for water, steam and water are, in general, equivalent reactants at the same pressure.

Stainless steel is an important structural and cladding material which is used in many water-cooled reactors. For this study, 304 stainless steel (19 w/o chromium, 10 w/o nickel, <2 w/o manganese, remainder iron) was chosen since this alloy is often used in reactor construction and it is typical of a broad class of stainless steels.

a. Experimental

The apparatus and method are similar to that used previously (ANL-6543, p. 185 and ANL-6800, p. 331) for studies of the uranium-steam reaction. In the present series of experiments, disc-shaped samples of 304 stainless steel, about 3/4 in. in diameter and 1/4 or 1/2 in. high, were supported on a fused silica pedestal. The pedestal was located inside a reaction vessel through which steam, at 1-atm pressure, was passed. The sample was heated by a single-turn induction coil which was external to the reaction vessel. The temperature was measured and controlled by a Pt-Pt, 10% Rh thermocouple which was imbedded in the center of the sample. After the steam passed the sample, it was condensed and the hydrogen produced by the metal-steam reaction was collected over water and measured continuously in a graduated vessel.

³Brewer, L., and Searcy, A. W., J. Am. Chem. Soc. 73, 5308 (1951).

b. Reaction Rate Determinations

The results of typical experiments at 1100 and 1200°C are shown in Figure V-4. The initial reaction was nearly parabolic (slope of 1/2 on the log-log plot in Figure V-4). The reaction, however, accelerated slightly after 10 to 20 min. The reaction rate at temperatures below 1100°C was very low.

Figure V-4
REACTION OF 304 STAINLESS
STEEL AT 1100 AND 1200°C
WITH STEAM

108-7454 Rev.

At 1300°C, the initial reaction rate depended upon the rate at which the sample was heated. The results of two experiments at 1300°C are shown in Figure V-5. The conditions of the experiments were identical

Figure V-5
REACTION OF 304 STAINLESS
STEEL AT 1300°C WITH STEAM

108-7822

except that the sample in experiment 1 was brought to temperature in 3 min and the sample in experiment 2 was brought to temperature in 5 min. This small difference in heating rate caused a large difference in the initial reaction rate, although the reaction rates in the two experiments approached the same value after about 20 min. The reaction approached a linear rate after the initial period.

No quantitative reaction rate information could be obtained at temperatures greater than 1300°C by the volumetric method. Samples heated to 1400°C underwent rapid swelling and foaming. A sample which was heated to 1400°C in steam for 1 min is compared in Figure V-6 with a sample which had been at 1100°C for 30 min. The sample which had been at 1100°C was coated uniformly with an oxide scale. The sample which had been at 1400°C was converted into an irregular mass of oxide-covered metal particles, and the reaction rate, as judged by the hydrogen evolution, increased sharply because of the increased surface area formed during the swelling and foaming process. It was evident, however, that as the sample disintegrated all control of sample temperature was lost because of the loss of inductive coupling between the induction coil and the sample. The swelling and foaming phenomenon was also observed to occur when the stainless steel samples were heated to 1400°C in air.

Figure V-6

APPEARANCE OF 304 STAINLESS STEEL AFTER EXPOSURE TO STEAM

c. Metallographic and Electron Probe Microanalyzer Studies

A metallographic examination of samples heated to 1300°C, slowly (5 min) and rapidly (3 min) showed the presence of segregated areas at the surface of the sample. These areas were approximately 60 μ deep and 200 μ wide on the rapidly heated sample and were sparsely scattered over large areas of unaltered material. In the slowly heated samples, the altered area nearly covered the sample, with only minor areas of unaltered material on the surface.

A detailed study of one of the altered areas was carried out using an electron probe microanalyzer.* The results of this analysis are shown in Figure V-7. In this figure, the distance axis has an arbitrary zero near the edge of the sample, and progresses inward toward the center of the sample. The sample analysis at about 70 μ is representative of the matrix material. Since each of the analysis curves was made on a separate traverse of the sample with the beam held stationary, small errors in registration are probable.

Figure V-7
ELECTRON MICROPROBE SCAN OF
AN AREA OF SEGREGATION AT THE
SURFACE OF 304 STAINLESS STEEL
AFTER REACTION WITH STEAM FOR
5-MINUTE HEATUP TIME TO 1300°C

Table V-3 shows the results of the electron microprobe analysis at arbitrary points throughout the traverse. The data for oxygen were obtained by difference, it being assumed that there were no other materials present. From the data, these areas are primarily metallic and show a marked reduction in the iron content with a concomitant increase in the content of alloying agents, which probably accounted for the protective nature of these segregations.

3. Studies of Metal-Water Reactions by the High-Pressure Furnace Method (R. E. Wilson, C. Barnes)

It was shown in the previous section that the stainless steel-steam reaction can not be studied at temperatures greater than 1300°C by the volumetric method because of the rapid swelling and foaming of the steel which causes a loss of electrical coupling between the induction

*Electron probe microanalyzer study performed by N. Stalica.

heating coil and the sample. In order to continue the studies, it was necessary to begin development of an experimental method in which the sample would be in a constant-temperature environment so that the disintegration of the sample would not alter the sample temperature.

Table V-3

ELECTRON MICROPROBE ANALYSIS OF 304 STAINLESS STEEL

(Sample exposed to steam at 1300°C)

Arbitrary Traverse, Distance from Edge of Sample (μ)	Composition (a/o)			
	Iron	Chromium	Nickel	Total Metal Oxygen
10	27	7	31	65 35
20	38	37	33	108 -
30	40	40	6	86 14
40	45	35	16	96 4
50	49	30	12	91 9
60	58	26	11	94 6
70	70	27	11	108 -

An additional reason for providing means whereby metal-water reactions can be studied under isothermal conditions and over a wide range of pressures is to allow the study of the aluminum-water reaction. In recent TREAT experiments (ANL-6725, p. 212), it was discovered that pressure had a marked effect on this reaction. It was, therefore, decided to construct a furnace in which metal samples could be exposed to a high-temperature high-pressure steam environment.

A diagram of the furnace, which is now under construction, is shown in Figure V-8. The unit was designed for temperatures as high as 1900°C and pressures up to 1000 psi. Inside the bell jar and separated by a ceramic tube are two high pressure zones, an internal steam-filled zone and an external argon-filled zone. The pressure in each zone will be automatically matched to avoid stressing the ceramic tube. A crucible containing the sample will be rapidly elevated from a moderate temperature region, where the reaction rate is negligible, into the high-temperature region by an external crank mechanism. Some unreacted steam and the hydrogen generated by metal-water reaction will be removed continuously from the top of the steam zone, and the quantity of hydrogen will be determined as a function of time.

The high-pressure furnace will also be used to simulate the environment experienced by power reactor fuel following a loss-of-coolant accident. In such a situation, the fuel will 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 will reach the melting point of the metal cladding in roughly 10 min.

The physical characteristics of the cladding meltdown process are, in general, not known under these conditions. Experiments will be performed with UO_2 pellets clad with stainless steel and with Zircaloy. Uniform heating will be achieved either by slowly elevating samples into the hot zone of the furnace or by increasing the furnace temperature or both.

Figure V-8

HIGH-PRESSURE FURNACE FOR STUDIES OF MOLTEN METAL-STEAM REACTIONS

108-7179-T-2

4. Thermal Decomposition of Steam (M. Kilpatrick, S. K. Lott)

It is well known that when steam is passed over white-hot platinum wires hydrogen and oxygen are formed, and that under proper conditions, amounts of dissociation products are obtained which correspond to the dissociation equilibrium at the temperature of the wire.⁴ The degree of dissociation of water vapor at one atmosphere pressure, as shown in Figure V-9, begins to be appreciable at 1600°K and is considerable at 3000°K.⁵

Since the dissociation of steam on a metal surface may be important in the study of metal-water reactions, a brief investigation of the kinetics of the reaction in a flow system was undertaken.

a. Apparatus

The apparatus (shown in Figure V-10) consisted of an electrically heated 3-liter steam boiler (A), connected to a quartz tube (B) by

⁴ Langmuir, I., J. Amer. Chem. Soc. 28, 35 (1906).

⁵ Dorsey, N. E., Properties of Water Substance, Reinhold Publishing Corporation, New York, 1940, p. 29.

a ball joint. In the quartz tube, the specimen in the form of a cylinder or cube (C) was mounted on a two-hole alumina rod (D) which carried the Pt-Pt, 10% Rh thermocouple wires for connection to a potentiometer or recorder. The bottom of the quartz tube fitted into a female ball joint on a brass cup (F) which was connected to a copper tube that led to the gas burette (G). A copper spiral (H) which was soldered to the copper tube carried cooling water to condense the steam. The induction coil (E) was connected to a Reeve Electronic Generator.

Figure V-9
DISSOCIATION OF WATER
VAPOR AT ONE ATMOSPHERE

108-7824

Figure V-10
APPARATUS FOR STUDIES OF THE THERMAL
DECOMPOSITION OF STEAM

TO POTENTIOMETER
AND RECORDER

108-7427-T-3

To carry out an experiment, the polished and weighed specimen was mounted at (C), the boiler (A) was heated, and the apparatus steamed out to remove air. The experiment was started by turning on the induction heater and rapidly bringing the specimen to the desired temperature, as indicated by the thermocouple on a recorder chart, and observing the evolution of gas with time. At the end of the experiment, the sample was removed and weighed and the gas sample was analyzed with a mass spectrograph. The readings of gas evolved were corrected to standard conditions and were plotted against time.

b. Results with Platinum and Iridium Surfaces

Analysis of the noncondensable gas produced with platinum and iridium specimens indicated a hydrogen-to-oxygen ratio very close to 2:1. Typical results for the gas

Figure V-11

RATE OF DECOMPOSITION OF STEAM OVER PLATINUM IN A FLOW SYSTEM

(Steam at one atmosphere)

108-7430-T-2

evolved versus time over platinum

cylinders are given in Figure V-11.

The straight lines in Figure V-11 indicate that the reaction is zero order at constant flow rate, pressure, and temperature. Results with iridium cylinders and platinum cubes were nearly identical.

These experiments were carried out with steam at a constant pressure close to one atmosphere and a constant flow rate. To determine the effect of flow rate, specimens of varying cross sections can be used in the same quartz tube or specimens having identical dimensions can be used in quartz tubes of different diameters. Experimental arrangements used are illustrated in Figure V-12.

The flow rate was determined at constant boiling rate by weighing the condensate during a time interval before the experiment and during the experiment, and by calculating the number of liters of steam passing through the free space between the specimen and the quartz tube. The flow rate is defined as liters per minute per square centimeter of free cross-sectional area.

Figure V-12
CROSS SECTIONS OF SAMPLES
AND QUARTZ TUBES USED IN
STEAM DECOMPOSITION
EXPERIMENTS

The data were then plotted according to the Arrhenius equation. The plots for a platinum cylinder at three flow rates are shown in Figure V-13 while the Arrhenius parameters for the platinum cylinder, the platinum cube, and the iridium cylinder are given in Table V-4. Velocity constants calculated with the Arrhenius equation for 1500 and 1800°K are given in Table V-5 in order to illustrate the effect of flow rate and to facilitate comparison of the platinum results with those of iridium.

Figure V-13
DECOMPOSITION OF
STEAM OVER A
PLATINUM CYLINDER

Table V-4

**ARRHENIUS PARAMETERS^a FOR THE THERMAL DECOMPOSITION
OF STEAM OVER PLATINUM AND IRIIDIUM**

Flow Rate [liters/(min)(sq cm)]	Number of Data Points	(Temperature range 1200-1700°C)		Activation Energy, E (kcal/mole)
		Pre-exponential Factor, A [g moles H ₂ /sq cm/(min)]		
Platinum Cylinder (dia. 6.35 mm, length 10 mm, flat top)				
7.8	8	1.3 ± 0.2 ^b	36.6 ± 0.7 ^b	
15.7	11	1.7 ± 0.6	38.0 ± 1.3	
55	8	6.5 ± 1.4	39.5 ± 1.0	
Iridium Cylinder (dia. 6.35 mm, length 10 mm, rounded top)				
7.5	10	1.0 ± 0.5	36.3 ± 1.5	
15	11	2.0 ± 0.6	38.0 ± 1.0	
62	11	1.8 ± 0.4	34.7 ± 0.7	
Platinum Cube (9.97 mm on edge)				
10	7	0.4 ± 0.2	32.4 ± 1.9	
34	11	1.1 ± 0.4	36.0 ± 1.2	

^aThe Arrhenius equation is as follows:

$$\text{Hydrogen Produced, moles H}_2\text{/sq cm)(min)} = A \exp (-E/RT)$$

where A is pre-exponential factor, E is activation energy, R is gas constant, and T is absolute temperature.

^bStandard deviations obtained by least squares analysis of data.

Table V-5

**VELOCITY CONSTANTS AT 1500 AND 1800°K FOR THE THERMAL
DECOMPOSITION OF STEAM OVER PLATINUM AND IRIIDIUM**

Flow Rate [liters/(min)(sq cm)]	Velocity Constant [moles H ₂ /(sq cm)(min)]	
	1500°K	1800°K
Platinum Cylinder (dia. 6.35 mm, length 10 mm, flat top)		
7.8	6.17 x 10 ⁻⁶	4.78 x 10 ⁻⁵
15.7	4.98 x 10 ⁻⁶	4.17 x 10 ⁻⁵
55	11.1 x 10 ⁻⁶	10.5 x 10 ⁻⁵
Iridium Cylinder (dia. 6.35 mm, length 10 mm, rounded top)		
7.5	5.46 x 10 ⁻⁶	4.15 x 10 ⁻⁵
15	5.74 x 10 ⁻⁶	4.82 x 10 ⁻⁵
62	16.0 x 10 ⁻⁶	11.1 x 10 ⁻⁵
Platinum Cube (9.97 mm on edge)		
10	7.30 x 10 ⁻⁶	4.46 x 10 ⁻⁵
34	6.43 x 10 ⁻⁶	4.82 x 10 ⁻⁵

The results given in Tables V-4 and V-5 indicate that the reaction over platinum is very nearly identical with that over iridium. The differences between results with each specimen were probably due to

differences in specimen geometry. The results can probably be explained on the basis that an equilibrium of water dissociation products is rapidly formed and maintained at the hot metal surface and that the dissociation products then diffuse through the thermal boundary layer at a rate determined by the sample geometry and the steam flow rate. This is consistent with the fact that the apparent energy of activation of the thermal decomposition reaction, 32 to 40 kcal/mole (see Table V-4), is very similar to the apparent activation energy for the equilibrium dissociation of steam, 41 kcal/mole (see Figure V-9).

c. Results with Other Surfaces

Experiments were also carried out with palladium (m.p. 1552°C). A 2:1 mixture of hydrogen and oxygen was also obtained. At temperatures above 1400°, black specks came over with the steam-gas mixture. As the meniscus of the water in the burette dropped, the specks adhered to the walls of the burette and fairly soon the gas bubbles came over with no change in the burette reading, and finally, with gas coming over, the meniscus rose, indicating less gas in the burette. On standing, the hydrogen completely combined with the oxygen. Examination of the black specks by X-ray diffraction analysis eliminated the possibility that the specks were PdO or PdO₂; a palladium line indicated that they were palladium black. Hence, it was observed that steam was decomposing over palladium at 1500°C and that in the same apparatus palladium was catalyzing the recombination of hydrogen and oxygen at 23°C. Because of this recombination, no quantitative decomposition data were obtained.

Studies with readily oxidizable metals such as molybdenum, tungsten, tantalum, niobium, and zirconium showed that only hydrogen is evolved, but a less readily oxidizable metal, nickel, gave 3 to 10% oxygen over the temperature range 1300-1425°C.

An attempt was made to determine if the equilibrium between oxygen, hydrogen, and steam is rapidly established and maintained at a nonmetallic surface. In order to use inductive heating of the material, a metallic core was necessary. Experiments were carried out in Al₂O₃ and MgO crucibles with fitted covers and nickel cores over the temperature ranges 1500 to 1850°C and 1250 to 1600°C, respectively. Analysis of the gas evolved gave hydrogen-to-oxygen ratios of 5.21 and 5.35, indicating that the crucible material was permeable to steam, which reacted with the nickel. In another experiment, a fused transparent magnesium oxide crucible was used with a nickel core over the temperature range 1400-1750°C, as measured with an optical pyrometer. Only 16 cc of gas was evolved in 90 min. The temperature of the surface, however, was uncertain because of the temperature drop from the metal core to the nonmetallic surface.

5. Studies of Metal-Water Reactions by the Laser Heating Method
(L. Leibowitz, L. Mishler)

Experiments are continuing on the use of laser beam heating in the study of rates of chemical reaction and heat transfer between individual metal particles and water. The laser beam is focused on a small submerged particle of metal which as a result is heated very rapidly, within about 1 msec. This rapid heating simulates the rapid contacting of heated metal that would result from a violent meltdown in a water-cooled nuclear reactor. Rational analysis of reactor accidents requires information on the rate of exchange of both chemical and thermal energy from metal particles to water. The laser heating method was adopted to provide a rapid heating method for materials which cannot readily be examined by such techniques as condenser discharge (ANL-6687, p. 187) or induction heating.

The experimental arrangement and procedure have been described in some detail (ANL-6800, p. 327). The sample is placed in a quartz cell containing water, the system is degassed, the cell is sealed off under vacuum, and the metal is then heated by a focused beam from a ruby laser. The contents of the cell are analyzed for hydrogen to determine the extent of reaction.

The initial experiments were designed to examine the effect of variations of laser output energy on the extent of reaction for zirconium and aluminum. A constant sample size was used, and the energy was varied from that just necessary to achieve melting to the highest available. With zirconium, 1-mm squares of 5-mil (0.013-cm) foil were used; with aluminum, 1-mm squares of 1-mil (0.0025-cm) foil were used. These quantities of metal, when melted, would yield spheres, respectively, 620 and 360 μ in diameter.

The results of the first series of experiments are summarized in Table V-6. In all cases, the metal residue consisted of a single particle.

Table V-6

EXTENT OF REACTION FOR ALUMINUM
AND ZIRCONIUM HEATED UNDER
WATER BY A LASER BEAM

<u>Series I</u>		
<u>Run No.</u>	<u>Laser Output (joules)</u>	<u>Reaction (%)</u>
<u>Aluminum 360 μ Spheres</u>		
L-31	10	7.3
L-29	18	6.8
L-26	25	10.5
L-27	29	7.4
<u>Zirconium 620 μ Spheres</u>		
L-30	19	31
L-25	25	32
L-28	32	33

It is clear from these results that, over quite a wide energy range, the extent of reaction is independent of laser output. In the absence of suitable temperature measurements, it was thought that some estimate of temperature, however crude, would be valuable. The minimum laser output energy which would just melt the sample was fairly easy to establish for zirconium but not for aluminum. In run L-30, a laser output of 19 joules was enough to bring the temperature of the zirconium to its melting point, 1850°C. Since the total energy needed just to melt the amount of zirconium involved is known, the percent of the laser output absorbed can be readily computed. Assuming the same percentage of the laser output to be absorbed in runs L-25 and L-28, we can calculate the approximate temperatures reached. They are 2700 and 3600°C, respectively. These values should be understood to be estimates of the order of the temperature range.

When these experiments were completed, several changes were made in the laser head: the ruby was refinished, the cavity replated, and an overvoltage trigger was acquired. As a result, the maximum power obtainable was approximately doubled. It was, therefore, decided to repeat the experiments with the 360- μ dia. aluminum particle. These results are summarized in Table V-7. This second group of results confirm quite clearly that the extent of reaction is independent of laser output energy. There was a slight increase in the average percent reaction, 8.0% in Series I to 10.3% in Series II, for which no explanation can be offered.

Table V-7

EXTENT OF REACTION FOR ALUMINUM
HEATED UNDER WATER BY A LASER BEAM

Series II

(Aluminum 360 μ spheres)

<u>Run No.</u>	<u>Laser Output (joules)</u>	<u>Reaction (%)</u>
L-36	15	10.0
L-40	48	9.5
L-43	41	11.4

The residues from all of these runs were recovered, mounted in plastic, and examined metallographically to study further the extent and character of the reactions. Typical photomicrographs of spheres formed in one zirconium run and one aluminum run are shown in Figure V-14.

The appearance of the zirconium particle is very similar to the appearance of those found in condenser discharge experiments (ANL-6548). In the laser experiments, zirconium has regularly shown uniform oxide coatings on spherical residues. The internal metal shows the typical structure of zirconium after a transition from the beta to the alpha phase. An

X-ray diffraction examination of a group of these spheres showed the presence of monoclinic ZrO_2 and of alpha zirconium. Those phases had also been found in the condenser discharge work. Indeed, for this zirconium particle size, 25% reaction was predicted in ANL-6548. The observation of 32% reaction (based on hydrogen analysis) agrees well with that calculation.

Figure V-14

METAL SPHERES FORMED BY LASER MELTING
OF METAL FOIL SQUARES UNDER WATER

- (a) Zirconium, Particle Diameter 620μ
(Oxide film thickness, 42μ)
(b) Aluminum, Particle Diameter 360μ

Run L-30

(a)

100 μ

Run L-27

(b)

100 μ

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It also is possible to calculate from the photomicrograph the percent reaction. Assuming the oxide to be pure ZrO_2 and the internal metal to be pure zirconium, about 20% reaction was computed. This low value is partly a result of rounding of the edges of the sectioned sample during polishing which therefore decreased the apparent oxide film thickness and partly due to oxygen solubility in zirconium metal. The diffuse image at the edge of the sample shows the rounding of the sample that occurred.

The aluminum sample was polished with MgO and treated with Keller's etch (1% HF, 1.5% HCl, 2.5% HNO₃ in water). This sample presents an appearance which is quite different from that of zirconium. No clear oxide film is present, although considerable internal structure can be seen. In general, it has been difficult to observe an oxide film on aluminum specimens.

Another method for obtaining information on reaction rates is the use of high-speed motion pictures taken during each run. After the metal sample is heated by the laser beam, a bubble of hydrogen and water vapor is seen to grow around the hot particle. In some cases, this bubble will grow and then collapse to a very small volume. The growth and collapse may be repeated two or three times. This behavior has also been observed in underwater explosions.⁶

In addition to taking motion pictures of the experiments carried out in degassed, closed cells, motion pictures were also taken of particles heated in open tubes beneath a column of water. Using 2-mm squares of 5-mil (0.013-cm) thick zirconium foil, bubble growth and collapse was observed to occur periodically in 5-mm ID tubes containing a 4-cm column of water. It was possible, by careful measurements from the film, to obtain a record of bubble volume as a function of time. It was assumed that the bubbles were symmetrical in calculating their volumes. These results are plotted in Figures V-15 and V-16. The laser output energy in all three open-tube runs (Figure V-16) was the same. From the appearance of the residue in run WH-2, poor alignment evidently caused lowered heating of the metal in that run.

Figure V-15
BUBBLE VOLUME GENERATED
BY LASER BEAM HEATING OF
METAL PARTICLES
(Closed-cell experiments)

108-7825

⁶Cole, R. H., Underwater Explosions, Princeton University Press, Princeton, N. J., 1948.

Figure V-16

BUBBLE VOLUME GENERATED BY LASER BEAM HEATING OF METAL PARTICLES

(Open-tube experiments)

108-7826

suitable for measuring the temperatures of these heated particles will be completed shortly.

6. Studies of the Meltdown of Oxide Core-Metal Clad Fuel Pins in TREAT (R. C. Llimatainen, F. J. Testa, J. Hepperly)

The use of the TREAT (Transient REActor Test facility) reactor at the National Reactor Testing Station, Idaho, to study the reaction of various metals with water is continuing. The technique consists of subjecting fuel specimens immersed in water to a transient nuclear burst. The objectives of the program are:

- to determine the extent of reaction between the metal 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; this is accomplished by such means as metallographic and particle size evaluations.

Analysis of the dynamics of this process is being undertaken. As a first approximation, the analysis given by Cole⁶ was applied. This assumes immediate release of the explosive energy and no subsequent reaction or slow energy transfer and is based simply on inertia of the water flowing out from and then back into the explosive bubble. The periods predicted from this model are roughly 50 msec for the closed-tube experiments and 3 msec for the open-tube experiments. As order of magnitude estimates, these values are in fair agreement with the observed periods of 26 and 5 to 10 msec, respectively, for the two types of tests.

Experimental work has begun on the next phase of this study, namely, the determination of the effect of variation of particle size on the extent of reaction. It is also hoped that the task of constructing a high-speed two-color pyrometer

Figure V-17

"TAPER SEAL" HIGH PRESSURE AUTOCLAVE ASSEMBLY FOR METAL-WATER REACTION STUDIES IN TREAT

DESIGN PRESSURE 9000 PSI @ 1000°F

108-7479-T

on the autoclave walls by the heated fuel or cladding material during the experiments. A strain gage pressure transducer was connected to the autoclave by stainless steel tubing; the transducer was outside the reactor core (32 in. above the autoclave). Tests reported previously (see ANL-6800, p. 355) have indicated that there is no loss of recording fidelity by the remote location of the transducer. On the other hand, previous experiments in which the transducer was located within the reactor core resulted in excessive extraneous output caused by the gamma and neutron flux. A second pressure transducer was located in close proximity to the first one

Results of previous studies with oxide core-metal clad specimens have been summarized in ANL-6250.* Some of the previous experiments have been with a pure UO_2 core and some have been with a mixed oxide core containing 81.51 w/o ZrO_2 , 8.69 w/o U_3O_8 , 9.06 w/o CaO , and 0.74 w/o Al_2O_3 . Results were reported for oxide pellets clad with both 304 stainless steel and Zircaloy-2. Additional results, especially in the very energetic range, are reported in the following paragraphs.

In each of the experiments, a single pressed and sintered pellet of oxide material, 0.375 in. dia. and 0.535 in. long, was enclosed completely within a stainless steel or Zircaloy can. End caps were welded so that there was no prior access of water to the oxide pellet and in such a way that there was a minimum of extraneous weld metal at the ends of the specimens. Cladding thickness was 20 mils, and the oxide-clad gap was nominally 1 mil and was filled with helium.

The specimens were loaded into a high-pressure autoclave of the type shown in Figure V-17. Fuel pins were located under water in a graphite crucible to prevent attack of the fuel or cladding material during the experiments. A strain gage pressure transducer was connected to the autoclave by stainless steel tubing; the transducer was outside the reactor core (32 in. above the autoclave). Tests reported previously (see ANL-6800, p. 355) have indicated that there is no loss of recording fidelity by the remote location of the transducer. On the other hand, previous experiments in which the transducer was located within the reactor core resulted in excessive extraneous output caused by the gamma and neutron flux. A second pressure transducer was located in close proximity to the first one

*Values given for nuclear energy input have been changed slightly in the light of more extensive calibrations (see The Technology of Reactor Safety, Vol. 2, Chap. 17, "Chemical Reactions," in press).

in order to show the nature and degree of the "radiation signal" in the absence of a changing pressure.

Generally, two particle size determinations were made for UO_2 core pins. One was performed on the fuel sample after the irradiation and the other after a treatment with boiling concentrated nitric acid which resulted in dissolution of the UO_2 . The mixed oxide material could not be dissolved in this way so that only one particle size determination on the fuel sample was made. The particle size determinations were accomplished by sieving and the results reported as the Sauter mean diameter, d_{sv} . The extent of metal-water reaction was determined by mass spectrometric analysis of the gaseous contents of the autoclave for hydrogen.

The results of the experiments with both the stainless steel- and Zircaloy-clad specimens are summarized in Table V-8. Photographs of the residue, graphs of the particle size distribution, and the pressure traces from the experiments are given in Figures V-18 through V-24. The fuel specimen in each of the runs was reduced to one large fragment and a considerable quantity of powdered material. The particle size determination showed that, in general, the oxide core material was more finely divided than the cladding material. The pressure traces indicated that no explosive pressure rises had occurred. The maximum rate of pressure rise occurred in run CEN-170 and was only 6.0 psi/msec.

Table V-8

TREAT MELTDOWN EXPERIMENTS WITH OXIDE CORE FUEL SPECIMENS

CEN Run No.	Fission Energy Input (cal/g)	Adiabatic Core Temp. (°C)	Reactor Characteristics			Appearance of Specimen after Transient	Mean Particle Diameter (mils)	Peak Autoclave Pressure (psi)	Percent of Metal Reacted
			Characteristics		Core Fuel Pins				
			Period (msec)	Int. Power (MW-sec)					
Stainless Steel Clad, UO ₂ Core Fuel Pins									
Clad: Stainless steel-304, 20 mils thick, ends capped									
Core: UO ₂ , 11.2% enriched (Runs CEN-169 and 174), 20% enriched (Run CEN-170), 0.375 in. dia. x 0.53 in. long.									
169	617	3300 ^a	42	768	Fragmented	26 (59) ^b	305	29.8	
170	655	3300 ^a	51	606	Fragmented	10 (82) ^b	718	31.7	
174	688	3300 ^a	39	860	Fragmented	10 (57) ^b	199	35.5	
Zircaloy-2 Clad, UO ₂ Core Fuel Pins									
Clad: Zircaloy-2, 20 mils thick, ends capped									
Core: UO ₂ (11.2% enriched), 0.375 in. dia. x 0.53 in. long.									
181	287	2700	72	323	Fragmented	56 (70) ^b	61	23	
175	450	3300 ^a	52	505	Fragmented	29 (34) ^b	180	63	
173	771	3300 ^a	39	867	Fragmented	26 (46) ^b	480	80	
Zircaloy-2 Clad, Mixed Oxide Core Fuel Pins									
Clad: Zircaloy-2, 20 mils thick, ends capped									
Core: 81.5 w/o ZrO ₂ , 9.06 w/o CaO, 0.74 w/o Al ₂ O ₃ , 8.69 w/o U ₃ O ₈ (93% enriched), 0.33 in. dia. x 0.53 in. long.									
168	787	3300 ^a	41	985	Fragmented	15	100	29.6	

^aPartly vaporized.

^bAfter dissolution of UO_2 .

Figure V-18
304 STAINLESS STEEL-CLAD, UO₂-CORE FUEL PIN
AFTER TREAT TRANSIENT CEN-169
(617 cal/g UO₂)

Fuel Pin after Transient

Particle Size Distribution

Figure V-19
304 STAINLESS STEEL-CLAD, UO₂-CORE FUEL PIN AFTER
TREAT TRANSIENT GEN-170
(655 cal/g UO₂)

Fuel Pin after Transient

108-6825

Particle Size Distribution

SS Clad Only

108-7877

Figure V-20
304 STAINLESS STEEL-CLAD, UO₂-CORE FUEL PIN
AFTER TREAT TRANSIENT CEN-174
(688 cal/g UO₂)

Fuel Pin after Transient

108-7047

Particle Size Distribution

108-7878

Figure V-21
ZIRCALOY-2-CLAD, UO₂-CORE FUEL PIN
AFTER TREAT TRANSIENT CEN-181
(287 cal/g UO₂)

Particle Size Distribution

Figure V-22

ZIRCALOY-2-CLAD, UO₂-CORE FUEL PIN
AFTER TREAT TRANSIENT CEN-175

(450 cal/g UO₂)

Fuel Pin after Transient

108-7229

Oscillograph Record

Particle Size Distribution

UO₂ Core and Zr-2 Clad

108-7880

Zr-2 Clad Only

Figure V-23
ZIRCALOY-2-CLAD, UO₂-CORE FUEL PIN
AFTER TREAT TRANSIENT CEN-173
(771 cal/g UO₂)

Fuel Pin after Transient

Particle Size Distribution

UO₂ Core and Zr-2 Clad

108-7881

Zr-2 Clad Only

Figure V-24
ZIRCALOY-2-CLAD, MIXED OXIDE-CORE FUEL PIN
AFTER TREAT TRANSIENT CEN-168
(787 cal/g mixed oxide)

Fuel Pin after Transient

108-6823

Oscillograph Record

Particle Size Distribution

Mixed Oxide Core and Zr-2 Clad

108-7882

The results with the mixed oxide core specimens and the pure UO_2 core specimens could not be compared directly on the basis of fission energy input because of large differences in the specific heat of the two fuel materials. The calculated relationship of adiabatic temperature to energy input is plotted in Figure V-25 where the large difference is apparent. In order to compare results, and adiabatic temperature basis was used. The

extent of metal-water reaction was, therefore, plotted in Figures V-26 and V-27 as a function of fission energy input. One energy abscissa was used for the pure UO_2 data and another for the mixed oxide data. The abscissas were scaled so that the same temperature scale (with the melting temperature as a fixed point of correspondence at an average melting temperature of 2700°C) applied approximately to both sets of data. Compared on this basis, the results for both the Zircaloy-2 and stainless steel-clad specimens (see Figures V-26 and V-27) were independent of whether pure UO_2 or mixed oxide core was used. The extents of reaction for the Zircaloy-clad specimens and the stainless steel-clad specimens were nearly a linear function of energy input.

Figure V-25

PEAK ADIABATIC CORE TEMPERATURE VS
ENERGY INPUT FOR UO_2 AND MIXED OXIDE

108-7829

108-7830

Figure V-26

MELTDOWN EXPERIMENTS IN TREAT ON UO_2 -
AND MIXED OXIDE-CORE, 304 STAINLESS STEEL-
CLAD FUEL PINS SUBMERGED IN WATER

Figure V-27

MELTDOWN EXPERIMENTS IN TREAT ON UO₂- AND MIXED OXIDE-CORE, ZIRCALOY-2- CLAD FUEL PINS SUBMERGED IN WATER

108-7831

7. Studies of Preirradiated Fuel Meltdown in TREAT (R. C. Liimatainen, F. J. Testa, J. Hepperly)

Most of the meltdowns conducted in the TREAT metal-water program have been on unirradiated fuel. The main purpose of this study is to compare data on the amount of molten metal-water reaction and change in geometry for preirradiated fuel with previous data obtain in TREAT for unirradiated, clean fuel samples.

The first meltdown experiment with preirradiated fuel was described in the previous summary report, ANL-6800, p. 353. That experiment was conducted with an unclad metallic pin having the composition 93.5 w/o uranium (20% enriched)-5 w/o zirconium-1.5 w/o niobium, and which had been irradiated in MTR to 0.3% burnup of the uranium atoms present. Two additional experiments with this material have been completed and are reported herein. Two experiments have also been completed with undamaged fuel plates salvaged from the SL-1 reactor. These specimens were clad plates having a center section of 81 w/o aluminum-17 w/o uranium (fully enriched)-2 w/o nickel, and clad with X8001 aluminum. The SL-1 material had been irradiated to 2.2% burnup of the uranium atoms present.

Data were obtained on both the extent of metal-water reaction and on the release of fission products. The amount of chemical reaction

was measured by the hydrogen evolved, and the activity release was determined by analyzing the preirradiated fuel before and after the TREAT transient.*

The analytical procedure was first to dissolve the fuel sample by treatment with hot $3\text{M HCl} + 0.5\text{M HF}$. Following the dissolution, the uranium was oxidized by $3\text{M H}_2\text{O}_2$. Aliquots of the solution containing the uranium, zirconium, niobium, and fission products were then taken and specific analyses performed. The uranium was determined colorimetrically. Gross beta and gamma counting were done on a proportional counter and a well type scintillation counter, respectively. The fission product cesium was determined by first extracting with sodium tetraphenyl boron in amyl acetate to achieve a separation from other fission products and then counting the cesium-137 gamma. Fission product strontium was determined by first adding strontium carrier to an aliquot of the acid solution of the sample and then scavenging with ferric hydroxide to remove zirconium, niobium, ruthenium, and the rare earths from the solution. Then the strontium was precipitated as the carbonate, filtered, dried, weighed, and mounted for beta counting. In samples such as these which have received two irradiations (the first one in the MTR of long duration and the second one in TREAT lasting about 1 sec), it is important to differentiate between ^{89}Sr and ^{90}Sr to get meaningful data on fission product release as a result of TREAT meltdowns. To accomplish this, the samples were counted within 4 hr of the separation of the strontium and then were recounted one week later to allow the yttrium to grow into equilibrium. The second count gave the sum of the activities of ^{89}Sr , ^{90}Sr , and ^{90}Y . The difference between the two counts gives a measure of the ^{90}Sr . Fission product cerium was determined by first extracting with diethylhexyl phosphoric acid in toluene from the acid solution made 0.01M . Then the total rare earths and yttrium were stripped out with 8M HCl . An aliquot of the strip solution was plated and counted on a single channel gamma analyzer for ^{144}Pr which is a measure of the activity of the parent ^{144}Ce . From these analyses, the percent activity release was computed from the following relationship:

$$\% \text{ Release} = \frac{\text{Activity in fuel pin before meltdown in TREAT} - \text{Activity in particles of fuel after destructive TREAT meltdown}}{\text{Activity in fuel pin before meltdown in TREAT}} \times 100$$

The results of the experiments with preirradiated fuel specimens are summarized in Table V-9, while Figures V-28, V-29, V-30, and V-31 show the appearance of the samples after meltdown. The extent of metal-water reaction is plotted as a function of fission energy input for the uranium alloy specimens in Figure V-32 and for the SL-1 fuel plate specimens

*We wish to acknowledge the cooperation of the Analytical Group of the Chemical Engineering Division who performed the radiochemical separations and counting.

in Figure V-33. The results in each case are compared with correlations representing the nominal behavior of cold, clean specimens as determined in previous studies. The comparisons indicated that the preirradiation had no effects on the extent of reaction. The appearance of the residue was similar to that of unirradiated specimens that had been subjected to TREAT transients, indicating that there was no effect of preirradiation on the nature of the meltdown.

Table V-9

TREAT MELTDOWN EXPERIMENTS WITH
PREIRRADIATED FUEL SPECIMENS

(Water initially at room temperature)
(Initial helium overpressure of 20 psia)

CEN Run No.	Fission Energy Input (cal/g)	Reactor Characteristics		Appearance of Specimen after Transient	Percent of Metal Reacted
		Period (msec)	Int. Power (Mw-sec)		
<u>Unclad Uranium-Zirconium-Niobium Fuel Pins</u>					
	93.5 w/o uranium (20% enriched), preirradiated to 0.3% burnup-5.0 w/o zirconium-1.5 w/o niobium; 0.2 in. dia. x 0.5 in. long.				
171	150	96	168	globule and some fines	10.5
167 ^a	270	84	300	fragmented	22.6
172	394	63	438	fragmented	51.3
<u>Clad Aluminum-Uranium Alloy Plates (salvaged from SL-1)</u>					
Clad: X8001 aluminum, 20 mils thick Core: aluminum-17 w/o uranium (93% enriched), preirradiated to 2.2% burnup-2 w/o nickel; 0.5 in. x 0.75 in. x 0.080 in.					
180	520	43	691	globule and some fines	10.0
182	745	39	985	globule and some fines	23.8

^aPreviously reported in ANL-6800, p. 353.

Figure V-28

PREIRRADIATED URANIUM-ZIRCONIUM-
NIOBIUM ALLOY FUEL PIN AFTER
TREAT TRANSIENT CEN-171

(150 cal/g alloy)

108-6838-A

Figure V-29

PREIRRADIATED URANIUM-ZIRCONIUM-
NIOBIUM ALLOY FUEL PIN AFTER
TREAT TRANSIENT CEN-172

(394 cal/g alloy)

108-7046-A

Figure V-30

PREIRRADIATED ALUMINUM-URANIUM
ALLOY (SL-1) FUEL PLATE AFTER
TREAT TRANSIENT CEN-180

(520 cal/g alloy)

108-7325-A

Figure V-31

PREIRRADIATED ALUMINUM-URANIUM
ALLOY (SL-1) FUEL PLATE AFTER
TREAT TRANSIENT CEN-182

(745 cal/g alloy)

108-7447-A

Figure V-32

TREAT MELTDOWN EXPERIMENTS
WITH PREIRRADIATED URANIUM-
ZIRCONIUM-NIOBIUM FUEL SAMPLES

108-7832

Figure V-33

TREAT MELTDOWN EXPERIMENTS
WITH PREIRRADIATED ALUMINUM-
URANIUM ALLOY (SL-1) FUEL SAMPLES

108-7833

The results of the fission product analyses for the uranium alloy fuel are summarized in Table V-10. The analyses indicated that there was an extensive release of all three of the nuclides studied.

Table V-10

FISSION PRODUCT RELEASE FROM TREAT MELTDOWNS
OF PREIRRADIATED U-Zr-Nb ALLOY FUEL PINS IN WATER

Type of Activity	Original Activity (cpm/mg U)	171		167		172	
		Activity ^a (cpm/mg U)	% Release	Activity ^a (cpm/mg U)	% Release	Activity ^a (cpm/mg U)	% Release
¹³⁷ Cs γ	8.0 x 10 ⁶	1.3 x 10 ⁵	99	1.3 x 10 ⁵	99	1.4 x 10 ⁵	98
⁹⁰ Sr β	1.8 x 10 ⁶	4.0 x 10 ⁴	98	4.1 x 10 ⁴	99	4.6 x 10 ⁵	74
¹⁴⁴ Ce γ	3.4 x 10 ⁶	1.3 x 10 ⁵	96	2.0 x 10 ⁶	41	2.3 x 10 ⁵	93
total β	20 x 10 ⁶	8.8 x 10 ⁶	56	15 x 10 ⁶	25	7.7 x 10 ⁶	67
total γ	11 x 10 ⁶	2.5 x 10 ⁶	77	2.7 x 10 ⁶	75	1.8 x 10 ⁶	84
energy (cal/g)		150		270		394	
% metal-water reaction		10.5		22.6		51.3	

^aActivity in the melted particles after the destructive power excursion experiment in TREAT.

B. Transient Heat Transfer (L. Baker)

1. Calculation of the Pressure History of a Water-Cooled Reactor during an Excursion
(R. O. Ivins, L. Baker)

A mathematical model describing the transient heat transfer and pressure generation in a water-cooled reactor undergoing an excursion is being developed. An objective of this investigation is to study the role of rapid steam formation as a pressure producing mechanism in water-cooled reactor meltdown accidents. The initial effort is directed at simulating the SPERT-1D destructive transient which employed a metallic plate type core.⁷ The development of the mathematical model is described in several sections which follow:

a. Growth of a Steam Film on a Rapidly Heated Plate at Constant Pressure

In developing a mathematical model for a violent pressure surge produced during the meltdown, several assumptions were made at the outset. These are as follows:

1. A steam film is formed at the fuel surface and is of uniform thickness.
2. The vapor obeys the ideal gas law.
3. The temperature gradient across the steam film is constant.
4. The thermal conductivity and specific heat of the vapor are constant.
5. Radiative heat transfer can be neglected.

Some of the assumptions, particularly 4 and 5, may be discarded in future, more refined calculations. The model implied by the assumptions is illustrated in Figure V-34. The rate of heat transfer from the plate to the

Figure V-34

DIAGRAM OF STEAM FILM AT A RAPIDLY HEATED SURFACE

108-7834

⁷Miller, R. W., Spano, A. H., Dugone, J., Wieland, D. D., and Haughtaling, J. E., Trans. Am. Nucl. Soc. 6 (1), 138 (1963).

steam is as follows using the assumption of a constant temperature gradient across the film:

$$\frac{dQ}{dt} = kA \left(\frac{T_w - T_s}{X} \right) \quad (3)$$

where Q = thermal energy, cal,

t = time, sec,

k = thermal conductivity of vapor, cal/(cm)(sec)(°K),

A = plate area, sq cm,

T_w = plate surface temperature, °K,

T_s = temperature at liquid-vapor interface, °K, and

X = vapor film thickness, cm.

It was also assumed that some of the heat is used to form new steam and some is used to superheat steam. The total heat content, Q , of the steam film is obtained by an integration over the film noting that the vapor density at any point in the film is PM/RT :

$$Q = \int_0^X L \left(\frac{PM}{RT} \right) A \, dx + \int_0^X C_p (T - T_s) \left(\frac{PM}{RT} \right) A \, dx \quad (4)$$

Latent Heat Sensible Heat

where Q = heat required to create steam film from water at T_s , cal,

L = heat of vaporization at T_s , cal/g,

P = pressure in steam film, atm,

M = molecular weight of water, 18 g/mole,

R = gas constant, 82.06 (cc)(atm)/(mole)(°K) or 1.987 cal/(mole)(°K),

C_p = specific heat of steam, cal/(g)(°C),

T = temperature at point x , and

x = distance from plate, cm.

The expressions in Equation 4 may be integrated noting that

$$T = (T_w - T_s) \left(1 - \frac{x}{X} \right) + T_s \quad (5)$$

to yield

$$Q = PAX \left[\frac{LM}{R(T_w - T_s)} \ln \frac{T_w}{T_s} + \frac{C_p^M}{R} - \frac{C_p^M T_s}{R(T_w - T_s)} \ln \frac{T_w}{T_s} \right]. \quad (6)$$

Latent Heat Sensible Heat

It is convenient at this point to define a dimensionless function of T_w and T_s as follows:

$$F = \left[\frac{M(L - C_p T_s)}{R(T_w - T_s)} \ln \frac{T_w}{T_s} + \frac{C_p^M}{R} - 1 \right]. \quad (7)$$

The heat content then becomes

$$Q = \frac{PAX(F+1)}{K_1} \quad (8)$$

where $K_1 = \text{constant}$, $41.29 \text{ (cc)(atm)/cal}$.

If we now stipulate constant pressure conditions, Equation 8 can be differentiated and equated to the right hand side of Equation 3:

$$\frac{dQ}{dt} = kA \frac{(T_w - T_s)}{X} = \frac{PA(F+1)}{K_1} \frac{dX}{dt}. \quad (9)$$

Equation 9 can now be solved to yield

$$X^2 = \frac{2k(T_w - T_s)K_1 t}{P(F+1)}. \quad (10)$$

It is now possible to compare steam film growth rates calculated from Equation 10 with those calculated by Hamill and Bankoff.⁸ The treatment by Hamill and Bankoff began with the differential equation for heat conduction. Their treatment, therefore, did not require an assumption of a linear temperature change across the film (assumption 3). Although their treatment is more general, it is much more complex and does not appear readily adaptable to the more important case of varying pressure. In order to achieve a numerical comparison, Equation 10 was recast into the symbolism used by Hamill and Bankoff. Instead of the vapor film thickness X , they used the mass of steam as an index of growth. The mass of steam is related to the film thickness according to our development as follows:

$$\text{Mass} = \left[\frac{PM}{R(T_w - T_s)} \ln \frac{T_w}{T_s} \right] X. \quad (11)$$

Substituting Equation 11 into Equation 10, the latter becomes

⁸Hamill, T. D., and Bankoff, S. G., Chem. Eng. Sci. 18, 355 (1963).

$$(\text{Mass})^2 = 4 \beta'^2 \left(\frac{\text{PM}}{RT_s} \right) \frac{k}{C_p} t \quad (12)$$

where β'^2 = Hamill and Bankoff's growth constant and

$$\beta'^2 = \frac{\ln U_w}{2 \left(\frac{L}{C_p T_s} - 1 \right) + \frac{2(U_w - 1)}{\ln U_w}} \quad (13)$$

where $U_w = T_w/T_s$.

Hamill and Bankoff's second order analytical approximation for the growth constants was given as follows:

$$\beta'^2 = \frac{\ln U_w}{2 \left(\frac{L}{C_p T_s} - 1 \right) + \frac{4(U_w - 1 - \ln U_w)}{(\ln U_w)^2}} \quad (14)$$

Numerical agreement was checked for steam at 1 atm ($T_s = 100^\circ\text{C}$, $L/C_p T_s = 3.85$) and at 1000 psia ($T_s = 285^\circ\text{C}$, $L/C_p T_s = 2.02$) and for several values of T_w , 200, 400, and 800°C .

The numerical results were as follows:

Pressure (psia)	Plate Temp. T_w ($^\circ\text{C}$)	β'^2	
		Hamill and Bankoff (Equation 14)	This Treatment (Equation 13)
14.7	200	0.030	0.030
14.7	800	0.122	0.114
1000	400	0.045	0.044
1000	800	0.143	0.135

The comparison of the results indicates nearly perfect agreement at the low plate temperatures and a somewhat imperfect agreement at the higher plate temperature (where the temperature across the vapor film would deviate from linearity to a significant extent). It is likely, however, that a more serious deviation from linearity is caused by the variation of thermal conductivity with temperature which has been ignored in both treatments.

b. Energy Balance over the Steam Film for a Varying Pressure

From the first law of thermodynamics, the equation

$$E_2 - E_1 = \Delta Q - \Delta W \quad (15)$$

where E = internal energy, and

W = mechanical work

is used to develop an energy balance over the steam film. The kinetic energy of the steam film was neglected. The development is considered for a small, but finite, time interval, Δt . The heat added to the film is given by Equation 3 as follows:

$$\Delta Q = kA \frac{(T_w - T_s)}{X} \Delta t. \quad (16)$$

The mechanical work is given simply as

$$\Delta W = \frac{PA \Delta X}{K_1}. \quad (17)$$

The internal energy, E , may be obtained by noting that the total heat required to create the steam film from water at T_s at constant pressure (Equation 4 or 8) can be related to the enthalpy, H . The internal energy is the enthalpy less the product of the pressure and the volume:

$$E = H - PAX \quad (18)$$

and, therefore, from Equation 8:

$$E = \frac{PAX (F)}{K_1}. \quad (19)$$

The energy balance, Equation 15, then becomes

$$P_2 X_2 F_2 - P_1 X_1 F_1 = \frac{kK_1 (T_w - T_s)}{X} \Delta t - P \Delta X. \quad (20)$$

Equation 20 relates the pressure, P , and the steam thickness, X , as a function of time. A second expression necessary to obtain a numerical solution was derived as shown in the following section.

c. Acoustic Constraint for a Submerged Reactor Core

A physical model, shown in Figure V-35 based on the SPERT-1 reactor was used to develop an equation which would describe the acoustic constraint imposed on the steam film. As the reactor core undergoes an excursion and a steam film begins to form on the surface of fuel plates, the necessary volume for expansion can be obtained only from compression of water and reactor parts and from the flow of water away from the reactor core. It will be assumed that pressure can be relieved

spherically in all directions from the reactor core. Water then flows across the boundary defined by the reactor core which has a total surface area a^* (see Figure V-35). The linear velocity of water flow is given by the acoustic equation⁹

$$U = \frac{\Delta P K_2}{\rho_w C} \quad (21)$$

where U = acoustic water flow velocity, cm/sec,

ρ_w = water density, g/cc,

C = velocity of sound in water, 1.524×10^5 cm/sec,

K_2 = constant, 1.013×10^6 dynes/(sq cm)(atm),

and

$$\Delta P = P - P_0 \quad (22)$$

where P = pressure within reactor (function of time), atm, and

P_0 = original pressure of water (at time zero), atm.

The assumption is made that the pressure is uniform within the core. The rate at which water leaves the core can be equated to the rate of change of the quantity of water in the core as follows:

$$-\rho_w a^* U = \frac{d}{dt} [\rho_w (V - AX) + \rho_v AX] \quad (23)$$

where V = volume within core available to water or steam, cc, and

ρ_v = average density of vapor.

Figure V-35
DIAGRAM OF SPERT-1 REACTOR

108-7452 Rev.

Several assumptions are used to simplify Equation 23. These are:

$$\rho_w = \rho_0 (1 + \beta P), \quad \rho_w \gg \rho_v, \quad \text{and } 1 \gg \beta P, \quad (24)$$

where ρ_0 = original water density,

β = compressibility of water, $50 \times 10^{-6} \text{ atm}^{-1}$, and

P = pressure, atm.

Using these assumptions and noting that $C^2 = K_2/\rho_0\beta$, Equation 23 becomes

$$\frac{dx}{dt} = \beta \left(\frac{V}{A} - X \right) \frac{dP}{dt} + \frac{a^*}{A} \beta C (P - P_0). \quad (25)$$

Equations 23 and 25 ignore the compressibility of the metal reactor parts within the core because of the relatively small values of metal compressibilities.

Under many circumstances, it is necessary to consider the gas content of the reactor core. The gas can be either condensable (steam) or noncondensable (radiolytic or corrosion products). If the compression of this gas can be described by the perfect gas laws, then the quantity of gas (expressed in cc, at the original pressure and temperature) times the compressibility of a perfect gas ($1/P$) should be added to the first term of Equation 25.

$$\frac{dx}{dt} = \left[\beta \left(\frac{V}{A} - X \right) + \frac{V' P_0}{A P^2} \right] \frac{dP}{dt} + \frac{a^*}{A} \beta C (P - P_0) \quad (26)$$

where V' = volume of core gas at pressure P_0 , cc.

The acoustic constraint equation applies only for a limited period of time. Two factors must be considered in determining this time. The first factor is the sonic loading time of the water column above the core. Since sound travels at approximately 5 ft/msec in water, the loading time of the SPERT reactor, in Figure V-35, is 2 msec. The other factor to be considered is the time required for the pressure disturbance to reach a stationary surface, such as the tank wall, and be reflected back into the core. This round trip time is also approximately 2 msec in the SPERT case. In the SPERT case, it was concluded, therefore, that an acoustic constraint equation (Equation 25 or 26) is applicable without complication for 2 msec from the time the core pressure first begins a significant rise as a result of steam formation.

d. Solution of Equations for SPERT-ID Transient

The pressure events noted during the SPERT experiment are given in Figure V-36. The first pressure pulse was limited to a peak value of about 35 psig. The second pressure pulse occurred about 15 msec later and the peak pressure was estimated to be between 3000 and 4000 psig. The second pressure pulse occurred at a time when the reactor power was at a very low level as indicated by the power curve given in Figure V-36. Temperature-time curves for fuel plate surfaces were calculated by Zivi and Wright.¹⁰ The calculated curve for the 8th decile of power distribution of the transient is given in Figure V-37. This calculation was taken to represent the nominal behavior of fuel plates in the central 35% of the core in which fuel melting was observed to occur. The calculated temperature shows that fuel melting began at 6 msec (3 msec after peak power) and that the final temperature of 800°C was reached at 11 msec (8 msec after peak power, 7 msec before the large pressure pulse).

108-7451 Rev.

Figure V-36

EXPERIMENTAL PRESSURE AND POWER FOR SPERT-1D DESTRUCTIVE TEST

Figure V-37
CALCULATED FUEL PLATE
TEMPERATURE HISTORY FOR
SPERT-1D EXPERIMENT

108-7456 Rev.

¹⁰Zivi, S. M., and Wright, R. W., Kinetic Studies of Heterogeneous Water Reactor, STL-6306, June 1963.

The preliminary calculations were designed to test the hypothesis that the second and larger pressure pulse resulted from the sudden dispersal of the molten portion of the reactor core, exposing fresh surface of molten metal to water. The temperature of the molten metal was assumed to be 800°C (see Figure V-37), and the temperature decrease of the fuel plates resulting from the heat transferred from the metal to the steam was ignored.

The pressure in the core and the steam film thickness were calculated for a 2-msec period using Equation 20, the energy balance, and Equation 25, the acoustic constraint. The equation was put into the finite difference form, while the energy balance is already in that form. The two equations were combined to result in two new expressions; one of these was used to obtain a value for the film thickness and the other, a quadratic equation, was used to calculate the pressure. These equations were:

$$X_{n+1} = X_n + \beta \left(\frac{V}{A} - X \right) (P_{n+1} - P_n) + \frac{a^*}{A} \beta C (P_n - P_0) \Delta t \quad (27)$$

$$P_{n+1}^2 + \left[\frac{X_n}{\beta \left(\frac{V}{A} - X_n \right)} - P_n + \frac{\frac{a^*}{A} C \Delta t (P_n - P_0)}{\left(\frac{V}{A} - X_n \right)} + \frac{P_n}{F_{n+1}} \right] P_{n+1} = \left[\frac{\frac{kK_1 \Delta t}{X_n} (T_w - T_s) + P_n X_n F_n - \frac{a^*}{A} \beta C \Delta t P_n (P_n - P_0) + \beta \left(\frac{V}{A} - X_n \right) P_n^2}{\beta \left(\frac{V}{A} - X_n \right) F_{n+1}} \right]. \quad (28)$$

The equations were solved alternately on a CDC-3600 digital computer* using an initial time interval of 10^{-6} sec. Since the equations are undefined at the start, when $X = 0$, it was necessary to make an arbitrary assumption that the pressure increases during the first two time intervals were equal. With this assumption, it was possible to begin iterative calculations with the third time interval.

The calculated model was based only on the molten portion of the core which was assumed to be a sphere with a radius of 19.07 cm. The peripheral surface area, a^* , was therefore 4.56×10^3 sq cm. Calculations were performed using (1) a heat transfer area A equal to the original plate area in the molten portion of the core, 7.67×10^4 sq cm, (2) an area which was assumed to have increased by a factor of 5, and (3) an area which was assumed to have increased by a factor of 10.

*Programming was done by Ruth Fu of Applied Mathematics Division.

One set of calculations were made assuming that any steam generated within the central region of the reactor core during the first pulse and the period between the pulses had condensed prior to the explosive pressure rise. Another set of calculations were performed on the assumption that steam was present in the reactor core and acted as compressible gas. For these calculations, Equation 26, in finite difference form, was used.

An estimate of the quantity of steam present in the reactor core at the time of the second pulse was given by Zivi and Wright¹⁰ as 6 liters. This was based on the observation that the reactor power was at a low level and was not rising. This shut-down condition implied that approximately \$4 of reactivity had been compensated by void. Using an average void coefficient of 0.067, it was concluded that 6 liters of void was present. If it is also assumed that the void was distributed uniformly throughout the core, then the central 35% of the core contained 2.1 liters of steam. One of the calculations was therefore performed assuming that 2.1 liters of steam was in the molten portion of the core ($V' = 2100$ cc). Another calculation was performed assuming $V' = 210$ cc. This calculation and the calculations without steam in the central core region are based on the demonstrated tendency of steam formed at rapidly heated surfaces in subcooled water to condense almost completely and then re-form in a periodic manner. This was shown by the laser studies (see Figure V-16) and by recent in-pile capsule tests by Wentz.¹¹

The results of the calculations are given in Table V-11 and Figure V-38. The peak pressures and the rise time of the pressure (time for pressure to rise from 10 to 90% of peak) are given in Table V-11. The results for extensive core breakup (a tenfold increase in area) approach reported experimental estimates of 3000-4000 psi (200-267 atm) and 150- μ sec rise time. These preliminary calculations, therefore, indicate that the

Table V-11
COMPUTER SIMULATION OF DESTRUCTIVE
(SECOND) PRESSURE PULSE
IN SPERT-1D REACTOR EXPERIMENT

Surface Area Factor	Initial Steam Void Volume (cc)	Peak Pressure (atm)	Pressure Rise Time ^a (μ sec)
10	0	184	10
10	210	73	260
10	2100	40 ^b	1600 ^b
5	0	116	10
5	210	46	260
5	2100	19 ^b	1600 ^b
1	0	40	10
1	210	14	370
1	2100	34 ^b	1600 ^b

^aTime to rise from 10 to 90% of peak pressure.

^bStill rising after 2000 μ sec (2 msec).

Figure V-38
COMPUTED PRESSURE-TIME
CURVES FOR DESTRUCTIVE
(SECOND) PRESSURE PULSE
IN SPERT-1D REACTOR
EXPERIMENT (PLATE)

108-7835

second pulse in the SPERT test could have been a steam explosion caused by the sudden breakup of the molten portion of the core. The principal difficulty at present lies in the fact that considerable void in the core was required to account for the shut down condition of the reactor at the time of the second pressure pulse. The calculations show that a large void volume prevents a sharp explosion. The possibility remains, however, that the steam void at the central molten portion of the core may have condensed and thereby caused core breakup and a violent steam explosion.

C. Metal Oxidation and Ignition Kinetics

(L. Baker)

1. Uranium-Plutonium Alloy Ignition Studies (J. G. Schnizlein, D. F. Fischer)

Interest is being shown in zero power critical experiments with a uranium-plutonium alloy with an atomic ratio of about 2:1. The known pyrophoricity of such a binary alloy has prompted a study of the effect of small additions of other elements on the pyrophoricity of the uranium-plutonium alloy. The additives studied were aluminum, carbon, copper, molybdenum, zirconium, and iron. Iron was studied because a U. S. Patent¹² indicated that addition of 6 a/o (1.5 w/o) iron provided improved oxidation resistance.

The initial studies of this problem (reported in ANL-6800, p. 376) indicated that addition of 6 a/o of either iron or molybdenum to the

¹²U. S. Patent 2,902,362, Sept. 1, 1959.

uranium-30 a/o plutonium alloy achieved good resistance to ignition; however, the ignition characteristics with the iron alloy were adversely affected by the presence of moisture in the air.

The experiments were carried out primarily by the burning curve method, wherein the sample is heated at 10 degrees per minute in a flowing, oxidizing atmosphere. The burning curve is the temperature-time record of the specimen as measured by a thermocouple inserted into the specimen. The data presented in ANL-6800, p. 376 were obtained with cylindrical samples 6 mm in diameter by 6 mm in height which were prepared by chill casting.

In an effort to determine whether fabrication procedure and aging had any effect on ignition characteristics of uranium-30 a/o plutonium-6 a/o iron alloy, a rod of this alloy was prepared by injection casting. The alloy had an extremely coarse grain structure in contrast to the fine grain structure obtained by chill casting. Although the injection-cast material was too brittle to be used as a fuel, it was realized that the production of plates for zero power experiments would involve slower cooling rates than those used in the small-scale preparation of chill-cast samples. Accordingly, an ignition experiment was performed in dry air (<5 ppm moisture) on an injection-cast sample which had been aged approximately four months. This sample ignited at 300°C (see Figure V-39). It was at this temperature that notable reaction had occurred for the fresh chill-cast sample that did not ignite even though heated up to 820°C in dry air.

Figure V-39

BURNING CURVES OF U-30 a/o Pu AND
U-30 a/o Pu-6 a/o Fe ALLOYS
IN DRY AIR (<5 ppm MOISTURE)

Also included in Figure V-39 are burning curves for an aged sample of chill-cast iron alloy and a fresh injection-cast sample, as well as a burning curve for the binary alloy uranium-30 a/o plutonium for comparison. The chill-cast ternary material that had been aged had a greater specific area than the other specimens used in this study. This material underwent marked self-heating at 240°C followed by rapid reaction. It is not clear whether this less desirable behavior is due to the increased specific area or the aging of the alloy.

A fresh injection-cast ternary sample studied within a week of fabrication ignited at 240°C compared to 300°C for the aged sample. It is doubtful that aging would improve the ignition resistance of the alloy, so it must be assumed that the difference in ignition temperature is due to variation in the fabrication of the two castings.

A tentative conclusion from these experiments is that the ignition temperature can be increased somewhat by the addition of 6 a/o iron to uranium-30 a/o plutonium alloys, but that the method of fabrication is very important. One chill-cast sample of uranium-30 a/o plutonium-6 a/o iron did not ignite in dry air even though heated to 820°C, but a similar sample did ignite at about 300°C in wet air containing 20,000 ppm moisture. In dry air the injection-cast samples ignited at temperatures between 240 and 300°C and the binary alloy ignited at 157°C.

A recent communication from Winfrith, England,¹³ reports some results on uranium-25 a/o plutonium-4 a/o iron and uranium-25 a/o plutonium-8 a/o iron alloys. The investigators concluded that these alloys are more pyrophoric than delta-stabilized plutonium and give ignition temperatures near 300°C in dry air and below 300°C in moist air. However, the method of fabrication, which is not reported, may be the cause of the apparent increase in pyrophoricity.

Some fuel plate samples of a uranium-18 a/o plutonium-14 a/o iron alloy were prepared. This composition corresponds to the (U, Pu)₆Fe intermetallic. Although chill cast, the cooling rate was intermediate to laboratory chill-cast and injection-cast specimens. Samples for ignition experiments were prepared as 10-mm squares 2.1 or 5.3 mm thick with unmachined cast surfaces and as a machined 6 x 6 mm right cylinder. The thick square (0.44 sq cm/g specific area) and the cylinder (0.5 sq cm/g specific area) ignited at 300°C in dry air. The thin slice (specific area 0.83 sq cm/g) ignited at 275°C in dry air. An injection-cast cylinder of the same composition and another of uranium-18 a/o plutonium binary both ignited at 300°C. Burning curves are presented in Figure V-40. The conclusion is that addition of iron to the uranium-18 a/o plutonium alloy does not offer any advantage of ignition resistance.

¹³Smith, R., to Thalgott, F. W., private communication, February 17, 1964.

Figure V-40
BURNING CURVES OF U-18 a/o Pu
AND U-18 a/o Pu-14 a/o Fe ALLOYS
IN DRY AIR

108-7837

Because the addition of 6 a/o molybdenum to the uranium-30 a/o plutonium had also shown improved ignition behavior in a fresh chill-cast sample, the effects of injection casting and aging for this combination were examined. Burning curves in dry air for 6 x 6 mm right cylinders of fresh and aged chill-cast and injection-cast samples are compared in Figure V-41. The injection-cast molybdenum alloy is less subject to ignition than the injection-cast iron ternary alloy.

Since it is of interest from a nuclear physics point of view to keep the molybdenum content low, ternary alloys were also prepared with 4.5 and 3 a/o molybdenum. In these experiments the plutonium content was set at 20 a/o and chill castings were made by production methods. Burning curves for these uranium-20 a/o plutonium ternaries containing 6, 4.5, and 3 a/o molybdenum are compared in Figure V-42 with that for a uranium-18 a/o plutonium binary alloy. It is evident that the resistance to ignition is decreased by decreasing the molybdenum content, but that even the lowest molybdenum content is considerably superior to the binary.

Titanium or vanadium additions were suggested as lower atomic mass additives. Ternary alloys were prepared and tested in dry air. Burning curves in Figure V-43 illustrate that the resistance to ignition of uranium-20 a/o plutonium-6 a/o titanium and uranium-20 a/o plutonium-6 a/o vanadium is better than the binary but not as satisfactory as the uranium-20 a/o plutonium-6 a/o molybdenum.

Figure V-41
BURNING CURVES FOR
U-30 a/o Pu-6 a/o Mo
(6 x 6 mm dia. right cylinders
in dry air <5 ppm)

108-7838

Figure V-42
BURNING CURVES OF U-Pu-Mo
TERNARY ALLOYS WITH VARIED
MOLYBDENUM CONTENT
(Samples 10 x 10 x 6 mm in dry air)

108-7839

Figure V-43

BURNING CURVES OF U-18 a/o Pu,
U-20 a/o Pu-6 a/o Ti, U-20 a/o Pu-6 a/o V,
AND U-20 a/o Pu-6 a/o Mo

(Samples 10 x 10 x 6 mm in dry air)

108-7840

Several conclusions may now be made relative to this study of the ignition behavior of ternary uranium-plutonium alloys. Although 6 a/o of titanium or vanadium in the ternary uranium alloy containing 20 a/o plutonium, and 6 a/o of aluminum, carbon, copper, or zirconium in the ternaries containing 30 a/o plutonium improved the resistance to ignition, ternaries containing 6 a/o iron or molybdenum exhibited the greatest resistance. However, the ternary containing iron with 30 a/o plutonium showed considerable sensitivity to the mode of fabrication, and the ternary containing iron with 18 a/o plutonium showed no improvement of ignition behavior compared to binary uranium-18 a/o plutonium. Ternary uranium alloys containing 6 a/o molybdenum and either 20 or 30 a/o plutonium were much improved, being nearly as resistant to ignition as uranium. Ternary uranium alloys with 20 a/o plutonium and either 4.5 or 3 a/o molybdenum showed somewhat less resistance to ignition than did the corresponding alloy with 6 a/o molybdenum but showed greater resistance than the binary uranium-18 a/o plutonium.

2. Uranium-Molybdenum Alloy Oxidation Studies (J. G. Schnizlein, D. F. Fischer)

There has been considerable interest in the use of uranium-10 w/o molybdenum alloy as core material in various nuclear facilities. To assist in a hazards evaluation for one of these proposed assemblies, material supplied by the Lawrence Radiation Laboratory, Livermore, California has been subject to high-temperature oxidation studies.

These experiments have been performed on the Ainsworth recoding thermobalance (see ANL-6413, p. 172, for apparatus description). Two types of runs were carried out. In the first series, the furnace was heated at a uniform rate of 10 degrees per minute to approximately 750°C and then more slowly to 800°C where it was held constant as the reaction continued. The sample temperature was measured continuously.

For this first series of experiments, samples (1-cm cubes) of bare metal were tested both in dry air (<5 ppm moisture) and in air saturated with water at room temperature (~20,000 ppm moisture). In addition, a sample with a 2-mil nickel plating was tested in wet air.

The oxidation data (shown in Figure V-44) for the bare samples showed excellent agreement, indicating negligible effect of moisture on the oxidation behavior. No weight gain was detected until the sample was above 350°C. The oxidation rates at 770°C were approximately 0.4 mg/(sq cm)(min).

Figure V-44
OXIDATION OF URANIUM-
10 w/o MOLYBDENUM ALLOY

108-7841

The nickel-plated sample showed no weight gain until the temperature reached 760°C. The rate increased smoothly, and the sample self-heated to 945°C. The oxidation rate was approximately 72 mg/(sq cm)(min) at 925°C. This rate is higher than would be expected for unalloyed uranium. The nickel coating apparently provided a temporary protection from oxidation, but subsequently had a deleterious effect, as evidenced by the high rate of reaction.

In the second type of experiment, also carried out in the thermobalance, isothermal oxidation rate data were obtained. The bare samples were shielded from oxidation by a helium atmosphere while being heated to experimental temperature. These isothermal oxidation experiments were performed in moist air (saturated at room temperature to contain about 20,000 ppm moisture) at 300, 400, 450, 500, 600, and 700°C. When the air was admitted, slight self-heating was observed. Even at 700°C, this self-heating only caused the sample temperature to increase 25 degrees momentarily. The sample temperature was controlled at 700°C after 3 min of oxidation.

The data are presented in Figure V-45 as a plot of log of weight gain/sq cm vs log of time. At 300°C, the oxidation is initially linear at 1.74×10^{-3} mg/(sq cm)(min) for 80 to 100 min, after which an oxide coating which is then about 1.5μ thick becomes protective; this results in a decreasing reaction rate. Because of this unusual behavior, the run was repeated. Nearly identical results were obtained. The initial linear rate at 300°C is only 17% of the initial linear rate expected for unalloyed uranium. It may be speculated that the increased protectiveness resulted from an increase in the concentration of molybdenum at the metal surface as the uranium was preferentially oxidized.

Figure V-45
AIR OXIDATION OF
URANIUM-10 w/o MOLYBDENUM
ALLOY CUBES

At 400 and 450°C, the reaction was essentially parabolic with rate constants of 5.5 and 14 (mg O₂/sq cm)²/min, respectively. These rates are in fair agreement with an extrapolation of parabolic data obtained for pure uranium in air at temperatures from 600 to 1000°C (see ANL-6725, p. 201).

At 500 and 600°C, linear rates are observed for the entire run with rate constants of 0.039 and 0.31 mg/(sq cm)(min). At 700°C, the oxide coating formed was very protective; the oxidation followed a nearly cubic rate law for 200 min, and then accelerated to a final linear rate of about 0.07 mg/(sq cm)(min).

The experimental results, although complicated, indicate that there is little if any ignition hazard with massive pieces of the uranium-10 w/o molybdenum alloy. The isothermal oxidation studies have shown that a partially protective oxide is formed at temperatures up to 450°C. In general, the linear oxidation rates are at least an order of magnitude lower than those of unalloyed uranium.

The effects of prolonged thermal cycling have not been investigated. The possibility, therefore, remains that the oxidation behavior of uranium-10 w/o molybdenum alloy could be altered by thermal cycling. Severe thermal cycling will be produced by continued operation of a critical assembly at the Lawrence Radiation Laboratory. Should this cycling result in extensive cracking or crumbling of the metal, an ignition hazard could develop as a result of the increased surface area available for oxidation. Thermal cycling might also lower the protectiveness of oxide films, and, in addition, might cause deterioration of the nickel plating.

3. Thermal Conductivity of Metal Powders (D. Swift, P. Krause)

An investigation of the thermal conductivity of metal powders has been undertaken to better understand powder ignition phenomena. The increased use of reactive metal powders in metallurgical processes has increased the importance of understanding the mechanism of air ignition. Previous ignition studies with uranium,¹⁴ zirconium (ANL-6560, p. 145), and uranium monocarbide powders (ANL-6379, p. 192) have been reported. The results of the uranium experiments have been interpreted¹⁴ in terms of the Frank-Kamenetskii theory of thermal explosions.¹⁵ This theory defines a criterion for ignition in terms of the geometry of the system, the rate and heat of reaction, and the thermal conductivity. It is thus desirable

¹⁴Tetenbaum, M., Mishler, L., and Schnizlein, J. G., Nucl. Sci. Eng. 14, 230 (1962).

¹⁵Frank-Kamenetskii, D. A., Diffusion and Heat Exchange in Chemical Kinetics, Princeton University Press (1955).

to know how thermal conductivity of powder depends on particle size, temperature, and the extent of oxidation on the surface of the particles. The effect of gas pressure is important in determining the relative contributions of gas and solid to the overall conductivity and in developing a general correlation of the results.

A transient line source method was chosen as the experimental method. The theory of the method and the experimental apparatus were described in the previous summary report (ANL-6800, p. 383). Preliminary results with nickel powders and with uranium powders were also presented in that report. Experimental studies with uranium and zirconium powders have now been completed and are described in the following paragraphs. Preliminary analysis of the results using a theoretical model is also described, and the application of the data to the prediction of ignition temperature of uranium powders is discussed.

a. Results with Unoxidized Uranium Powders

The uranium powder used was in the form of spherical particles prepared by the Linde Company. The material was the same as that used in the ignition studies.¹⁴ The powder was packed into the thermal conductivity cell so that there was 0.60 solid volume fraction. The conductivities were first measured at atmospheric pressure in nitrogen gas and at several temperatures as shown in Figure V-46. Three mesh fractions were used and it was found that thermal conductivity increased with increasing particle size and was a linear function of temperature.

108-7854

Figure V-46
THERMAL CONDUCTIVITY OF
UNOXIDIZED URANIUM POWDER
IN NITROGEN AT
ATMOSPHERIC PRESSURE

According to the kinetic theory of gases, the thermal conductivity of a gas is independent of the pressure.¹⁶ The thermal conductivity of a gas-powder system, however, is dependent on the pressure at lower pressures, because the mean free path of the gas becomes appreciable in comparison with the particle size, so that free molecular conduction is experienced. At very low gas pressure, the thermal conductivity of a powder is no longer pressure-dependent. At this point, heat conduction occurs

¹⁶Jeans, Sir James, Kinetic Theory of Gases, Cambridge (1959), p. 47.

by particle contact only. The limiting value of conductivity at very low pressure will be represented by k_0 [cal/(cm)(sec)(°C)] in the following paragraphs.

At high pressure, thermal conductivities of powders are also expected to become pressure-independent. Under these conditions, the mean free path of the gas is small in comparison with the particle size. The observed conductivity is some combination of the gas and solid conductivities which are both pressure-independent. The limiting high-pressure conductivity will be represented by $\bar{k}$.

Variation of thermal conductivity with nitrogen gas pressure for five uranium powder fractions is plotted in Figure V-47. At high pressure ($>10^3$ mm), the thermal conductivities have reached a value independent of pressure; the larger size particles had a higher conductivity. At pressures below 10^{-4} mm, the conductivities were also constant. The larger values found for the larger particle sizes indicate that particle contact is more effective for heat transfer with these powders.

Figure V-47

THERMAL CONDUCTIVITY OF UNOXIDIZED URANIUM POWDER AT 25°C IN NITROGEN

108-7846

The results, plotted in Figure V-47, also show that the pressure above which the thermal conductivity is constant decreases with increasing particle diameter. This limiting pressure has been called the "breakaway pressure" by Deissler and Eian¹⁷ and it can be characterized by the ratio of the mean free path, λ , to the particle diameter, d . This ratio, λ/d , is called the Knudsen number. Breakaway pressures for the uranium powder corresponded to a Knudsen number of about 4×10^{-3} , while breakaway pressures for magnesium oxide powder as measured by Deissler and Eian corresponded to a Knudsen number of 7×10^{-4} .

¹⁷Deissler, R. G., and Eian, C. S., NACA RM E52C05, (1952).

b. Results with Oxidized Uranium Powders

Thermal conductivity measurements were performed at atmospheric pressure and 280°C with two particle size fractions of uranium powders which had been oxidized to various degrees as a function of the extent of oxidation. The procedure for oxidizing the uranium powders is described in ANL-6800, p. 388. Results are given in Figure V-48 and indicate that the conductivity at first decreases sharply as the extent of oxidation increases and then decreases more slowly as the composition approaches that of UO_2 .

Figure V-48

THERMAL CONDUCTIVITY OF OXIDIZED URANIUM POWDER IN NITROGEN AT 280°C AND ONE ATMOSPHERE

108-7847

The dependence of conductivity on pressure for preoxidized uranium was also determined, using -70 +80 mesh powder and -230 +325 mesh powder in nitrogen at 25°C. The results for the -70 +80 mesh fraction are given in Figure V-49. It was found that the limiting high-pressure conductivity $\bar{k}$ decreases as the extent of oxidation increases; however, the limiting low-pressure conductivity k_0 does not depend upon the extent of oxidation. Since the oxides of uranium have lower thermal conductivities than the metal, it appears that there is better particle-to-particle contact between the oxidized particles than between the metal particles. The very low values of k_0 in relation to $\bar{k}$ indicate that particle-to-particle contact contributes little to the thermal conductivity at ordinary pressures.

Figure V-49

THERMAL CONDUCTIVITY OF
OXIDIZED URANIUM POWDER
IN NITROGEN AT 25°C

(-70 +80 mesh)

108-7848

c. Results with Zirconium Powders

The zirconium powder used was in the form of spherical particles prepared by the Linde Company. Thermal conductivity at 24°C as a function of pressure was determined in helium, nitrogen, and argon for a -70 +80 mesh fraction. The results, shown in Figure V-50, were similar to those reported previously for nickel (see ANL-6800, p. 386) in that the thermal conductivity decreased in the same order as the conductivity of the gas, namely $\text{He} > \text{N}_2 > \text{Ar}$. However, the conductivities approached the same k_0 value at low pressures for all three gases showing that k_0 is in fact a contact conductivity.

Figure V-50

THERMAL CONDUCTIVITY OF ZIRCONIUM POWDER
IN VARIOUS GASES AT 24°C

(-70 +80 mesh)

108-7849

Values of $\bar{k}$ were determined for a number of unoxidized zirconium powders in order to determine the variation of conductivity with average particle diameter. These experiments were performed in nitrogen at 100 psig and 25°C in order to determine the limiting high-pressure conductivity. The results are compared with similar results for uranium powders in Figure V-51 where it is shown that the limiting conductivity increases with particle size for both metals.

Figure V-51

THERMAL CONDUCTIVITY OF URANIUM AND
ZIRCONIUM POWDERS AT 25°C IN NITROGEN
AT HIGH PRESSURE (100 psig)

The thermal conductivity results with oxidized zirconium powders were similar to those with uranium in that the conductivity decreases with increasing extent of oxidation. Conductivity changes with zirconium, however, were more gradual than with uranium. The zirconium results are plotted in Figure V-52. A more compact oxide is formed on

Figure V-52

THERMAL CONDUCTIVITY
OF OXIDIZED ZIRCONIUM
POWDER IN NITROGEN
AT 25°C AND
ONE ATMOSPHERE
(-70 +80 mesh)

zirconium than on uranium, and this probably accounts for the decreased effect of preoxidation on the thermal conductivity.

d. Theoretical Correlation of Powder Thermal Conductivities

A number of papers have been published containing theoretical treatments for prediction of powder thermal conductivities. The less complicated theories generally assume a particular stacking arrangement of the particles, and the theoretical expressions involve only the bulk conductivities of the solid and the gas and the void fraction. Examples of these are the treatments of Deissler and Eian,¹⁷ Rayleigh,¹⁸ Russell,¹⁹ and Woodside.²⁰ This type of treatment is only applicable for prediction of $\bar{k}$. In general, there is no way of predicting k_0 for a given system. Conductivity values in the transition region between k_0 and $\bar{k}$ depend upon the thermal accommodation coefficient of a solid-gas system. More complicated treatments such as that of Masumuni and Smith,²¹ which take into account particle contact conductivities and accommodation coefficients, are not suitable for prediction.

The randomly arranged spherical powders used in the experimental studies had a void fraction of approximately 0.40. A theoretical model should, therefore, have the same void fraction. Among the regular packing arrangements of spheres, the orthorhombic structure with a void fraction of 0.395, appears to be best suited for the development of a model. The unit cell for the orthorhombic model is shown in Figure V-53. The assumption is made, along with Deissler and Eian, that there is no bending of the heat flux lines. It is also assumed that there are only point contacts between particles so that no heat flows directly from particle to particle. The unit cell is assigned an area of unity normal to the heat flux and a temperature difference of unity is imposed across the unit cell. The thickness, Z , of the unit cell is then calculated to be 0.76 unit. The heat flux through an infinitesimal area $r \, dr \, d\theta$ is then given in terms of Z_s , the distance from the top of the cell to the surface of sphere, and T_s , the temperature at the surface of the sphere as follows:

$$\frac{dq}{r \, dr \, d\theta} = k_s \frac{(1 - T_s)}{Z_s} = k_g \frac{T_s}{0.76 - Z_s} \quad (29)$$

where q = heat flux,

k_s = thermal conductivity of solid, and

k_g = thermal conductivity of gas.

¹⁸Rayleigh, Lord, Phil. Mag. 34, 481 (1892).

¹⁹Russell, H. W., J. Amer. Ceramic Soc. 18, 1 (1935).

²⁰Woodside, W., Can. J. Physics 36, 815 (1958).

²¹Masumuni, S., and Smith, J. M., I and EC Fundamentals 2, 136 (1963).

The total heat flow is found by integrating Equation 29, using the substitution

$$Z_s = \sqrt{0.577 - r^2}. \quad (30)$$

Expressing the result in terms of the overall conductivity $\bar{k}$ yields

$$\frac{\bar{k}}{k_g} = 0.577 \pi \left\{ \left(\frac{k_g}{k_s} - 1 \right)^{-1} - \left(\frac{k_g}{k_s} - 1 \right)^{-2} \ln \frac{k_g}{k_s} \right\} + 0.093. \quad (31)$$

Equation 31 indicates that the limiting high-pressure conductivity of powders depends only on the gas and solid conductivity values. Equation 31 cannot be used to explain the increase in conductivity with particle size noted in Figure V-51 since particle size does not appear in the equation. In order to compare the experimental conductivities with Equation 31, the conductivity of -70 +80 mesh uranium and zirconium powders were used.

Figure V-53
ORTHORHOMBIC UNIT CELL FOR
THERMAL CONDUCTIVITY CALCULATION

108-7852

The limiting conductivities for uranium and zirconium powders are compared in Figure V-54 with a line calculated from Equation 31 (solid line) and with the correlation developed by Deissler and Eian¹⁷ (dashed line). The results show excellent agreement with Equation 31. Solid conductivities used were 0.074 and 0.050 cal/(cm)(sec)(°C) for uranium and zirconium, respectively.²²

In order to test Equation 31 further, $\bar{k}$ was measured for a number of other spherical powders including nickel, aluminum, copper, magnesium, and glass. The conductivities were measured in a number of gases including hydrogen, helium, nitrogen, methane, argon, and freon-12,

²²Metals Reference Book, Vol. II, Butterworths, Washington, 1962, p. 696.

and the points corresponding to these values of $\bar{k}$ are also shown in Figure V-54. The point at the lower left of Figure V-54 is the measured $\bar{k}$ for the glass spheres with water in the interstices instead of a gas. The experimental points in Figure V-54 show considerable scatter, but they appear to fit the predicted line based on the orthorhombic model better than they fit the curve predicted by Deissler and Eian.

Figure V-54

TEST OF EQUATION FOR POWDER THERMAL CONDUCTIVITY, $\bar{k}$, ORTHORHOMBIC MODEL

108-7853

Experiments with glass spheres of three sizes were conducted at 25°C in N₂ as a function of gas pressure. It was interesting to note, as shown in Figure V-55, that the values of $\bar{k}$ and k_0 for the powders were not size dependent. It was thus concluded that the dependence of $\bar{k}$ upon particle size for the uranium and zirconium powders was not merely a characteristic of the apparatus or measuring technique. Figure V-55 also shows the decrease of breakthrough pressure with increasing particle size, consistent with the concept of a critical value of the Knudsen number.

Figure V-55

THERMAL CONDUCTIVITY OF GLASS MICROSPHERES IN NITROGEN AT 25°C

108-7855

The correlation summarized in Figure V-54 does not include results of conductivity measurements with oxidized particles. In order to include these results, it is necessary to estimate an effective conductivity for the partly oxidized solid particles. Methods of achieving this are presently under study.

e. Application of Conductivity Results of Uranium Powder Ignition Behavior

Uranium powder ignition behavior has been interpreted¹⁴ using the Frank-Kamenetskii theory of thermal explosion.¹⁵ This theory, originally developed for homogeneous gas phase reactions, resulted in the following ignition criterion:

$$\delta = \frac{QE}{kRT_0^2} r^2 n A \exp\left(-\frac{E}{RT_0}\right) \quad (32)$$

where δ = a dimensionless constant, 0.88 for slab geometry, 2.0 for cylindrical geometry, and 3.32 for spherical geometry,

Q = heat of reaction of uranium with oxygen, 8100 cal/g O_2

E = activation energy, cal/mole,

k = thermal conductivity, cal/(cm)(sec)(°K),

R = gas constant, 1.99 cal/(mole)(°K),

T_0 = ignition temperature, °K

r = dimension, cm (half-thickness for slab, radius for cylinder or sphere).

n = reactive surface area per unit volume, sq cm/cc, and

A = pre-exponential factor in linear oxidation rate equation, $g O_2/(\text{sq cm})(\text{sec})$.

Studies of the isothermal oxidation of uranium up to 300°C²³ (see also ANL-5974, p. 45) have shown that the reaction occurs in two linear stages. The reaction rate during the second stage was nearly an order of magnitude greater than that during the initial stage. The oxidation rates were expressed in Arrhenius form:

$$\text{Rate} = A \exp\left(-\frac{E}{RT}\right). \quad (33)$$

The following constants were reported (ANL-5974, pp. 52, 54) for the reaction with O_2 at 800 mm:

²³Leibowitz, L., Schnizlein, J. G., Bingle, J. D., and Vogel, R. C., J. Electrochem. Soc. 108, 1155 (1961).

First Stage: $A = 5.17 \text{ g}/(\text{sq cm})(\text{sec})$, $E = 18.7 \text{ kcal/mole}$
 Second Stage: $A = 350 \text{ g}/(\text{sq cm})(\text{sec})$, $E = 20.5 \text{ kcal/mole}$.

Ignition temperatures were calculated from Equation 32, using slab geometry to represent the case of a shallow powder bed in the same manner as in Reference 14. Accordingly, one-half of the experimental critical height was used for dimension r . Results are given in Table V-12 where it appears that the experimental ignition temperatures are intermediate between those based on first-stage oxidation rates and those based on second-stage rates. This result implies that the complexity of the reaction kinetics prevents an unequivocal test of Equation 32. Additional studies of the detailed progression of the reaction are evidently required.

Table V-12

COMPARISON OF EXPERIMENTAL AND THEORETICAL
IGNITION TEMPERATURE FOR URANIUM POWDER

Mesh Size	Average Particle Diameter (μ)	Specific Surface (sq cm/cc)	Thermal Conductivity ^a [cal/(cm)(sec)(°C)]	Experimental		Theoretical Ignition Temperature	
				Critical Height (cm)	Ignition Temperature (°C)	Using First Stage Rate Constants (°C)	Using Second Stage Rate Constants (°C)
-12 +14	1500	25.2	1.35×10^{-3}	0.88	320	342	242
-18 +20	840	42.4	1.30×10^{-3}	0.68	310	340	241
-40 +45	390	102	1.17×10^{-3}	0.43	295	338	239
-80 +100	149	238	1.0×10^{-3}	0.29	270	328	234
-120 +140	115	338	9.5×10^{-4}	0.24	260	326	232
-200 +230	62	574	8.4×10^{-4}	0.18	255	324	230

^aInterpolated from data given in Figure V-46.

Ignition experiments with preoxidized uranium powders (ANL-6333, p. 201) have shown that slightly oxidized powders have lower ignition temperatures than unoxidized powders. As the powders are further oxidized, the ignition temperature levels off, then slowly increases. Thermal conductivity variation with extent of preoxidation (shown in Figure V-48) decreases monotonically, indicating that thermal conductivity variations alone do not explain the observed ignition temperature variations.

Further attempts to understand powder ignition behavior quantitatively can now be carried forth without uncertainty regarding values of thermal conductivity and their dependence upon temperature, pressure, particle size, and extent of prior oxidation.

4. Aluminum-U₃O₈ Thermite Reaction (L. Baker, J. D. Bingle)

Aluminum-uranium oxide cermets are used quite extensively as a nuclear fuel. Because of abnormal dimensional growth during

fabrication procedures with UO_2 ,²⁴ in contrast to that of fuel elements containing U_3O_8 ,^{25,26} the latter oxide is the one commonly used. However, this leads to a fuel element in which there remains the potential for an exothermic thermite reaction between the components. It is essential to evaluate the safety implications of this potential energy.

Previous work has shown some significant differences in experimental findings. In this laboratory (see ANL-6800, p. 390), results utilizing both slow and fast heating techniques indicated that a maximum thermal effect occurred for specimens in the composition range 60 to 75 w/o U_3O_8 , with sample temperatures peaking at about 400 to 600°C above the furnace temperature. A maximum self-heating rate of 150°C per second was measured with an electronic two-color pyrometer.

In contrast, other investigators had reported²⁷ that violent reactions occurred with mixtures containing from 74.5 to 89.8 w/o U_3O_8 . The reactions were initiated at specimen temperatures of 820 to 1050°C, depending upon the particle sizes of powders used to prepare the pressed compacts. It was also reported in that study that surface temperatures as high as 2200°C were reached during ignition, while self-heating rates, as deduced from high-speed motion pictures of the ignitions, were of the order of several thousand degrees per second.

The overall reaction involved, as previously reported (ANL-6800, p. 399) may be described by the following equation:

However, this can be divided into two separate reactions as follows:

Rough calculations based on thermodynamic and stoichiometric considerations indicate that enough heat is evolved in the overall reaction, if released adiabatically, to cause a temperature increase of about 2000°C for 75-85 w/o U_3O_8 specimens. Approximately three-fourths of this heat is produced by the reduction of the U_3O_8 to UO_2 (Equation 35) even though this

²⁴Waugh, R. G., The Reaction and Growth of Uranium Dioxide-Aluminum Fuel Plates and Compacts, ORNL-2701, 1959.

²⁵Beaver, R. J., and Cunningham, J. E., Recent Developments in Aluminum Base Fuel Elements for Research Reactors, Fuel Elements Conference held at Gatlinburg, Tenn., May 14-16, 1958, TID-7559 (part 1), p. 40, 1959.

²⁶Belle, J. (ed.), Uranium Dioxide: Properties and Nuclear Applications, United States Government Printing Office (1961), p. 369.

²⁷Fleming, J. D., and Johnson, J. W., Aluminum- U_3O_8 Exothermic Reactions, Nucleonics 21 (5), 84 (1963).

results in the consumption of only a small fraction of the aluminum. Thus, a temperature rise of 1500°C added to the initiating temperature (~900°C) gives a resultant value of about 2400°C for the maximum temperature after this part of the reaction is completed. If we assume that the further reaction of UO_2 with aluminum (Equation 36) proceeds more slowly, the temperature of 2400°C might not be exceeded. In any case the calculated value is in better agreement with the experimental peak temperatures reported by Fleming and Johnson than those heretofore achieved in this Laboratory.

The studies during this reporting period have, therefore, been designed to evaluate causative factors for the considerable difference in experimental findings between the two studies as represented by the peak temperatures recorded. Several approaches were tried, including varying the powder particle size, testing for oxygen release during the reaction, and pre-heating of the specimens in a nitrogen-containing atmosphere. In addition, preliminary experiments with compacts in the range of fuel material (40 w/o U_3O_8) were initiated.

a. Effect of Particle Size of Powders

As noted in ANL-6800, p. 391, work in this laboratory had been entirely done with -400 mesh ($12\ \mu$ average particle size) powders, in contrast to Fleming and Johnson's work, in which the maximum effect was observed for a -200 +270 mesh size (53 to $74\ \mu$) fraction. Thus, studies with coarser powders were undertaken to see if this factor was an important consideration in achieving the maximum possible reaction.

A series of 10 experiments was carried out utilizing -100 +200 mesh (74 to $149\ \mu$) and -270 +325 mesh (44 to $53\ \mu$) powders of U_3O_8 and aluminum. Several additional runs were also conducted with the -400 mesh powders. These all were done primarily at the 75 and 85 w/o U_3O_8 concentrations in an air environment in the Marshall furnace by the plunging method previously described. Without exception, the coarser powders gave decreased reaction as measured by the maximum temperatures achieved, compared with the -400 mesh powders. Typical temperature-time curves for several 75 w/o U_3O_8 specimens compacted from the various size powders, as shown in Figure V-56 illustrate this fact. Thus, the -400 mesh particle size powders were confirmed as having maximum reactivity. Consistently, however, the -400 mesh samples yielded temperature peaks of about 1700°C, approximately 500°C below those reported by Fleming and Johnson.

b. Determination of Oxygen Release

Several experiments were subsequently carried out in an argon atmosphere in which the off-gas was examined for evidence of oxygen. It was noted that possible oxygen release during reduction of the U_3O_8 to

UO₂ (Equation 35) could significantly decrease the amount of energy available from that reaction. The flowing argon off-gas was channeled through copper turnings heated to 400°C. Oxygen metered into the gas stream was shown to be picked up by the turnings in a test of this technique. However, no trace of oxygen was found in the off-gas in several typical runs, and this approach was abandoned.

Figure V-56
TEMPERATURE-TIME TRACES OF
75 w/o U₃O₈-Al PELLETS PLUNGED INTO
PREHEATED 1250°C FURNACE
(Pellets prepared from powders
of indicated mesh size)

108-7843

c. Effect of Sample Pretreatment

In an recent article²⁸ reporting studies of the inhibition of the UO₂-aluminum reaction, two methods were detailed which were successful in suppressing this reaction. The methods employed were (1) heating the aluminum powders in nitrogen prior to mixing and compaction or (2) sintering the pressed pellets in a nitrogen-containing atmosphere. Consequently, both of these techniques were employed to ascertain their suitability for the U₃O₈-aluminum system.

Figure V-57 compares temperature-time traces of three 85 w/o U₃O₈-aluminum pellets after insertion in the 1250°C Marshall furnace.

²⁸Rollig, H. E., On the Compatibility of Uranium Dioxide and Aluminum: 2. Communication: Studies on the Inhibition of the UO₂-Aluminum Reaction in Dispersion-Type Fuel Elements, *Kernenergie* 7 (1), 11 (1964); (translated by E. K. Wilip, ANL-TRANS-18, April 1964).

All pellets were prepared from -400 mesh powders of the two constituents, thoroughly mixed, and compacted with a force of 20,000 lb. One of the specimens received no other treatment, the second was prepared from aluminum powder previously heated in air at 600°C for 4 hr, and the third was heated in air at 600°C for 4 hr after being pressed into a pellet. All three give evidence of two separate temperature excursions. This seems to be peculiar to the 85 w/o U_3O_8 pellets, as those containing 75 w/o or less U_3O_8 give a single, sharper temperature rise. In Figure V-57 no real difference can be seen in the traces of the nonpretreated sample and the one prepared from aluminum powder previously heated in air. However, the specimen which had been sintered at 600°C after pressing shows a much more violent temperature excursion during its second peak. Two-color pyrometer readings indicated a maximum temperature of approximately 2000°C with a heating rate measured in thousands of degrees per second. This was not an isolated phenomenon, but was observed in each of several experiments run with sintered 85 w/o U_3O_8 -aluminum specimens. A 75 w/o U_3O_8 -aluminum sample, also previously sintered, exhibited an accentuated single peak with a maximum temperature near 1900°C and a fast heating rate.

Figure V-57
TEMPERATURE-TIME TRACES OF
85 w/o U_3O_8 -Al PELLETS PLUNGED INTO
PREHEATED 1250°C FURNACE

108-7844

It is now believed that we are obtaining results compatible with those reported by Fleming and Johnson.²⁷ Perhaps their slow-heatup experiments served to presinter the samples. Our previous slow-heatup experiments may not have recorded this effect for several reasons: (1) the two-color pyrometer was not employed during those tests and the shielded

thermocouples which were employed do not have a fast response, (2) our previous slow-heatup experiments were not done with 85 w/o U_3O_8 specimens which should have greatest reactivity, and (3) few experiments were carried very far beyond the first temperature excursion and so any subsequent, more violent peak may not have been reached.

d. Studies with 40 w/o U_3O_8 -Aluminum Compacts

It is now evident that U_3O_8 -aluminum cermets containing large concentrations of U_3O_8 have a potential for rather violent reactions. Similar studies have been initiated with compacts having a concentration of 40 w/o U_3O_8 , which has more practical application for nuclear fuels. Preliminary experiments indicate increased reactivity of sintered samples over unsintered ones for this concentration also. For example, Figure V-58 illustrates the temperature-time traces for 40 w/o U_3O_8 -aluminum specimens, both unsintered and sintered, which were plunged into a furnace preheated to either 1000 or 1250°C. It will be noted from the figure that the maximum temperatures involved are considerably lower than those reached by the 75-85 w/o U_3O_8 specimens. The self-heating rates, even for the sintered samples, are only of the order 100-200°C per second. Nevertheless, appreciable reactivity is evident.

Figure V-58

TEMPERATURE-TIME TRACES OF 40 w/o U_3O_8 -Al PELLETS PLUNGED INTO PREHEATED FURNACE

(Pellets prepared from -400 mesh powders)

108-7845

VI. ENERGY CONVERSION* (C. E. Crouthamel)

Development of the basic physical chemical data needed to design both the hydride and several bimetallic regenerative cells has been continued. These cells could be applied in a closed Carnot cycle to the conversion of reactor heat into electrical energy. The overall maximum efficiency of the cycle is the Carnot efficiency, Eff, which is given by the equation

$$\text{Eff} = \frac{T_2 - T_1}{T_2}$$

T_1 is the cell operating temperature at which the cell reactions are conducted isothermally and reversibly, and T_2 is the high temperature at which isothermal regeneration of the cell reactants from the cell product is accomplished. The regenerated cell products are separated at or near T_2 before they are returned to their respective compartments in the cell to prevent spontaneous recombination, which would occur at some temperature below T_2 . The upper limit of T_2 is set at about 1000°C. This limit is a reflection of the availability of suitable materials for containment and is not inherent in the known cell reactions which could be utilized in the regenerative cell. Fused salt hydride and bimetallic cells are expected to operate in the temperature range of 300-500°C. Thus, the overall Carnot maximum efficiency is expected to be around 50%. Modern steam plants actually achieve 40% efficiency, whereas a regenerative cell might be expected to achieve 25% efficiency, i.e., one-half the Carnot maximum.

The regenerative cell would be expected to achieve the conversion of heat to electricity with virtually no mechanical parts and would be amenable to operation of systems over a wide range of sizes and operating specifications.

Comparison of regenerative cells with other direct conversion systems, i.e., metal vapor turbines and thermionic diodes, reveals that the regenerative cell cycles alone have the capability of operating efficiently at the low maximum temperatures of 800 to 1000°C. Thus, regenerative cell closed systems are expected to have less difficult materials problems and relatively long operating lifetimes.

Two main types of regenerative emf cells are being studied. They are the bimetallic concentration cells and the hydride cell.

A bimetallic cell consists of two liquid metal electrodes in contact with a fused salt electrolyte which is stable with respect to the anode. Therefore, the electrolyte usually contains only salts of the anode metal. The

*A summary of this section is given on pages 41 to 43.

overall cell reaction is

The interaction energy of the dissolved metal A is usually very strong, and as a result compounds may be formed in the liquid state, e.g., Li_3Bi , in the lithium-bismuth cell. This strong interaction is the effect which produces a useful voltage in the bimetallic cell. However, it had not been realized that in many instances this leads to the appreciable solubilization of the cathode metal in the electrolyte. Thus, we found that a variety of intermetallic compounds are soluble in fused salts. We first re-examined the lithium-bismuth cell experiments reported previously (ANL-6800, p. 405) and were able to demonstrate: (1) that the cell design prevented the back diffusion of appreciable bismuth to the anode and (2) that liquid lithium saturated with Li_3Bi is an ideal solution and has little effect on the cell voltages. Therefore, the previously reported lithium-bismuth cell data are not in error.

Solubility and absorption spectra of Li_3Bi , Li_2Te , and Cs_2Te have been obtained. Observations on a variety of other intermetallic-fused salt solutions are reported. There is no doubt that this phenomenon will be of importance in bimetallic cell design. Although irreversible transfer of the cathode metal to the anode is now known to be possible, the usefulness of the bimetallic cells need not be appreciably diminished if the components are properly selected.

The solid-liquid equilibria phase diagram of LiH-NaCl has been completed. This completes a series of phase diagrams obtained in conjunction with the lithium hydride cell studies. The completed series, which comprised studies of LiH-LiCl , LiH-LiBr , and LiH-NaCl , reveals some very interesting results. All systems show positive deviations from ideal solution behavior which can be quantitatively accounted for by assuming dimerization for lithium chloride and lithium bromide and a monomeric association for sodium chloride.

The standard emf of the lithium hydride cell has been obtained by cell measurements over a temperature range of $510-610^\circ\text{C}$. The data appear to be consistent with calorimetric data in the literature.

The hydrogen permeation studies with vanadium metal are reported. A cell run of 540 hr was successful and indicated that a vanadium diaphragm behaved as a reversible H_2, H^+ electrode and was capable of supporting 130 ma/cm^2 at half open-circuit voltage.

The sodium-bismuth system has been investigated using the mass spectrometer and the Knudsen effusion cell. The vapor pressures of sodium and bismuth are calculated as a function of composition.

Engineering studies have been initiated during this period. The sodium-bismuth cell was selected for initial work as the best compromise among a number of variables in cell operating characteristics, regeneration parameters, and corrosion.

A. Bimetallic Cells and Intermetallic Compounds in Fused Salt Systems

1. Bimetallic Cell Studies, Li-Bi System (M. S. Foster and R. Eppley)

Since our discovery¹ that the intermetallic compound Li_3Bi is soluble in molten LiCl-LiF , a question has existed concerning the effect that this might have on the emf of the lithium-bismuth cell and on the calculations of the thermodynamic properties (ANL-6800, p. 405) of the lithium-bismuth system. In the lithium-bismuth cell experiments, a reference electrode consisting of bismuth liquid saturated with solid Li_3Bi was used. There can be little doubt that some Li_3Bi dissolved in the cell electrolyte (fused LiCl-LiF) and was then carried by diffusion and convection to the anode. The anode was either pure liquid lithium or a saturated solution of lithium in bismuth.

In two experiments, which are described below, it has been shown that this intermetallic compound solubility has not produced an appreciable effect on the cell voltages measured and that there is no error in the previously reported thermodynamic values as a result of the dissolution of the intermetallic compound in the electrolyte. For the first experiment, a cell was set up which was identical with that used in the study of the reference electrode, viz.,

The isotope ^{210}Bi was used as a tracer in the liquid bismuth cathode alloy. The lithium anode, contained in a porous BeO cup, was periodically sampled while the cell temperature was varied over the same range as had been used in previous studies. Analysis of these samples by beta counting showed that at no time did the bismuth content exceed 0.012 a/o in the lithium anode (see Table VI-1). The value of 0.012 a/o bismuth was obtained at a cell

Table VI-1

BACK DIFFUSION OF BISMUTH FROM A Li_3Bi -SATURATED LIQUID
BISMUTH CATHODE TO A LIQUID LITHIUM ANODE

Temperature (°C)	Bi (a/o) Found in Anode	Time after Run Started (hr)
575	0.006	19.2
547	0.006	26.9
653	0.008	121.3
549	0.007	164.4
866	0.012	168.6

¹M. S. Foster, C. E. Crouthamel, D. M. Gruen and R. L. McBeth, J. Phys. Chem., **68**, 980 (1964).

temperature of 866°C after 168 hr of operation. Thus, it is seen that very little Li_3Bi transferred (through the solution and through the porous beryllia wall) to the lithium anode under the conditions of the experiment.

In the second experiment, the magnitude of the effect on the cell potential of bismuth in the lithium anode was measured. The following cell was used:

The overall composition of the anode was 85 a/o lithium, and the cathode was 60 a/o lithium. The cell emf was very steady and reproducible with temperature cycling. The results show that within experimental error, the emf of this cell is identical with the emf of the cell in which the anode contained pure lithium, i.e.,

This demonstrates that the excess chemical potential of lithium in a lithium-rich liquid saturated with Li_3Bi solid is zero, i.e., the solution is essentially an ideal solution. The effect on the cell voltage of such an ideal solution is negligible. Thus, a calculation shows that even at 15 a/o bismuth dissolved in the lithium anode, a decrease in cell voltage for an ideal solution would be of the order of 2 mv.

2. Solubility and Spectrum of Li_3Bi in $\text{LiCl} - \text{LiF}^*$

Work at this site on the solubility of intermetallic compounds in liquids was preceded by other investigations. Zintl et al.² observed that a large number of intermetallic compounds form solutions in liquid ammonia. They found that NaBi and Na_3Bi_5 are soluble in liquid ammonia whereas Na_3Bi is not soluble. Later, Heymann et al.³⁻⁵ conducted what appear to be the first investigations of intermetallic solubility in fused salt media. These were distribution studies of two liquid metal phases in a third fused salt phase. The results led Heymann and associates to the conclusion that intermetallic compounds were formed as dissolved species in the salt phase. However, the importance of this discovery appears to have been overlooked; no further observations or studies have appeared in the literature in the past

*In cooperation with D. Gruen and R. McBeth of the Chemistry Division.

²Zintl, E., J. Goubeau, and W. Dullen Ropt, Z. Physik. Chem., 154A, 1-46 (1931).

³Heymann, E., and H. P. Weber, Nature 141, 1059 (1938).

⁴Heymann, E., and H. P. Weber, Trans. Faraday Soc. 34, 1492 (1938).

⁵Heymann, E., R. J. L. Martin and M. F. R. Mulcahy, J. Phys. Chem. 47, 473 (1943).

21 yr. In addition to its potential importance in the design and operation of bimetallic cells, the solubility of bimetallic compounds in fused salts has other interesting aspects. Examples are the possibility of studying inter-metallic compounds through the absorption spectra and Raman spectra and the possibility of a convenient method of growing single crystals.

The possibility that Li_3Bi is soluble in LiCl-LiF was recognized during the study of the bimetallic concentration cell

over the temperature range of 500 to 1000°C, when it was noted that the electrolyte became intensely red in color. Analysis of the electrolyte revealed the presence of both lithium and bismuth in the solution. Solubility and spectrophotometric measurements were undertaken to gain a better understanding of the nature of the fused salt solution.

The possibility of cosolubility of lithium and bismuth was investigated. First, the solubilities of high-purity, activated bismuth in LiCl-LiF eutectic (70 m/o LiCl) at 600, 800, 900, and 1000°C were measured. These solubilities were found to range from 1×10^{-3} to 2×10^{-3} w/o bismuth (approximately 2×10^{-4} to 4×10^{-4} m/o bismuth). The liquid bismuth metal equilibrated with the fused lithium salts gave colorless solutions.

Figure VI-1

SOLUBILITY OF Li_3Bi IN MOLTEN LiCl-LiF

Next, high-purity lithium (99.99% purity, with sodium and potassium content each less than 30 ppm) was combined with high-purity neutron-activated bismuth in an inert-

atmosphere box. The product is a two-phase mixture with an overall composition of 70 a/o lithium and consisting of solid Li_3Bi saturating the bismuth liquid metal. This mixture was equilibrated with molten LiCl-LiF eutectic mixture and was sampled at temperatures between 600 and 1000°C. The bismuth content was determined by monitoring ^{210}Bi tracer, and the lithium metal content was determined by acid titration of hydrolyzed samples of the fused salt solutions. The average Li:Bi ratio calculated from these data was 3.0 ± 0.1 . The solubility data are shown in Figure VI-1 as mole percent Li_3Bi vs $1/T$, °K. The heat of fusion of $\text{Li}_3\text{Bi}(s)$ calculated

from the solubility line and assuming that Li_3Bi forms an ideal solution in LiCl-LiF is 9.4 kcal/mole.

Equilibration of the Li_3Bi with the LiCl-LiF eutectic mixture resulted in clear, deep-red solutions. The solutions contained from about 350 to 2000 times the bismuth content found in the solutions equilibrated with pure bismuth at the same temperatures. When the clear, red solutions were allowed to come in contact with air, they quickly became colorless and contained a fine dispersion of insoluble black precipitate (assumed to be elemental bismuth).

The lithium content of about 0.3 m/o at 640°C in LiCl-LiF (calculated from the curve in Figure VI-1) appears to be of the same order of magnitude as that found by Bredig and coworkers⁶ at Oak Ridge for the solubility of lithium in LiCl at the same temperature, namely, 0.5 m/o. A single experiment in our laboratory showed the solubility of pure lithium in LiCl-LiF eutectic to be 0.1 m/o at 600°C . A lower solubility in the mixed eutectic than in LiCl is reasonable, based on Bredig's data which show that for a particular alkali metal, the fluoride has the least solubility of all the halides for the metal. At 1000°C , Bredig reports a solubility of lithium in LiCl of 2 m/o compared with 4 m/o lithium found in fused LiCl-LiF saturated with $\text{Li}_3\text{Bi(s)}$ in this study.

For observation of the absorption spectra of Li_3Bi in LiCl-LiF , solutions were prepared and placed in rectangular sapphire absorption cells. The sapphire cell was placed in a quartz outer envelope having a square bottom. This assembly was evacuated and placed in the heated sample chamber of a Cary Model 14H spectrophotometer.

The spectrum of the Li_3Bi red solution was measured at 525°C in the range 350-2000 $\text{m}\mu$. The spectrum is characterized by an intense absorption band whose long wavelength edge is located at 610 $\text{m}\mu$ at 525°C . Preliminary studies of the temperature shift of the band have shown that the band edge shifts about 40 $\text{m}\mu$ to lower energies for each 100°C rise in temperature.

The absorption spectrum of lithium in LiCl has been reported by Young,⁷ and the absorption spectrum of bismuth in BiCl_3 by Boston and Smith.⁸ Both of these spectra have their absorption maxima at 555 $\text{m}\mu$. The solubility data and the absorption spectra strongly suggest that an Li_3Bi species exists in the fused salt.

⁶A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *J. Phys. Chem.* **66**, 572 (1962).

⁷J. P. Young, *J. Phys. Chem.* **67**, 2507 (1963).

⁸C. R. Boston and G. P. Smith, *J. Phys. Chem.* **66**, 1178 (1962).

3. Solubility of Li-Bi Intermetallic Compounds from a 50 a/o Alloy in LiCl-LiF

At temperatures between 505 and 610°C, the system with an overall composition of 50 a/o lithium in bismuth consists of a solid Li_3Bi phase and a liquid bismuth-rich phase saturated with $\text{Li}_3\text{Bi(s)}$. Above 610°C, the bimetallic system exists as a single liquid phase. Therefore, the solubility of 50 a/o lithium-bismuth alloy in fused salt would be expected to be the same as that of $\text{Li}_3\text{Bi(s)}$ at temperatures between 505 and 610°C, and to be lower than the solubility of Li_3Bi at higher temperatures.

The solubility of lithium and bismuth from a 50 a/o lithium-bismuth alloy in LiCl-LiF eutectic has been measured. The bismuth content was determined by a complexometric titration, and the lithium content by a hydrogen evolution-gas chromatographic technique. The results are shown in Figure VI-2 and are compared with those previously obtained for a 70 a/o lithium-bismuth system. Note that the ordinate values are given in terms of log m/o bismuth. The plot is made in this manner because the average Li:Bi ratio was not very constant, being 1.7 ± 0.6 . This may be due to the solubility of more than one species, e.g., Li_3Bi and LiBi . However, it is more likely that the variations in the Li:Bi ratios are due to difficulties encountered with lithium analyses by the hydrogen evolution-gas chromatographic method.

Figure VI-2

SOLUBILITY OF Bi FROM Li-Bi ALLOYS (X_{Li} = atom fraction Li) IN LiCl-LiF

4. Alkali Metal Tellurides in Molten Salt Solutions

The probability of success of utilizing bimetallic cells in a closed heat cycle is reduced if the anode metal or intermetallic compound solubility in the cell electrolyte reduces the cell operating efficiency. Such an irreversible transfer of the metals comprising the anode and the cathode must be minimized by careful selection of the metals and cell electrolyte. Earlier work on the solubility of intermetallic compounds in fused salts is discussed near the beginning of this section of this report.

Intermetallic compound behavior in fused salt media is not an unrelated study to the regenerative cell program. The bimetallic cells are one of the very few cell types

which offer promise as high power density devices because of the simplicity of the cell (no junction potential) and high exchange currents at the liquid metal electrodes.

In an effort to determine the nature and scope of the phenomena involved in the solubility of intermetallic compounds in molten salt solutions, the investigation of several types of compounds was begun, starting with perhaps the most ionic compounds - the alkali metal tellurides, M_2Te , where M is an alkali metal. Later studies will be made of alkali metal intermetallic compounds involving Bi, Pb, Tl, Hg or Cd, Sn, etc. in various molten salt media. These studies will include measurements of solubilities, absorption spectra, electromigration, and Raman spectra.

The absorption spectrum of Li_2Te in a LiCl-LiF solvent (80 m/o LiCl, m.p. 505°C) has been measured in a fused silica absorption cell. These solutions, which are clear red, were filtered through a fine-porosity fritted disc of silica. They are relatively stable in fused silica absorption cells, though at high temperatures (up to 1000°C) some decomposition occurs, as evidenced by the formation of a thin tellurium mirror in the upper, cooler end of the tube attached to the heated cell. Some etching of the cell also occurs at higher temperatures (probably as a result of the Li_2Te or the LiF in the solvent).

Figure VI-3

ABSORPTION SPECTRUM OF Li_2Te IN LiCl-LiF AT 525°C AND IN CsCl AT 700°C

The spectrum of Li_2Te in

LiCl-LiF at 525°C (see Figure VI-3)

is characterized by an absorption peak at 469 $m\mu$, an absorption minimum at 385 $m\mu$, and an intense absorption band (charge transfer band) whose long wavelength edge is located at 377 $m\mu$.

The peak with a maximum at 469 $m\mu$ has a half-width of about 70 $m\mu$. The molar absorptivity determined at Li_2Te concentrations of 0.07, 0.1, and 0.13 mole per liter was found to be 25.1, 24.0, and 33.4, respectively. The analyses of these solutions consisted of a colorimetric determination of tellurium (using thiourea), and the calculation of the concentration of the absorbent of the concentration of the absorbent

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was based on the assumption that the ratio Li:Te = 2. Although analytical difficulties were encountered and corrections were required for the slight etching of the cell, it is believed that these data do not indicate a concentration dependence of the absorptivity.

From a knowledge of the molar extinction coefficient, ϵ , as a function of wavelength in terms of frequency, $\tilde{\nu}(\text{cm}^{-1})$, the oscillation strength for the transition may be calculated⁹ from the relationship:

$$f = \frac{2303 \text{ m}_e C}{\pi N e^2} \left[\frac{9 n_0}{(n_0^2 + 2)^2} \right] \int \epsilon d \tilde{\nu}$$

$$= 4.319 \times 10^{-9} \left[\frac{9 n_0}{(n_0^2 + 2)^2} \right] \int \epsilon d \tilde{\nu}$$

The term in brackets is an internal field correction factor in terms of the refractive index, n_0 , of the solvent. Ignoring this correction term (which ranges from 0.69 to 0.86 for solvent with $1.3 \leq n_0 \leq 1.6$), we find that $f = 8.45 \times 10^{-4}$.

From the concentration of tellurium in a LiCl-LiF solution saturated with Li_2Te at $\sim 525^\circ\text{C}$, the solubility of Li_2Te was estimated to be 2.62 moles per liter. The tellurium analysis was accomplished by a permanganate titration.

Solutions of Li_2Te in LiCl-KCl (59 m/o LiCl, m.p. 354°C) have also been prepared and studied. These solutions, which are red to orange, are similar to the solutions in LiCl-LiF, although the corrosive character at higher temperatures is somewhat reduced. The spectrum at 500°C is almost the same as in LiCl-LiF except that the absorption maximum is slightly shifted to $485 \text{ m}\mu$ (from $469 \text{ m}\mu$ at 525°C in LiCl-LiF). Between 700 and 800°C , an unusual broadening of this peak toward longer wavelengths was noted, indicating that perhaps a lower energy transition was becoming involved. At higher temperatures, the shift of the charge transfer band to lower energy effectively precluded any definitive observations. It should be noted that if a cation shift were expected due to the 41 m/o KCl in the solvent, the predicted shift would be toward lower energy (longer wavelength). The solubility of Li_2Te in LiCl-KCl was estimated to be 0.57 mole per liter at 400°C .

Also, CsCl was used as a solvent because of its noncorrosive character toward fused silica and its lower affinity for water than lithium salt melts (the latter must be purified by HCl or Cl_2 treatment prior to use). One of the disadvantages of CsCl is its higher melting point (646°C), which precludes measurements on solutions much lower than 650°C .

A comparison of the spectrum of Li_2Te in LiCl-LiF and in CsCl is shown in Figure VI-3. In the spectrum of Li_2Te dissolved in CsCl at 700°C , two peaks are visible - one at $\sim 465 \text{ m}\mu$ and another at $\sim 635 \text{ m}\mu$ - in

⁹W. Kauzmann, "Quantum Chemistry," Academic Press, Inc., New York, 1957, p. 581.

addition to the charge transfer band whose wavelength edge is at $\sim 300\text{ m}\mu$. The peak at $465\text{ m}\mu$ agrees quite well with that observed for Li_2Te in LiCl-LiF . However, as will be seen later, this peak may not be assigned to Li_2Te at this time. The longer wavelength peak is ascribed to the effect of CsCl . The solution, when concentrated, is the color of permanganate, while the solidified solution is black. The solubility of Li_2Te in CsCl at 700°C was calculated to be 8.9 moles per liter by a permanganate titration of tellurium.

The spectrum of Cs_2Te in CsCl has been observed. The solution is blue and at 700°C exhibits two absorption peaks in addition to the charge transfer band whose long wavelength edge is at $\sim 340\text{ m}\mu$. One peak is located at $635\text{ m}\mu$ and a weaker peak is seen at $465\text{ m}\mu$. It is not likely that the weaker peak at $465\text{ m}\mu$ is due to a Li_2Te impurity in the Cs_2Te or a lithium-salt impurity in the CsCl because of the small extinction coefficient previously noted for Li_2Te in LiCl-LiF .

Figure VI-4

RELATIVE SOLUBILITIES OF ALKALI METAL TELLURIDES AND Li_3Bi IN VARIOUS SOLVENTS

Studies are underway to determine the lithium and tellurium in samples of Li_2Te in CsCl and for lithium (impurity) and tellurium in the samples of Cs_2Te in CsCl . In a preliminary experiment, the quantity of tellurium (determined by permanganate titration) of a solution of Cs_2Te in CsCl indicated that the solubility of Cs_2Te is about 1.7 moles per liter at 700°C . This value must be regarded as tentative since it is possible that the CsCl was not saturated with Cs_2Te . The relative solubilities of the alkali tellurides and Li_3Bi in various solvents are shown in Figure VI-4.

5. Observations on Other Intermetallic Compounds

Some exploratory experiments have been carried out in the laboratory on a group of alkali metal and bismuth, tin, lead, cadmium, and tellurium intermetallic compounds. The results of these experiments are summarized in Table VI-2.

It was noted that the compound LiCd and the analogous compound, LiZn , exhibit a red coloration in the solid form. In LiCd , a thermochromic effect was observed which is quite

striking; the silver liquid alloy, changes first to red just below the melting point and then to gold at room temperature. Ketelaar¹⁰ comments that both of these compounds probably have d-electrons involved in their bond formation. The liquid solution of LiCd in LiCl-LiF is clear yellow.

Table VI-2

OBSERVED COLORS OF SOLUTIONS OF INTERMETALLIC
COMPOUNDS IN SALTS

<u>Compound</u>	<u>Solvent</u>	<u>Comment</u>
Li ₃ Bi	LiCl	{ Red solutions. Grey solid upon freezing.
Li ₃ Bi	LiCl-LiF (70 m/o - 30 m/o)	
Na ₃ Bi	NaCl-NaF (50 m/o)	
		Very dark green solution at 675°C.
Li ₇ Sn ₂	LiCl-LiF (70 m/o - 30 m/o)	Orange-brown color up to 800°C.
Li ₁₀ Pb ₃	LiCl-LiF (70 m/o - 30 m/o)	Solution is similar to that of Li ₇ Sn ₂ , but darker brown.
LiCd	LiCl-LiF (70 m/o - 30 m/o)	Yellow solution - grey on freezing. LiCd(s) alone is rose to gold colored with decreasing temperature of the solid.
Li ₂ Te	LiCl-LiF (70 m/o - 30 m/o)	Red solutions.
Cs ₂ Te	CsCl	Blue solutions.

None of the pure metals - Cd, Sn, Bi, Pb, or Te - form colored solutions when contacted with molten LiCl-LiF eutectic.

B. Lithium Hydride-Alkali Halide Solid-Liquid Equilibrium Studies
(C. Johnson and J. Allen)

In evaluating the potential of lithium hydride as a fluid for use in direct energy conversion devices, it is important to be able to define the thermodynamic and physical properties of lithium hydride in fused salt systems. The solid-liquid equilibrium in simple eutectic systems is one way these data can be obtained. The LiH-LiCl and LiH-LiBr systems have already been completed. They were reported in ANL-6725, p. 228 and ANL-6800, p. 413, respectively, and both were found to be simple eutectic systems.

¹⁰J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., New York (1958), p. 350.

Thermal analysis studies now have been completed defining the solid-liquid equilibrium temperatures in the lithium hydride-sodium chloride reciprocal system. These data were obtained using the apparatus previously described in ANL-6596, p. 203 and the method described in ANL-6648, p. 214. The lithium hydride-sodium chloride system is a simple eutectic melting at 565.7°C and containing 55.3 m/o lithium hydride. The solid-liquid equilibrium data are plotted in Figure VI-5. No indication of the formation of a solid solution was obtained from either the thermal analysis data or X-ray powder patterns of the solid phase.

Figure VI-5

LiH-NaCl SOLID-LIQUID EQUILIBRIUM

In the reciprocal salt system lithium hydride-sodium chloride, the following equilibrium exists, $\text{LiH} + \text{NaCl} \rightleftharpoons \text{LiCl} + \text{NaH}$. The position of this equilibrium is controlled by usual factors, the stable pair being LiH-NaCl. However, of particular importance to the execution of the experiments were the stability of sodium hydride, its normal dissociation pressure, and its vapor pressure. Literature data¹¹ indicate NaH to have a hydrogen dissociation pressure of some 3000 mm at 600°C. In order to insure the retention of LiH and NaCl in the sample crucible, it was necessary to maintain a hydrogen pressure of about 3000 mm Hg over the sample. Even at these pressures there were some experiments in which appreciable quantities of sodium hydride and sodium metal

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were found condensed in the cooler portions of the equipment. Generally, however, no more than 50 mg of sodium hydride (1/1000 of the total sample) was distilled in a given experiment. The situation became more critical when the system was rich in sodium chloride. At high concentrations of sodium chloride, the solid-liquid equilibrium temperature increased so that the 3000 mm Hg of hydrogen pressure was no longer sufficient for maintaining the stable pair, LiH and NaCl, in the sample crucible. For operation at these higher temperatures, hydrogen pressures which would exceed the safety factor of the apparatus would have to be used. Therefore, the region from 75 to 100 m/o sodium chloride was not examined experimentally.

¹¹R. C. Werner and T. A. Ciarlariello, Metal Hydride Fuel Cells as Energy Storage Devices, E/Conf. 35/Gen/14, 23 May 1961.

From the solid-liquid equilibrium data, some of the thermodynamic properties of the system were calculated from the following:

$$\Delta\mu_1^M(X_2T_e) = \Delta H_f \left(\frac{T_e - T_{m_1}}{T_{m_1}} \right) + T_e \int_{T_{m_1}}^{T_e} \frac{dT}{T^2} \int_{T_{m_1}}^T \left(C_p^{(\ell)} - C_p^{(s)} \right) dT.$$

This equation has been described previously (ANL-6687, p. 194.) In this equation $\Delta\mu_1^M$ is the change in the chemical potential on mixing, ΔH_f is the molar change in enthalpy of the pure component on melting at its melting point T_{m_1} , and T_e is the equilibrium temperature of the two-phase system. The standard state of the component was chosen to be the pure supercooled liquid at the equilibrium temperature and atmospheric pressure. From this equation and the solid-liquid equilibrium data, calculations have been made of the chemical potentials for each component over the composition ranges in which these components precipitate from solution. These data are given in Table VI-3.

Table VI-3

THERMODYNAMIC PROPERTIES OF THE SYSTEM LiH-NaCl

LiH (m/o)	T_e (°K)	$\Delta\mu_{NaCl}^M$ (cal/mole)	$\Delta\mu_{LiH}^E$ (cal/mole)	$\Delta\mu_{NaCl}^E$ (cal/mole)	$\Delta\mu_{LiH}^E$ (cal/mole)
0.0	1074	-	-	-	-
5.0	1057	-108.4	-	-0.6	-
10.0	1038	-229.0	-	-11.6	-
15.0	1019	-349.7	-	-20.6	-
20.0	998.7	-477.8	-	-34.9	-
24.4	980.0	-595.5	-	-50.7	-
30.0	956.4	-743.7	-	-65.8	-
35.0	933.7	-885.2	-	-85.8	-
40.0	911.0	-1026	-	-101.4	-
45.0	887.7	-1170	-	-115.2	-
49.8	864.1	-1315	-	-131.2	-
55.2	838.9	-1468	-678.5	-129.3	312.1
60.9	848.8	-	-620.9	-	215.7
65.1	857.1	-	-573.3	-	157.8
69.9	867.5	-	-513.3	-	104.1
75.0	878.4	-	-451.0	-	51.2
80.0	892.7	-	-369.4	-	26.5
85.0	906.7	-	-289.8	-	3.0
90.0	923.7	-	-195.0	-	-1.6
95.1	940.4	-	-100.7	-	-6.8
100.0	959.3	-	-	-	-

Having calculated $\Delta\mu^E$ for both components it is of interest to find a function of $\Delta\mu^E$ and X , the mole fractions of the components, which will best fit the data in a normal least squares sense and allow examination of $\Delta\mu^E$ for one component in the presence of the other component. This was done by expressing the thermodynamic function ΔG^E in the following manner:

$$\Delta G^E = X_1 X_2 (\alpha + \beta X_1 + \gamma X_1^2),$$

from which the excess chemical potentials may then be expressed as:

$$\Delta\mu_1^E = X_2^2(\alpha + 2\beta X_1 + 3\gamma X_1^2),$$

$$\Delta\mu_2^E = X_1^2[\alpha - \beta + 2(\beta - \gamma)X_1 + 3\gamma X_1^2].$$

These equations must satisfy the Gibbs-Duhem equation within the assumption that the coefficients are independent of temperature. The values of the coefficients are $\alpha = -437$, $\beta = 1271$ and $\gamma = -40.5$. These data are given in Figure VI-6 where the excess chemical potential for each component is given as a function of composition. The circles are the experimental data points and the lines represent the least squares calculation for the function $\Delta\mu_i^E$; the lines are extrapolated into the region where experimental verification was not possible.

Figure VI-6

EXCESS CHEMICAL POTENTIALS OF LiH AND NaCl

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In the systems previously examined, namely, the lithium hydride-lithium chloride and the lithium hydride-lithium bromide systems, deviations of the calculated chemical potentials from ideality were positive and quite large for the lithium halide component in each binary. Such positive deviations are caused by London dispersion energy of interaction of next nearest neighbors or by association of one of the components. In the discussion that follows on the lithium hydride-lithium chloride system, all comments made about this binary also apply similarly to the data we have obtained on the lithium hydride-lithium bromide system.

If it is assumed that lithium chloride in the LiH-LiCl system is a dimeric species Li_2Cl_2 , the limiting value of the curve of temperature vs composition would be the line marked $\nu = 1/2$ in Figure VI-7. The limiting value of the same function for an ideal solution of un-ionized LiCl in lithium

hydride, or of Li_2Cl^+ and Cl^- in lithium hydride would follow the line marked $\nu = 1$. The fact that the experimental data approach the line marked $\nu = 1/2$ strongly suggests that lithium chloride may exist quantitatively as a dimeric species in dilute solutions in lithium hydride solvent.

Figure VI-7

LiH-LiCl SOLID-LIQUID
EQUILIBRIUM - UNDER
1 atm $\text{H}_2(\text{g})$

108-7331 Rev.

A study of the species present in the more concentrated region is illustrated in Figure VI-8. The line represents the calculated values of

Figure VI-8

COMPARISON OF EXPERIMENTAL
DATA FOR $\Delta\mu_{\text{LiH}}^E$ WITH VALUES
CALCULATED ASSUMING Li_2Cl_2
AND LiH SPECIES

$$[\Delta\mu_{\text{LiH}}^E = -RT \ln (X_{\text{LiH}} + 1/2 X_{\text{LiCl}})]$$

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$\Delta\mu_{\text{LiH}}^{\text{E}}$ on the basis of ideal solutions formed by the species Li_2Cl_2 and LiH . The circles are the experimental data. It is interesting to note how closely the experimental data follow the calculated line even up to a lithium chloride mole fraction of 0.6. This result certainly gives strong evidence that the species Li_2Cl_2 may exist in these solutions.

When lithium hydride is the solute in lithium chloride solvent, the limiting value of a curve of temperature vs composition approaches a value of $\nu = 1$ (Figure VI-7). For an ideal solution of either un-ionized lithium hydride in lithium chloride or of Li^+ and H^- in lithium chloride, the limiting value of this function would follow a line marked $\nu = 1$. Because of the common ion effect, one cannot, therefore, distinguish between ionized and un-ionized lithium hydride in this system. There is certainly strong indication from these data that dimerization of the lithium hydride in lithium chloride does not occur.

The lithium hydride-sodium chloride system presents a somewhat different condition from that seen previously for the other lithium hydride binaries. Not only are the deviations smaller in magnitude, but they are also dissimilar. $\Delta\mu_{\text{LiH}}^{\text{E}}$ deviates in a positive fashion from ideal solution behavior, while $\Delta\mu_{\text{NaCl}}^{\text{E}}$ deviates in a negative manner. With the larger Na^+ ion, simple ion pair association rather than polymerization is apparently sufficient to stabilize the system.

Assuming that sodium chloride is a monomeric species, NaCl , in very dilute solutions in lithium hydride and that the solution is ideal in terms of the species NaCl and LiH , then the limiting value of the curve of temperature vs composition would be the line marked $\nu = 1$, in Figure VI-5. The limiting value of the same function for an ideal solution of ionized Na^+ and Cl^- ions in lithium hydride would follow a line marked $\nu = 2$. The fact that the data approach the line marked $\nu = 1$ indicates that sodium chloride probably exists as an associated monomeric species in lithium hydride.

When lithium hydride is dissolved in sodium chloride, the limiting value approaches $\nu = 1$. Apparently, in this reciprocal salt system, lithium hydride also remains as an associated species.

In connection with this discussion, it is interesting to consider the work of Berkowitz and Chupka¹² on the mass spectrometric examination of the gas phase of the alkali metal halides. They found, for example, that lithium chloride has a dimer:monomer ratio of 2.50:1 for species present in the vapor phase when this vapor is in equilibrium with its condensed phase. Their data show that polymerization is a general characteristic of the lithium salts. The predominant species in the vapor phase over sodium, potassium, and rubidium salts, however, are monomers.

¹²J. Berkowitz and W. A. Chupka, J. Chem. Phys. **29**, 653 (1958).

C. Lithium Hydride Cell Studies
(C. Johnson, R. R. Heinrich)

1. Cell Studies

The anionic character of the hydride ion in the saline hydrides has been well established.¹³ More recently,¹⁴ the electrode reaction, $1/2 \text{H}_2 + e \rightarrow \text{H}^-$, has been utilized in a regenerative cell system. However, no thermodynamic calculations could have been made based on the emf data.

Many of the properties of lithium hydride have been extensively investigated.¹⁵ The purpose of this work was to attempt to establish by electrochemical emf measurements the standard emf of the lithium hydride cell as a function of temperature. If successful, this was to be followed by the determination of the activity of lithium hydride in fused salt solvent by cell emf studies. It is believed that the data presented show that the first objective has been achieved.

Initially, attempts were made to carry out the thermodynamic emf studies with cells utilizing gas diffusion diaphragms. Although thin 5- to 10-mil diaphragms of both pure iron and pure vanadium used as electrodes gave a voltage response to the hydrogen pressure with the expected theoretical Nernst slope, the behavior of the electrode was erratic under conditions which could not be fully defined. The difficulty was associated with the metal-fused salt-hydrogen gas interface of the hydride electrode. No stable insulator except frozen lithium salts is known for a cell containing a pure lithium anode. Fortunately, the lithium hydride tends to freeze at the surface and around the hydrogen electrode-fused salt-gas interface, providing a fused salt insulator. Nevertheless, even under these circumstances the cell voltage was somewhat lower than expected and too erratic for precise thermodynamic analysis.

Experiments were then conducted with iron flags at the fused salt-gas interface with pure hydrogen atmosphere in the furnace well for comparison with the diffusion electrode. The cell assembly is illustrated in Figure VI-9. The cells were operated in a furnace well attached to the floor of a high-purity helium-atmosphere box. The cells were isolated from the rest of the box atmosphere by a well cover which contained appropriate gas-tight electrical connections for the electrodes. The anode is

¹³Bardwell, D. C., J. Am. Chem. Soc. 44, 2499 (1922).

¹⁴Fuscoe, J. M., Carlton, S. S., and Laverett, D. P., Regenerative Fuel Cell Systems Investigations WADD Technical Report 60-442, AD-249256.

¹⁵Messer, C. E., Survey Report on Lithium Hydride, USAEC-NYO-9470, Oct. 27, 1960.

electrically insulated by use of high-fired beryllia tubing. Lithium metal ions are held on a sintered metal fiber sponge which in turn is held in a small stainless steel crucible. The interfacial tension of the lithium on the metal sponge is of such magnitude that the liquid metal is retained in place below the surface of the fused salt. The cathode is a 0.010-in. piece of Armco iron of 3-sq cm area.

Figure VI-9

LiH CELL ASSEMBLY

108-7466

The cell was assembled with both electrodes in their respective positions in the cell cover. The electrolyte was melted under one atmosphere of purified hydrogen gas and the cathode was lowered to a position to just intercept the surface of the electrolyte. The anode was held in the cooler zone of the cell assembly until electrolyte temperature equilibrium was reached. An initial emf of greater than 1 volt was observed when the cold anode was introduced into the melt. This thermocell effect was of short duration, decaying to the stable cell emf within 60-80 sec. Once the cold anode was introduced into the fused electrolyte, about 30 min was required for the electrolyte to return to its equilibrium temperature. At thermal equilibrium, the observed emf was very stable.

The cell may be represented as

Two successive cells gave 0.2908 ± 0.0002 volt at $813.0 \pm 0.5^\circ\text{K}$ and one atmosphere hydrogen pressure. The cell emf's were reproducible after temperature cycling; emf's were measured over the temperature range of 510 - 610°C . Figure VI-10 shows a plot of the emf vs temperature of the above cell. At the temperature of the experiments, solid lithium hydride was present in the electrolyte thereby fixing the thermodynamic activity of lithium hydride at unity. Assuming hydrogen acts as an ideal gas, its activity can be expressed as the ratio of the hydrogen pressures:

$$a_{\text{H}_2(\text{g})} = p/p^\circ = 1.$$

Figure VI-10

EMF-TEMPERATURE DATA FOR THE CELL:

108-7992

The standard free energy of formation of lithium hydride was calculated from these data and is compared below with known literature values.

ΔF_{f298}° (cal/mole)	Reference
-15,850	this work
-16,450	16
-16,800	17

Data have also been collected for the change of emf with temperature for various electrolyte compositions, each electrolyte composition being chosen to fix the lithium hydride activity at unity over a particular temperature range. The emf of the cell over this temperature range can be expressed as

$$\epsilon = 0.8808 - 7.291 \times 10^{-4} T$$

and

$$\left(\frac{\partial \epsilon}{\partial T} \right)_P = -7.291 \times 10^{-4} \text{ volt/degree}$$

16C. E. Messer and L. G. Fasolino. Report NYO-3956, Mar. 1954.

17Gunn, S.R., and Green, L. G., J. Am. Soc. 80, 4782 (1958).

where T is degrees, Kelvin. From these data, the standard enthalpy of formation and entropy of formation have been calculated to be

$$\Delta H_{f_{298}}^{\circ} = -21,180 \text{ cal/mole and } \Delta S_{f_{298}}^{\circ} = -17.9 \text{ eu.}$$

2. Hydrogen Permeation Studies

The practical application of a lithium hydride cell depends primarily upon the proper functioning of a hydrogen gas electrode. A diffusion electrode has the advantages of ease in defining and controlling the liquid-gas interface and greatly simplifying the operation of a hydride cell. This electrode must be of material which is compatible with the cell environment and in the case of a diffusion type electrode must exhibit a high permeability for hydrogen gas. Armco iron fulfills the former requirement but not the latter. Hydrogen permeation rates for 10-mil thick iron diaphragms at 550°C and one atmosphere pressure have been determined in this laboratory as 4.4×10^{-2} cc (STP) $\text{min}^{-1} \text{ cm}^{-2}$. The equivalent current density achievable, assuming 100 percent cell efficiency, is 6.3 ma/cm^2 . These current densities are about a factor of 20 lower than the minimum of 100 ma/cm^2 required for a practical cell. An iron diaphragm does have, however, the important property of being easily regenerated in a hydrogen atmosphere at moderate temperatures (650-700°C). That is, any surface oxide film can be reduced to iron metal by hydrogen gas at these temperatures.

Other metals which have the necessary properties for a hydrogen electrode are the group V-A metals, i.e., vanadium, niobium, and tantalum. Hydrogen has a high solubility in these metals and for this reason can be expected to be quite permeable to hydrogen. Unfortunately, these metals are also very sensitive to trace impurities which may exist in the hydrogen gas. Any oxygen or nitrogen impurity results in the formation of a very stable oxide or nitride on the metal surface and the presence of these compounds severely restricts the passage of hydrogen through the metal. These compounds cannot be reduced back to the metal by hydrogen gas and regeneration of such a diaphragm is difficult.

Experimental work on the permeation of hydrogen through vanadium has utilized a swage-type diaphragm holder for the containment of the thin diaphragm (Figure VI-11). The use of this apparatus circumvents the earlier problems associated with vanadium-to-stainless steel welds. Permeation rates of hydrogen through vanadium show some nonreproducible characteristics. With respect to hydrogen, vanadium is classified as an exothermic occluding metal; that is, a metal which absorbs hydrogen in large quantities with a negative temperature coefficient of solubility. Metals behaving in this way exhibit two unique permeation characteristics. Firstly, the metal must be "activated" at high temperatures (see Figure VI-12) in order to induce permeation, and secondly, if the metal is thermally cycled while charged with hydrogen the permeability decreases with time. Reactivation of the metal can only be achieved with difficulty at a temperature

higher than the initial temperature of activation. These characteristics are interpreted as being the result of the expansion and contraction of metal lattice and possibly the accumulation of surface contamination.

Figure VI-11

SWAGE-DIAPHRAGM ASSEMBLY FOR MEASUREMENT OF HYDROGEN GAS PERMEATION RATES

108-6906

Figure VI-12

HYDROGEN PERMEATION
ISOBARs FOR 0.010-IN.
THICK VANADIUM METAL

108-7137

Experiments for the determination of hydrogen permeation rates through niobium and tantalum were unsuccessful. Niobium permeation rates were about a factor of two greater than those obtained for iron and exhibited nonreproducibility. Permeation rates of hydrogen through tantalum were so low that they were beyond experimental detection. The reason for this type of behavior is again attributed to the sensitivity of the metal surface to trace contamination and the formation of stable oxides.

Operation of a lithium hydride cell with a vanadium metal diaphragm has been demonstrated by the successful run of a cell for a period of 540 hr at 535°C. When operated under resistive load, the average current density obtained was 130 ma/cm² at half open-circuit voltage and a hydrogen pressure of one atmosphere. This current density was achieved without making any attempt to activate the diaphragm at high temperature. The effect of hydrogen pressure on the cell voltage was studied. The slope of a plot of emf vs logarithm of hydrogen pressure corresponded to the expected theoretical (Nernst) slope of one, indicating the reversibility of the H₂(g), H⁺, V electrode.

D. Regeneration Studies, Sodium-Bismuth
(A. K. Fischer, J. Berkowitz,* W. Chupka*)

In order to calculate partial vapor pressures of components expected to exist at different stages of the thermal regeneration of the Na-Bi regenerative cell, it is necessary to identify and to obtain vapor pressure data for the various sodium and bismuth species existing in the vapor phase over various alloy compositions which may comprise the cell product. For this purpose, Knudsen effusion experiments using a mass spectrometer for analysis of the vapor are suitable in some temperature ranges of interest, although, at present, some assumptions regarding cross section ratios and fragmentation patterns are necessary in the interpretation of results. These qualifying factors, together with the exploratory nature of the work performed so far, serve to limit the reliance to be placed on the numerical values derived from the presently available results, but do not preclude some conclusions regarding the feasibility of regeneration of the Na-Bi bimetallic cell.

Under the vacuum conditions existing in the mass spectrometer (about 10⁻⁶ torr), Na₃Bi was found to vaporize by decomposition; no Na-Bi molecular species could be detected in the vapor either in the form of Na₃Bi or of NaBi. As can be seen from Table VI-4, the Na⁺ ion peak started registering at a temperature of about 546°K. It was only at a temperature of 690°K, some five hours later, that the Bi⁺ peak first appeared. In the interval, the atom fraction of sodium in the condensed phase in the cell had dropped from the original value of 0.75 to about 0.6.

*ANL Physics Division.

Table VI-4

RESULTS OF MASS SPECTROMETER EXPERIMENT ON Na_3Bi SHOWING PARTIAL PRESSURES OF VAPOR SPECIES AT VARIOUS TEMPERATURES AND ATOM FRACTIONS OF SODIUM (X_{Na}) IN THE RESIDUAL CONDENSED PHASE

Time (min)	T (°K)	P_{Na} (atm)	P_{Bi} (atm)	P_{Bi_2} (atm)	$P_{\text{Bi}} + P_{\text{Bi}_2}$ (atm)	X_{Na} (condensed phase)
1	546	4.75×10^{-9}				0.750
8	564	4.98×10^{-8}				0.750
13	576	3.54×10^{-7}				0.750
23	586	8.52×10^{-7}				0.748
104	615	1.19×10^{-6}				0.724
142	616	2.81×10^{-7}				0.721
273	613	1.82×10^{-7}				0.713
312	689	2.07×10^{-5}				0.633
316	690		1.26×10^{-8}		1.26×10^{-8}	~ 0.63
324	699	2.65×10^{-5}				0.443
352	640	4.16×10^{-7}				0.342
392	650-660		2.33×10^{-9}		2.33×10^{-9}	~ 0.31
404	670	8.66×10^{-7}				0.291
431	730		1.99×10^{-7}		1.99×10^{-7}	
439	734	1.84×10^{-7}				0.259
457	736		1.78×10^{-7}		1.78×10^{-7}	~ 0.24
466	737	1.00×10^{-6}				0.232
522	740		1.83×10^{-7}		1.83×10^{-7}	
528	740			7.64×10^{-8}		
536	743	6.96×10^{-7}	1.83×10^{-7}	7.64×10^{-8}	2.59×10^{-7}	0.105
563	798		1.27×10^{-6}			
566	799			5.43×10^{-7}	1.85×10^{-6}	~ 0.08
574	800		1.36×10^{-6}			
582	800	2.25×10^{-7}				0.063
608	856			2.11×10^{-6}	7.73×10^{-6}	~ 0.06
614	859		5.62×10^{-6}			
622	861	1.35×10^{-7}				
636	909			6.17×10^{-6}	$\sim 2.4 \times 10^{-5}$	0.049
641	921		1.80×10^{-5}			
648	924	1.19×10^{-7}				Na tailing
656	926		3.92×10^{-7}	Bi_2 gone by time 661		
664	926		1.06×10^{-7}		$\sim 1 \times 10^{-7}$	
670	926	5.87×10^{-8}				
676	926	5.69×10^{-8}				
679	926		2.76×10^{-8}		$\sim 3 \times 10^{-8}$	

In regard to the $\text{Bi}_2 \rightleftharpoons 2 \text{Bi}$ equilibrium which exists in the vapor phase in the Knudsen cell, there are uncertainties in the present interpretation of the mass spectrum which affect somewhat the quantitative value for total bismuth pressure but not the qualitative conclusion regarding cell

regeneration presented here. The uncertainty stems from assuming (1) that the additivity rule holds for the cross sections of Bi_2 and Bi for ionization by electron impact and (2) that there is no fragmentation of Bi_2 . The additivity rule is regarded as a good first approximation and states that $(\sigma_{\text{Bi}_2})/(\sigma_{\text{Bi}}) = 2$, where σ denotes the cross section. The partial fragmentation of Bi_2 is likely and would lead to a high apparent value for the Bi^+ ion current and a low value for the Bi_2^+ ion current. If it is assumed that 60% of Bi_2 is fragmented, the total bismuth pressure, $p_{\text{Bi}} + p_{\text{Bi}_2}$, plotted in Figure VI-13, would be raised about 15% in the region where Bi_2 was a significant contribution to the total bismuth pressure, i.e., in the region of the curve falling between about $X_{\text{Na}} = 0.2$ to 0.05. The part of the curve illustrating the preferential volatilization of sodium would not be affected. This feature provides some limited indication that regeneration of a Na-Bi cell is feasible.

Figure VI-13

PARTIAL PRESSURES OF SODIUM AND TOTAL BISMUTH VS ATOM FRACTION SODIUM IN RESIDUAL CONDENSED PHASE

(Temperature generally increasing
from left to right; see Table VI-4.)

108-7993

From phase diagram considerations, it is found that only the situation existing at the first Bi^+ measurement in Table VI-4 is one in which solid Na_3Bi may be expected to have been present. At this point (690°K), it may be calculated that for

$$\Delta F^\circ = 69.5 \text{ kcal}$$

or that for

$$\Delta F^\circ = 10.9 \text{ kcal.}$$

If the uncertainty in the partial pressure of monomeric bismuth were as high as one order of magnitude, the ΔF° values above would be off by $\pm 3 \text{ kcal.}$

E. Regenerative Emf Cells - Engineering Studies (J. C. Hesson, H. Shimotake)

Engineering studies were started during the past six months to investigate the feasibility of developing a practical thermally regenerative emf cell ultimately capable of being coupled to a reactor or other heat source. Both the bimetallic and lithium hydride cells are being studied.

This study involves the consideration of anode and cathode metal combinations including cell voltage measurements; electrolyte selection including stability, electrical ionic conductivity, and irreversible transfer of anode (and cathode) metals; cell configurations and geometry including electrical insulation; electrolyte and electrode mechanical positioning methods including the possible use of porous or sponge metals for the molten metal electrodes and perhaps a ceramic matrix for the electrolyte; electrode metal transfer to the regenerator and regeneration including heat exchange; cell and regenerator operating temperature; cell and regenerator efficiencies; corrosion; and perhaps cell stacking for higher series voltages and greater compactness.

Experimental Sodium-Bismuth Cells

Preliminary experimental sodium-bismuth bimetallic "open" cells (cells in open-top crucibles) have been operated with sodium chloride-62.5 m/o sodium iodide eutectic electrolyte, sodium hydroxide electrolyte, and sodium hydroxide-sodium iodide electrolyte. The cells have consisted of stainless steel (or tantalum) crucibles about $1\frac{7}{8}$ to $2\frac{1}{4}$ in. in diameter by 5 in. high into which the electrolyte was placed. For an experiment a crucible was placed in a stainless steel well connected to a helium inert-atmosphere box and was heated by a resistance furnace surrounding the well. The anode consisted of a stainless steel cup with a support rod attached and with a hole in the bottom. The bottom of the anode cup was dipped slightly into the electrolyte. In most of the experiments, a layer of porous stainless steel sponge was used to cover the hole in the anode cup to better retain the sodium which was placed in the cup, yet to allow contact with the electrolyte. In the experiments, cup holes of $1/4$, $3/8$, and $7/8$ -in. diameter were used.

The cathodes have consisted of $7/8$ -in. ID by $1\frac{1}{2}$ -in. deep stainless steel cups with hollow support rods which also served as thermocouple wells. Bismuth was placed in the cathode cups, which were immersed under the electrolyte. In some experiments, bismuth was placed directly into the $1\frac{7}{8}$ -in. diameter crucibles.

The cells have been operated at 575 to 685°C with the sodium chloride-sodium iodide electrolyte and at 300 to 500°C with the sodium hydroxide-sodium iodide electrolyte. With the $7/8$ -in. diameter anode

and 7/8-in. diameter cathode separated by 2 in. of electrolyte, cell resistances of from about 3 to 0.15 ohms over the temperature ranges have been experienced. Currents as great as 560 ma or 145 ma/cm² at 0.28 volt have been drawn from the cells.

In an experiment to determine open circuit voltages, anode and cathode cups consisting of alumina tubes with closed ends were dipped into the sodium chloride-sodium iodide electrolyte. A small hole was provided in each alumina tube to allow the electrolyte to enter the tubes from the crucible. Sodium was placed in the anode cup, and bismuth-sodium mixtures were placed in the cathode cup. Tantalum rods were used in the alumina tubes as electrical contacts. Figure VI-14 shows the open-circuit voltages obtained at 576°C as a function of mole fraction sodium in the bismuth cathode. From this graph, it is noted that at 586°C sodium is soluble up to about 55 m/o in the bismuth cathode, which indicates that the cell could be operated through this range without solid sodium-bismuth intermetallic compound formation. It is also seen that the cell voltage does not change greatly with percent sodium in the bismuth cathode between about 20 and 40 m/o sodium. For this reason, this would be a desirable cell operation and cathode regeneration range.

Figure VI-14

OPEN CIRCUIT POTENTIAL OF
SODIUM-BISMUTH CELL AS A
FUNCTION OF m/o Na IN
Bi CATHODE

Electrolyte: NaCl-62 m/o NaI

Temperature: 586°C

Anode and cathode separated by
small bridge hole to minimize
irreversible sodium transfer.

108-7994

VII. NUCLEAR CONSTANTS* (Donald C. Stupiegia)

In the preceding summary report (ANL-6800, p. 424), a discussion was given on the fast neutron cross section program in terms of the use of cross sections in the calculation of the breeding ratio of a fast reactor. The breeding ratio can be written

$$R = \frac{\nu - 1 - \alpha - A - \Lambda + F(\nu' - 1)}{1 + \alpha},$$

where, per fissionable nucleus fissioned, A is the number of neutrons captured by parasites, Λ is the number leaking out of the system, and F is the number of fertile nuclei fissioned. Also, ν and ν' are the average numbers of neutrons per fission in the fissionable and fertile species, respectively, and α is the ratio of the capture and fission cross sections of the fissionable species. Therefore, the breeding ratio of a reactor is a function of the fission and capture cross sections of the fissionable and fertile species and of the capture cross sections of reactor structural materials. The neutron reaction rates of various reactor materials need to be known as a function of neutron energy over the energy range occurring in fast reactors, that is, from 1 kev or lower to several Mev. Finally, a knowledge is needed of the cross sections for reactions which degrade the neutron energy spectrum of the reactor. These processes are elastic and inelastic scattering.

In the present program, neutron reactions are being studied as a function of neutron energy for reactor fuels, fertile nuclei, and reactor structural materials. Measurements of radiative capture cross sections have continued, and a new program has begun for the measurement of inelastic scattering cross sections as a function of neutron energy. In addition, preparations are being made for irradiations of uranium and plutonium isotopes in EBR-II in order to determine the ratio of capture and fission cross sections as a function of position in the reactor.

A. Capture to Fission Ratios in EBR-II

In calculating the breeding gain of a fast reactor, it is necessary to know the capture and fission cross sections of the fissionable and fertile species and the neutron spectrum of the reactor. For nuclides such as the higher plutonium isotopes, many of these data are not known. Because of the lack of sufficient quantities of these isotopes, it is not expected that monoenergetic capture and fission data will soon be available. An alternative experimental approach to this problem is now in progress, in which the ratio of capture to fission cross sections as a function of position in EBR-II is to be measured for plutonium and uranium isotopes.

*A summary of this section is given on page 43.

Samples of ^{233}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu and ^{242}Pu are now being inserted into stainless steel capsules, following which they will be loaded into special EBR-II fuel element tubes for placement in the reactor. Following irradiations of one to three months, the samples will be removed from the reactor and returned to Argonne for analysis. The number of fissions in the samples will be measured by separation and counting of fission product ^{137}Cs , and the number of captures will be assayed by the mass spectrometric analysis of the samples for the capture products.

In Table VII-1 is given a summary of the number of samples of each isotope to be irradiated, and their positions in the core and blankets. One additional type of irradiation has been suggested, namely that assemblies containing a moderator such as beryllium or carbon be inserted into the outer blanket and that ^{240}Pu , and perhaps other isotopes be irradiated in these assemblies. This experiment would give information on the capture-to-fission ratio in a neutron energy spectrum of much lower average energy, similar to that which would be found in a dilute fast reactor system.

Table VII-1

NUMBER OF SAMPLES OF URANIUM AND PLUTONIUM
IN THE CORE AND BLANKET REGIONS OF EBR-II

Isotope	Core	Blanket	
		Inner	Outer
^{239}Pu	8	1	4
^{240}Pu	4	1	2
^{242}Pu	6	1	4
^{233}U	6	0	2
^{235}U	6	1	2
^{238}U	3	0	2
			0

B. Neutron Inelastic Scattering

Neutron inelastic scattering is the main mechanism by which neutron energy degradation takes place in a fast reactor. When a neutron strikes a nucleus and a compound nucleus is formed which is in a highly excited state, the excitation energy may be released in a number of ways. A neutron may be emitted from the compound nucleus with the same energy as the incoming neutron; this is an elastic scattering event. If, however, the target nucleus has an excited state whose energy is lower than the energy of the incoming neutron, then a neutron may be emitted

with an energy decreased by the amount of that state. In this case the nucleus is left in an excited state, which then decays to ground state by the emission of a gamma ray. This is an inelastic scattering event.

In a fast reactor, one usually wants to use materials with a small inelastic scattering cross section to avoid excessive degradation of the average neutron energy. However, in some cases, such as in a reactor blanket, a degradation of neutron energy may be desirable, since this will increase the rate of capture in a fertile species.

The data obtained from an inelastic scattering experiment include measurements on either the product neutrons or the gamma rays from the de-excitation of the excited states of the target nucleus. An extensive program for the measurement of the neutrons from the reaction $(n, n'\gamma)$ is already in progress in the Reactor Physics Division. The program now beginning is directed toward measurements on the gamma rays. This work is being done with the 3-Mev nanosecond-pulsed Van de Graaff accelerator of the Reactor Physics Division, and is being carried out in cooperation with personnel of that Division.

Data sought in the $(n, n'\gamma)$ work include:

- (1) The cross section for the production of gamma rays as a function of neutron energy. This gives a measure of the inelastic scattering resulting in the production of each successive excited state of the target nucleus.
- (2) The cross section for the production of a given gamma ray as a function of angle of gamma-ray emission with respect to the direction of the neutron beam.

This work will therefore provide information needed for calculations on the neutron energy degradation in fast reactors. Further, the data will provide information for the testing of nuclear theory. From the data, one can predict the angular momentum and parity of the excited states of the target nucleus, and one can derive information about the distribution of energy levels in the compound nucleus.

Inelastic scattering in zirconium, niobium, holmium, copper, and rhodium is being studied. Gamma ray spectra have been obtained, but no results can be reported yet.

C. Radiative Capture Cross Sections

In the calculation of the breeding ratio of a reactor system, one of the required quantities is the capture cross section as a function of neutron energy for reactor structural materials. In the preceding summary report (ANL-6800, p. 425), some recent results of our radiative capture

cross section measurements were given. Among the elements discussed was the refractory metal, rhenium. Nearly complete results on the capture cross sections of both isotopes of rhenium can now be reported. Neutron irradiation of natural rhenium produces the following three reactions:

In Figure VII-1 are shown the radiative capture cross sections of ^{185}Re and ^{187}Re as a function of neutron energy between 4 kev and 2 Mev. The neutron energy spreads about each point are such that the spreads just overlap between adjacent points. The standard deviations of the cross section values are about $\pm 8\%$. In the previous summary report (ANL-6800, Figure VII-1, partial results for the capture cross sections of ^{187}Re were given, and are included in Figure VII-1 of the present report.

Figure VII-1
NEUTRON CAPTURE CROSS SECTIONS
OF RHENIUM

108-7995

In Figure VII-2 are plotted the total capture cross sections of natural rhenium as calculated from the previous graph. Also shown in the figure are the cross sections measured in the low energy region with the Oak Ridge fast chopper by R. C. Block et al (unpublished).

Figure VII-2

TOTAL NEUTRON CAPTURE
CROSS SECTION OF RHENIUM

108-7996

VIII. ANALYTICAL RESEARCH AND DEVELOPMENT*

(R. P. Larsen)

A. Determination of Burnup on EBR-II Fuel (R. P. Larsen and R. J. Meyer)

A program for the development of methods for determination of burnup on EBR-II fuel is being carried out by the Analytical Group. Although the primary objective of this program is the development of methods which will meet the needs of the EBR-II Fuel Processing Facility, these methods could also be used to provide information of great value to the metallurgists, reactor engineers, and reactor physicists. The methods which are being developed and the nuclear data being gathered should also find application to other fast reactors.

The definition of "burnup" used in this report is "number of fissions per 100 actinide atoms of the fuel charged to the reactor." In EBR-II, the number of actinide atoms is readily calculated from the elemental composition and the isotopic composition of the charged fuel. Both of these will be well known. The number of fissions will be determined by analyzing the discharged fuel for a particular fission product (the monitor) and dividing the number of atoms of this fission product by its fission yield.

1. Selection of a Burnup Monitor for EBR-II (R. P. Larsen)

There are certain restrictive conditions which must be met in selecting a fission product to monitor burnup in nuclear fuels. The fission yield of the monitor must be independent, or nearly so, of the energy of the fissioning neutron; the half lives of the monitor and its precursors must be such that there are no sizable in-pile or out-pile decay corrections; the monitor and its precursors must be retained in the fuel during irradiation; the monitor cannot be a constituent of the original fuel, and it must be removed in the fuel processing cycle.

In EBR-II none of the 85 or so fission product nuclides meet all of these restrictive conditions. However, two nuclides, technetium-99 (2×10^5 yr) and lanthanum-139 (stable) meet most of them. Technetium-99 is not removed in the free processing cycle, but this problem can be circumvented. Lanthanum-139 has volatile precursors, but their half-lives are very short.

To circumvent the problem of technetium-99 retention in the reprocessed fuel, a virgin pin will be included in each subassembly of reprocessed pins. Upon discharge of a subassembly from the reactor, the

*A summary of this section is given on page 43.

burnup for the virgin pin as determined by technetium-99 analysis can be related to the burnup for a reprocessed pin through a secondary analysis. Both pins will be analyzed for barium-140 (13 day), a fission product which is completely removed in the fuel processing cycle. The burnup in the reprocessed pin will be equal to the burnup in the virgin pin multiplied by the ratio of the barium-140 activity in the reprocessed pin to that in the virgin pin.

No loss of lanthanum-139 or its precursors (xenon-139, cesium-139 and barium-139) from the EBR-II fuel to the sodium bond is expected. The stable and long-lived xenon and cesium nuclides do, in time, diffuse out of the EBR-II fuel into the sodium, e.g., 25% of the cesium-137 (29.1 yr) was lost during a 4-month irradiation at 600°C to 2% burnup. However, the rapid decay of xenon-139 (41 sec) and cesium-139 (9.5 min) precludes their loss by diffusion. Although this conclusion has not been verified experimentally, it has been substantiated by observations of the behavior of the analogous mass-90 nuclides. Strontium-90 (26 yr) whose precursors, krypton-90 (33 sec) and rubidium-90 (2.9 min), are comparable in volatility and half-lives to the lanthanum-139 precursors, has not been found in sodium which contacted uranium-fission pins during simulated EBR-II irradiations (600°C, 2% burnup).

To establish technetium-99 and lanthanum-139 as burnup monitors for EBR-II, it was first necessary to develop reliable analytical methods and then to use these methods to obtain the best possible values for the uranium-235 fast fission yields of these two nuclides. The technetium work is being carried out by the Analytical Group of the Chemical Engineering Division at Argonne, Illinois, and is reported below; the lanthanum work is being carried out by the Analytical Group of the Idaho Division and will be reported in the Idaho Division's reports.

2. Technetium-99 as a Burnup Monitor (R. J. Meyer, R. D. Oldham and R. J. Popek)

The analytical method which will be used to determine technetium-99 in EBR-II fuel was originally developed and used to determine technetium in inactive fission alloys.¹ Separation from the fission constituents is effected by distillation of technetium sesquioxide from concentrated sulfuric acid; the technetium in the distillate is reacted with the chromogenic reagent zinc dithiol; the resulting complex is extracted into isoamyl acetate, and the absorbance is measured. In the analysis of irradiated samples, the distillation is carried out remotely; otherwise, the procedure is unchanged. The only active fission product in the distillates is antimony-125. The radiation level of the distillates is about 25 mr/hr.

¹R. J. Meyer, R. F. Oldham and R. P. Larsen, Separation and Spectrophotometric Determination of Technetium in Fission, Anal. Chem. 36, 1975 (1964).

The precision and accuracy of the technetium-99 method was tested by analyzing ten 133-mg samples of inactive fission, each containing 40 μg technetium (equivalent to 1% burnup) by the procedure used for active samples. This included distillation in the cave. The relative standard deviation for a single determination was 0.7% and there was no detectable bias.

3. The Uranium-235 Fast Fission Yield of Technetium-99
(R. J. Meyer, R. D. Oldham, R. J. Popek and J. Williams)

In order to use technetium-99 as a burnup monitor for EBR-II fuel, an accurate value for its fast fission yield is necessary. A direct determination of the yield has never been made. An approximation of the technetium-99 yield could be obtained by assuming that it is the same as the molybdenum-99 yield. There would be, however, two sources of error if this were done: the independent yield of technetium-99, though small, is probably not negligible, and the molybdenum-99 yield has not been determined with the necessary accuracy. The molybdenum-99 yield was determined by analyzing uranium-235 samples which had been irradiated in a fast flux for molybdenum-99; the number of fissions which occurred in these samples was determined by monitoring the flux with an in-pile fission counter. Molybdenum-99 (67 hr) has a particularly complex decay scheme, and there is reason to suspect the accuracy of the factors which were used to convert from measured counts to disintegrations of molybdenum-99. The problem is further complicated by the fact that the average energy of the neutrons was somewhat higher than that encountered in EBR-I or expected in EBR-II.

The uranium-235 fast fission yield of technetium-99 has been determined in our laboratory by analyzing irradiated, discharged EBR-I, Mark-III fuel by the method described in the preceding section. Since the burnup of this material was relatively low, 0.1%, the analyses were made with aliquots containing about 6 μg technetium instead of the optimum 30 μg . Despite this handicap, the precision for the average of 6 determinations was $\pm 0.7\%$. The number of fissions which had occurred in this sample of irradiated fuel was determined by radiochemical cesium-137 analyses. After correcting for in-pile and out-pile decay, the measured count rate was converted to atoms of cesium-137, using the Nuclear Chicago-ASTM Cesium-137 Standard. The fission yield used to convert the cesium-137 information to the number of fissions of uranium-235 was the value published by Kafalas and Crouthamel.²

The uranium-235 fast fission yield of technetium-99 calculated from the results of the above analyses is 5.2%. No estimation of error has been assigned to this value since there is reason to believe that the reported

²P. Kafalas and C. E. Crouthamel, J. Inorg. Nucl. Chem. 4, 239 (1957).
See also ERRATA, J. Inorg. Nucl. Chem. 5, 92 (1957).

value for the cesium-137 yield is somewhat low. The ratio of the cesium-137 yield to the technetium-99 yield calculated from the above analyses is 1.080 ± 0.010 .

4. Evaluation of Technetium-99 and Lanthanum-139 as Burnup Monitors for EBR-II Fuel
(R. P. Larsen)

Which of the two burnup monitors, technetium-99 or lanthanum-139, will be used for EBR-II fuel will depend on the number of samples submitted, the magnitude of the burnup, and the precision required. The technetium-99 analysis is relatively difficult to master but once mastered has the advantages of speed and simplicity of instrumentation. The lanthanum-139 analysis (mass spectrometric-isotope dilution) is relatively easy to execute up to the point of the mass assay since none of the purification steps need to be quantitative. However, extreme care must be exercised to prevent cross-contamination from natural lanthanum. It would appear on the basis of limited experience with the two methods that they are of comparable precision ($\pm 1\%$) when the burnup is 1% or more. At 0.1% burnup the precision of the lanthanum method is about $\pm 2\%$ while the precision of the technetium method is now $\pm 10\%$.

The accuracy with which burnup determinations can be made on EBR-II fuel is presently limited by the accuracy with which the technetium-99 and lanthanum-139 fission yields are known. Both values are dependent on the published value for the cesium-137 yield, and this value, on the basis of limited information, appears to be 5 to 10% low.

A program whose objectives are to determine more accurately the fast fission yields of technetium-99, lanthanum-139, and other fission products of potential use as fission monitors has been undertaken. An attempt will be made to irradiate gram-quantities of uranium-235, uranium-233, and plutonium-239 in EBR-II to a burnup of from 15 to 25% (several years of irradiation at full power will be needed to achieve this). The number of fissions will be determined by mass spectrometric-isotope dilution analyses; the amount of each fission product formed will be determined by chemical and/or mass spectrometric analyses.

B. Uranium-235 Thermal Fission Yield of Technetium-99
(R. J. Meyer, R. J. Popek and J. Williams)

The uranium-235 thermal fission yield of technetium-99 has also been determined. (This information was necessary for the determination of burnup for EBR-II fuel specimens which had been irradiated in thermal reactors.) Six sealed nickel capsules containing approximately 10 mg each of 47% enriched U_3O_8 were irradiated for 5 months in Argonne's CP-5 Reactor to a burnup of approximately 25% of the uranium-235. The

number of fissions which occurred in each capsule was calculated from pre- and post-irradiation mass spectrometric uranium analyses. An error analysis indicates that the error in the determination of the number of uranium-235 fissions per capsule is $\pm 0.3\%$ (1σ).

Technetium-99 was again determined spectrophotometrically. Separation of technetium-99 from the bulk of the nickel (capsule material) was effected by coprecipitation of technetium-99 with copper sulfide prior to the sulfuric acid distillation. Technetium-99 losses of from 5 to 10% occurred in the precipitation step, but the addition of a known quantity of technetium-95 (60 day) to the original aliquot allowed a yield determination to be made.

The value obtained for the uranium-235 thermal fission yield of technetium-99 is $6.07 \pm 0.08\%$ (1σ).

C. Uranium-235 Thermal Fission Yields of Cesium-133 and Cesium-137 (R. J. Meyer, G. W. Smith, R. J. Popek and J. Williams)

The uranium-235 thermal fission yields of cesium-133 and cesium-137 have also been determined using the capsules which were irradiated in CP-5 (Section B). Mass spectrometric analysis was used to determine the cesium isotopic distribution; mass spectrometric-isotope dilution analysis was used to determine the concentration of each cesium isotope. Aliquots containing $30\ \mu\text{g}$ of fission product cesium and identical aliquots to which a known amount of cesium-133 (standardized gravimetrically) had been added were passed through columns of ammonium phosphomolybdate. After thorough washing, the cesium was eluted with 11 M ammonium nitrate, the ammonium nitrate was destroyed with aqua regia, and the cesium was analyzed mass spectrometrically.

The possibility that cross-contamination from natural cesium (reagents and enviroins) might occur in the above separations was considered; it was checked by carrying previously isolated fission product cesium through the separation procedure and comparing the results of pre-separation and post-separation mass spectrometric analyses. The agreement between the two results showed that there had been no cross-contamination.

The values obtained for the uranium-235 thermal fission yields of cesium-133 and cesium-137 are given in Table VIII-1.

Table VIII-1

URANIUM-235 THERMAL FISSION YIELDS OF
CESIUM-133 AND CESIUM-137

<u>Capsule No.</u>	<u>Cesium-133</u>	<u>Cesium-137</u>
1	6.72 $\pm$ 0.05	6.29 $\pm$ 0.03
2	<u>6.79 $\pm$ 0.09</u>	<u>6.36 $\pm$ 0.05</u>
Average	6.75 $\pm$ 0.07	6.32 $\pm$ 0.04

The cesium-137 content of the irradiated capsules was also determined radiochemically using the standard perchlorate method. After corrections for chemical yield and cesium-134 content, the count rate on each sample was converted to atoms of cesium-137 by comparison with identically mounted and counted aliquots of the Nuclear Chicago-ASTM Cesium-137 Standard.* (This standard was standardized by mass spectrometric-isotope dilution analysis by B. F. Rider of the Vallecitos Atomic Power Laboratory.) The agreement between the results of the mass spectrometric and radiochemical analyses was better than 1%, which is less than the error of the radiochemical analysis.

*The Nuclear Chicago-ASTM Cesium-137 Standard as of 8-8-62, the day of certification, contained an amount of cesium-137 equivalent to $2.71 \pm 0.03 \times 10^{15}$ uranium-235 thermal fissions.