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Argonne National Laboratory

CHEMICAL ENGINEERING DIVISION
RESEARCH HIGHLIGHTS

May 1965-April 1966

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ARGONNE NATIONAL LABORATORY
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CHEMICAL ENGINEERING DIVISION
RESEARCH HIGHLIGHTS

May 1965-April 1966

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I. COMPACT PYROCHEMICAL PROCESSES

Compact pyrochemical processes have continued to be developed for recovery and purification of refractory fuel materials discharged from power reactors. Because inorganic, radiation-stable materials are employed in these processes, they can accommodate short-cooled, high-burnup metal and ceramic fuels, thus permitting rapid recycle of fuel. The resulting reduction of fuel inventories outside the reactor is one of the major economic incentives for the development of these processes. This is an especially important factor for fast reactor fuels which contain a high concentration of valuable fissionable isotopes and are thus subject to large inventory charges.

Other economic advantages are the avoidance or simplification of chemical conversions, the use of small process volumes (and, hence, compact processing equipment), the direct production of solid radioactive wastes, the decrease in criticality problems because of the absence of aqueous solutions, and, in some of these processes, the retention of valuable alloying elements. Because of the above characteristics, particularly the advantage of compact processing equipment, these pyrochemical processes are suited to use in small plants located on or near a reactor site. This concept of a close-coupled reactor and processing facility is being evaluated in Argonne's EBR-II reactor complex in Idaho.

During the past year, investigations of pyrochemical methods have been oriented toward the development of new and improved pyrochemical processes for efficient and economical reprocessing of future power reactor fuels. Since pyrochemical processes are most likely to be used for closed-cycle, on-site processing of future power reactor fuels, particular attention has been directed toward processes that are readily integrated with the other fuel cycle operations, such as fuel refabrication. The scope of the process development studies includes uranium, plutonium, and thorium fuels in the form of oxides, carbides, or metallic alloys.

In the process concepts currently under investigation, the fissile and fertile constituents of the fuel and the fission products are separated through differences in their partition behaviors between liquid metals and molten salts. In most cases, alloys of magnesium are used as the liquid metal phase, and $MgCl_2$, either alone or diluted with other chlorides, serves as the molten salt phase. The distribution coefficients and solubilities of the individual fuel constituents in the liquid metal-molten salt systems can be varied over a wide range by changes in the compositions of the salt and metal solvents and the temperature. Thus, by selecting the appropriate conditions, the process flowsheet can be designed to provide the separations required by a specific fuel cycle. It appears that separations of this type can be effected either by single-stage batch operations, or by continuous multistage techniques, as exemplified by packed columns.

The optimization of operating conditions and the development of plant-scale equipment for the skull reclamation process has also been continued. The skull reclamation process (discussed later in this section) is designed to recover the 5 to 10% uranium left in the zirconia crucible after the discharged fuel pins from the EBR-II reactor have been melt refined.

A. New Pyrochemical Processes for Future Fast Reactor Fuels

The general objective of the laboratory-scale investigations is the origination of new and improved pyrochemical processes for efficient and economical reprocessing of future power reactor fuels. This effort involves both supporting chemical studies and laboratory demonstrations of basic separation procedures used in conceptual processes.

1. Salt Transport Separations

Salt transport separations are pyrochemical separations based upon the selective transfer of solutes by equilibration of two liquid metal solutions with the same molten salt. When a liquid metal solution saturated with a particular solute is contacted with a molten salt, the equilibrium concentration of the solute in the salt phase is the product of its solubility in the metal phase and its distribution coefficient. Thus, upon equilibration of the salt phase with two metal phases of different composition, the solute will transfer to that metal phase over which the equilibrium concentration of the solute in the salt is lowest, and transfer will continue as long as there is a solute concentration gradient in the salt. The salt, in effect, serves only as a carrier for solute transfer between the liquid metal phases. To achieve rapid transfer of the solute, the salt phase is circulated between the metal phases. From a process standpoint, this separation has the outstanding advantage that only small solution volumes are required, since not all of the uranium or plutonium need be in solution at any one time. It also offers the possibilities of excellent separations and recoveries, and of continuous salt cycling in large-scale installations.

The salt transport concept has been applied as a potential method for processing uranium-plutonium fuels, utilizing the equilibrium relationships shown in Fig. I-1. In Fig. I-1, equilibrium concentrations¹ are given for uranium and plutonium in a $MgCl_2$ salt phase in contact with copper-magnesium and zinc-magnesium alloys. In this example, $MgCl_2$ is contacted with (1) a copper-8 w/o magnesium alloy containing uranium and plutonium at concentrations A and B, respectively, (2) a zinc-3 w/o magnesium alloy, and (3) a zinc-65 w/o magnesium alloy. Upon equilibration with the salt, uranium will transfer from the copper-magnesium alloy (point A) to the zinc-65 w/o magnesium alloy (point D), since the uranium concentration in the salt at point D is less than at points A or E. Plutonium, on the other

¹Based partially on estimated data.

hand, will transfer selectively to the zinc-3 w/o magnesium solution (point C) since its concentration in the salt at point C is less than at

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Fig. I-1. Plutonium and Uranium Concentration in MgCl_2 at Equilibrium above Saturated Alloys at 750°C . (Curves are based partially on estimated data and are intended for illustrative purposes only.)

molybdenum, and ruthenium. In the reduction step, uranium oxide, zirconium oxide, and nobler metal oxides in a 30 m/o MgCl_2 -30 m/o NaCl -40 m/o KCl salt were reduced by Cu-10 w/o Mg alloy. The reduced uranium metal was present largely as a precipitated phase in the Cu-10 w/o Mg alloy. The bulk of the cerium remained in the halide salt. The salt, containing cerium and MgO reaction product, was removed and discarded as waste. In the salt transport step, which followed the reduction step, uranium in the molten Cu-10 w/o Mg alloy was transferred incrementally to a molten Mg-35 w/o Zn alloy by cycling MgCl_2 between the two molten alloys, which were in adjacent vessels (see Fig. I-2). The charge of molten MgCl_2 was pressure-transferred through a transfer line alternately from one alloy to the other.

points B or F. In both cases an equivalent amount of magnesium is transferred in the opposite direction (i.e., to the copper-8 w/o magnesium alloy).

a. Laboratory Studies

Preliminary laboratory-scale experiments resulted in over 99% transfer of plutonium from a copper-33 w/o magnesium alloy to a zinc-5 w/o magnesium alloy with negligible uranium transfer. Pilot-plant studies confirmed the transfer of uranium from a copper-magnesium alloy to a magnesium-rich zinc alloy in accordance with the above principles. It was also shown that a highly satisfactory separation of zirconium (a fission product) from uranium is achieved by this process, since zirconium remains in the copper-magnesium alloy.

b. Engineering Demonstration of Salt Transport Processes

Engineering work related to the development of salt transport processes is underway. A demonstration run was completed using reduction and salt transport steps at 800°C to recover uranium from a $6\frac{1}{2}$ -kg unirradiated charge consisting of a mixture of oxides of uranium (5 kg), cerium, zirconium,

In each vessel, the salt and metal phases were mixed to promote chemical equilibration; then the phases were allowed to separate by settling.

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Fig. I-2. Schematic of Salt Transport Equipment

99% uranium recovery would have been achieved after about 22 transfer cycles. The rate of uranium transport tails off as the source solvent becomes highly depleted in uranium. A very satisfactory zirconium removal of ~99% was achieved. The engineering-scale run was very encouraging and has successfully demonstrated the salt transport principle.

Although salt transport investigations have thus far been limited to combinations of copper-magnesium and zinc-magnesium alloys, other liquid metal solvents may prove useful. For example, certain separations should be possible in systems involving combinations of cadmium-magnesium and zinc-magnesium alloys, or only zinc-magnesium alloys of different compositions.

2. Conceptual Pyrochemical Flowsheet for Oxide, Carbide, and Metal Fuels

A general type of flowsheet is being investigated for processing uranium and plutonium metal, oxide, or carbide core and blanket material discharged from fast breeder reactors. The flowsheet which is shown in Fig. I-3 is based on the salt transport concept described earlier. The process utilizes Cu-Mg and Zn-Mg alloys and a salt mixture of MgCl₂, NaCl, and KCl.² Because small volumes of metal and salt solutions are required and because separation factors are very high, the process is easily adapted to single-stage batch separations.

² Either MgCl₂-NaCl-KCl or MgCl₂ can be used as the salt phase. The ternary salt has a lower melting point and a lower vapor pressure. Magnesium chloride gives slightly higher distribution coefficients.

Equilibration time and settling time were 6 and 10 min, respectively, in the vessel containing Cu-Mg alloy and 6 and 5 min, respectively, in the vessel containing Zn-Mg alloy. The transfer of reduced uranium proceeded in accord with theory until 14 transfer cycles were completed, when the run was terminated. At this point, the net uranium transfer achieved was about 88% of the 5 kg charged. If the transfer had continued to proceed in accord with theory, a

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Fig. I-3... Conceptual Pyrochemical Process for Oxide, Metal, or Carbide Fuel from Fast Breeder Reactor Core

The flowsheet involves, first, an oxidative decladding operation in which oxide fuels are released from cladding. In this step, carbide and metal fuels are converted to oxides. These oxides are then reduced by a Cu-10% Mg alloy in the presence of a suitable molten salt. The highly electropositive fission elements, alkali, rare earth, and alkaline earth elements distribute strongly to the salt phase and are removed in it. Then, by taking advantage of the widely different distribution coefficients and solubilities for uranium and plutonium in zinc-magnesium phases of different compositions, the uranium and plutonium are separated by selective transfer to separate zinc-magnesium phases.

Plutonium and uranium are recovered from their solvent metals by retorting to remove volatile zinc and magnesium. After consolidation of the metal products in the desired proportions, by melting, the plutonium-uranium alloy is converted to oxides or to carbides or left as metal, as desired. The plutonium-uranium product is subsequently fabricated into fuel elements and recycled to the reactor core or blanket. The flowsheet shown would provide uranium and plutonium recoveries of 99% or better.

3. Integrated Fuel Cycle Studies

A major objective in the development of pyrochemical processes is to integrate the chemical separations process as closely as possible with the other operations of the fuel cycle so as to gain a complete fuel cycle of maximum economy and reliability. For the extensively recycled, high-burnup fuels expected to be used in future power reactors, the buildup of radioactive uranium and plutonium isotopes is expected to necessitate remote operation of the entire fuel cycle. It is therefore desirable that the product of the separations process be amenable to remote refabrication without further treatment. Decladding and reduction steps, as well as carbide preparation, oxide preparation, and waste consolidation steps are being evolved.

It appears that oxidative decladding may be applicable to oxide, carbide, or metallic fuels. This procedure yields a mixture of oxides of uranium, plutonium or thorium, and fission products. Early studies³⁻⁵ showed that uranium oxide, plutonium oxide, and thorium oxide are readily reduced by zinc-magnesium (5 to 15 w/o Mg) alloys in the presence of an

³Knighton, J. B., and Steunenberg, R. K., Preparation of Metals by Magnesium-Zinc Reduction. Part I, Reduction of Uranium Oxides, ANL-7057, June 1965.

⁴Hariharan, A. V., Knighton, J. B., and Steunenberg, R. K., Preparation of Metals by Magnesium-Zinc Reduction. Part II, Reduction of Thorium Dioxide, ANL-7058, June 1965.

⁵Knighton, J. B., and Steunenberg, R. K., Preparation of Metals by Magnesium-Zinc Reduction. Part III, Reduction of Plutonium Dioxide, ANL-7059, June 1965.

appropriate salt and form liquid metal solutions suitable for further pyrochemical processing. Since copper-magnesium and cadmium-magnesium alloys are also under consideration as solvents, reductions of uranium oxides by both of these solvents have been investigated briefly. Preliminary laboratory-scale studies indicate that reduction of uranium oxide by either of these alloys is possible. Additional work has also been performed on the reduction of uranium oxides by magnesium-rich (60 to 70 w/o) alloys with zinc. Under these conditions the reduced uranium metal is precipitated from the liquid alloy, thereby permitting the use of small volumes of the alloy. It was shown further that zinc in the absence of magnesium reduces U_3O_8 to UO_2 in the presence of molten chloride salts. This result is of particular interest in the EBR-II skull reclamation process (see Skull Reclamation Process section, this report), where this reaction apparently causes U_3O_8 particles to disintegrate, thereby releasing noble metal fission products which are extracted into the liquid zinc. Pyrochemical processes normally yield a metallic product. Experience with the oxidation of melt refining skulls, which are essentially metallic, indicates that a similar oxidation procedure may be suitable for the regeneration of an oxide fuel from a metallic product. In the case of carbide fuels, current studies indicate that metallic uranium and plutonium can be converted to the carbides by treatment with hydrogen and propane in a fluid-bed reactor (see Section IV of this report).

A method was reported previously (ANL-7020, p. 43) for consolidating rare earth fission product wastes into aluminum-magnesium alloys for long-term storage. In a laboratory demonstration experiment, an ingot consisting of 10 w/o cerium, 20 w/o magnesium, and 70 w/o aluminum was prepared, sectioned, and mildly irradiated to produce radioactive ^{141}Ce . An autoradiograph of the section, reproduced in Fig. I-4,

Fig. I-4

Autoradiograph of 10 w/o Cerium (activated)-20 w/o Magnesium-70 w/o Aluminum Alloy at Approximately 1.2X Magnification

shows the cerium to be reasonably well dispersed in the ingot as needle-like crystals of CeAl_4 . This alloy, therefore, is capable of containing relatively high concentrations of rare earth fission product elements; it also has attractive properties for the fixation of wastes in a medium that is suitable for both interim and ultimate storage. The aluminum-magnesium alloy, with the rare earth fission products, might also serve as a useful source of heat and radiation during the interim period before its permanent disposal.

4. Pyrochemical Processes for Carbide-type Reactor Fuels

The processing of carbide fuel (ThC_2 and UC_2), such as fuel for the High Temperature Gas Cooled Reactor (HTGR), by means of a pyrochemical process flowsheet has been considered. A conceptual flowsheet which utilizes fluid-bed and pyrochemical operations for the purification and recovery of HTGR fuel material and for its reconversion to the final carbide form is presented in Fig. I-5. In the first steps of the flowsheet, fluid-bed oxidation and chlorination of the spent fuel are carried out. Next, the pyrochemical steps of the process are employed. These consist of selective reduction of the chlorides of elements more noble than uranium and thorium (e.g., Mo, Ru, and Pd) by cadmium or a cadmium-zinc alloy. The noble metal fission products are extracted into the metal phase, which is then discarded as waste. Subsequently, the uranium and thorium chlorides are reduced by contacting with a reducing solution such as magnesium-cadmium. The bulk of the rare earth elements remain in the salt phase, while most of the uranium and thorium transfer to the metal phase. (A countercurrent extraction operation will be used for this step to achieve both a high recovery of uranium and a high removal of rare earth elements.) The complete process is shown in the flowsheet.

In order to determine the feasibility of the pyrochemical steps, a run was made in which batch extractions were employed, instead of batch countercurrent or continuous countercurrent extractions, to obtain information on the distribution coefficients and to indicate the possibility of achieving the desired results in a countercurrent operation. For experimental convenience in the run, a change was made in the noble metal extraction step (which in the conceptual flowsheet involves the reduction of the noble elements from a salt solution). In simulating this step, uranium, thorium, and cerium were oxidized by CdCl_2 from a Cd-3 w/o Zn solution containing thorium, uranium, cerium, and molybdenum. (Cerium was used as representative of the rare earth elements, and molybdenum as representative of the noble metal elements.) The result for the noble metal extraction step should be independent of whether thorium, uranium, and cerium in metal solution are oxidized and transferred to a salt solution or whether noble metals (e.g., molybdenum) in a salt solution are reduced and transferred to a metal solution.

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

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✓ Fig. I-5. Conceptual Process for HTGR Core Fuel

From the results of this run, the following conclusions were made:

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

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

(3) The pyrochemical steps should be easy to perform by the use of either batch or continuous operation.

B. EBR-II Fuel Cycle Development

1. Skull Reclamation Process

The skull reclamation process is an adjunct to the melt refining process (ANL-6875, p. 8) in the EBR-II fuel cycle and has been developed to recover uranium from the residue in melt refining crucibles for return to the main fuel stream. These residues, also known as skulls, consist principally of unpoured metal, some oxidized uranium, and oxidized rare earth and alkaline earth fission products that are concentrated in the skull material during melt refining. The process must effect a separation of uranium from the rare earth and alkaline earth metals and also from noble and refractory metal fission products (Zr, Mo, Ru, Rh, Pd, Nb, and Tc) that are not removed in melt refining. The removal of these elements in the skull reclamation process offsets their generation by fission of uranium in the reactor and serves to maintain their concentrations at nearly constant values in recycled fuel.

The skull reclamation process has been simplified since the last Highlights Report (ANL-7020, pp. 16-17). The revised flowsheet is presented in Fig. I-6. The major feature of the simplified flowsheet is complete elimination of the intermetallic compound precipitation step. With this elimination, it is possible to combine the reduction step with the uranium-zinc intermetallic compound decomposition step. (The latter step converts the uranium intermetallic precipitate to a uranium metal precipitate.) This is done in the modified uranium oxide reduction step by reducing the uranium oxides directly with a magnesium-rich solution and allowing uranium metal to precipitate as it is formed. Thus, the simplified flowsheet is shorter by two steps than its predecessor.

*Two different salts were employed: 47.5 m/o CaCl₂-47.5 m/o MgCl₂-5 m/o CaF₂ and 47 m/o MgCl₂-27.7 m/o NaCl-18.6 m/o KCl-6.7 m/o NaF

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✓ Fig. I-6. Simplified Liquid Metal Process for Reclamation of Melt Refining Skulls Generated in the EBR-II Fuel Cycle

A further simplification in the new flowsheet is the elimination of the three time-consuming cooling and heating cycles (between 800 or 700°C and 525 or 450°C) that were used in the original flowsheet (ANL-7020, Fig. I-7, p. 17). This has made it possible to process a batch of skull oxide (once the equipment is brought up to operating temperature) within 8 hr as compared with 18 hr by use of the previous flowsheet. In order to eliminate cooling after the noble metal extraction step, it was necessary to develop proficiency in the transfer of the waste zinc phase from beneath a liquid salt phase rather than from beneath a solidified salt layer. This latter operating change removes a restriction on the melting point of the salt system and widens the choice of salt compositions to include those with low melting points. In fact, the use of low melting point salt is advantageous in the simplified flowsheet, since it reduces the risk of the salt solidifying in the transfer line. Other advantages of the simplified flowsheet are reduced material consumption with a consequent smaller volume of wastes and increased uranium recovery.

a. Pilot Plant Studies

The pilot plant for the skull reclamation process was described in ANL-6875, p. 20, and ANL-6766, p. 23. Operation of the pilot plant was terminated during the past year. Engineering techniques developed during the pilot-plant demonstration runs are now being further developed in the EBR-II plant-scale experiments described in the following section.

In the pilot plant, the noble metal extraction, uranium oxide reduction, and uranium product dissolution steps were performed in a 9 $\frac{1}{2}$ -in. ID pressed-and-sintered tungsten crucible. The crucible was inductively heated in the bell jar furnace shown in ANL-6875, p. 21. The bell jar allowed the process steps to be conducted in an inert atmosphere and permitted pressurization of the system for transfer of molten metals or salts through a transfer line to a container outside the bell jar. Waste and product streams were moved from the process crucible by pressure transfer through the same molybdenum-30 w/o tungsten transfer line. Operation of the transfer line, which had been a problem in the early runs, was completely reliable in the last series of runs. The equipment was operated in a glovebox containing a dry (<150 ppm H₂O) nitrogen-argon atmosphere to eliminate moisture pickup by the hygroscopic salts.

Thirty-six engineering-scale runs were performed in the pilot plant. About 2 kg of skull oxide was processed in each run; in the full-scale (EDR-II) runs, about 5 kg of skull oxide is processed in each run. Eight of the runs were made using the new flowsheet (Fig. I-6); in six of these, the lower melting salt⁶ was employed. Because of the change to a low-melting salt flux, operating temperatures within the range of 650 to 800°C were investigated. Other variables investigated were reaction time, agitation intensity, and charge size. As would be expected, reaction time (for uranium oxide reduction or extraction of noble metals) and temperature are closely related: the higher the temperature, the shorter the reaction time. A reaction temperature of 750°C for the noble metal extraction and reduction steps is somewhat arbitrarily recommended as one which provides reasonably rapid reactions (complete within 1 to 2 hr) without incurring excessive vaporization of metal and salt phase constituents. Good agitation intensity is also necessary to effect the reactions within a short period of time.

The following conditions were recommended for initial operation of the plant-scale equipment:

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

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

⁶Composition: 47 m/o MgCl₂-27.7 m/o NaCl-18.6 m/o KCl-6.7 m/o NaF. This salt melts at about 495°C. The salt used in other runs has the composition 47.5 m/o CaCl₂-47.5 m/o MgCl₂-5 m/o CaF₂, and melts at about 600°C.

Process Performance: Uranium Recovery

A uranium recovery of 95% in the skull reclamation process is ample because probably less than 10% of the total EBR-II fuel will be cycled through this process. A uranium recovery of 95% in the skull reclamation process would provide an overall uranium recovery of greater than 99.5%. Achievement of a high uranium recovery in the skull reclamation process requires that certain conditions be met in the noble metal extraction and reduction steps. These conditions are stated below.

Noble Metal Extraction Step. To avoid loss of uranium in the waste metal, sufficient oxidizing power must be available to oxidize and to transfer to the salt phase (1) the uranium metal (and consequently all of the magnesium) present in the recycled product solution heel from the previous run and (2) any unoxidized uranium metal in the skull oxide charge. Considerable oxidizing power is available in the skull oxide through reactions such as:

If experience shows that the available oxidizing power is insufficient, an additional quantity of oxidant, such as ZnCl_2 , must be added. ZnCl_2 was usually employed in the pilot-plant runs. Uranium loss in the noble metal extraction step in the pilot-plant runs was no problem, being generally well under 0.5%.

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

The minimum loss of uranium in the 60 w/o Mg-Zn supernatant waste, which is determined by the solubility of uranium at 700°C , is about 1.4%. Any loss of uranium greater than this value would be the result of entrainment of the uranium metal precipitate. The minimum loss owing to solubility was achieved in runs in which moderate care was taken to allow the uranium to settle (0.5 hr) and to avoid its resuspension. In two runs made to determine whether the uranium was, in fact, easily suspended, the supernatant solution was stirred at 400 rpm during removal and most of the uranium was entrained in the supernatant metal. However, routine precautions should be sufficient to avoid uranium entrainment.

Process Performance: Fission Product Removal

Fission product removals were not significantly affected by the change to the new flowsheet. Removals may be summarized as follows:

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

Ruthenium--~90%

Molybdenum--~40-70%

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

Since the performance (e.g., mixing effectiveness, phase transfer efficiency, entrainment) of the skull reclamation process depends to a large extent on the physical features (such as size, shape, and agitator design) of the equipment employed, pilot-plant operations were terminated. Future efforts will be devoted to completing the development and testing of EBR-II plant-scale equipment.

b. Development of Plant Equipment for EBR-II Skull Reclamation Process

Plant equipment for processing skull oxide in the Fuel Cycle Facility in Idaho is being built and tested in a large inert atmosphere (argon) enclosure by the Chemical Engineering Division. This equipment, which was designed to be used in the Fuel Cycle Facility, is sized for operation with about 5.8 kg of skull oxide (~5 kg of uranium oxide). The principal equipment items currently being tested are the two furnaces that are required for processing the skull oxide: (1) a reduction furnace⁷ where the skull oxides are reduced and the uranium is purified to the extent necessary for return to the main fuel cycle, and (2) a retorting furnace where solvent metals are vaporized from the uranium and where the resulting uranium sponge is melted to consolidate it into an ingot. The performance of the reduction and retorting furnaces and the operation of the inert atmosphere enclosure are discussed in the three succeeding sections.

⁷Previously identified as "skull reclamation furnace."

(1) Reduction Furnace

The reduction furnace (ANL-7020, pp. 23-27) consists essentially of a large tungsten crucible (14-in. ID by $24\frac{1}{2}$ -in. inside height) contained in a Hastelloy C vessel which is equipped to provide for charging of materials, mixing of molten salt and metal phases, and transferring of metal and salt phases from the crucible to receivers outside the furnace. Ten shakedown runs were made in the reduction furnace to evaluate the process performance and mechanical reliability of the equipment. These runs were made generally according to the simplified flowsheet shown in Fig. I-6 except that ZnCl_2 was not used. The feed material in all runs consisted of unirradiated oxidized uranium-fissium alloy, together with small additions of cerium and zirconium oxides. Some variations in process and operating conditions were made to investigate their effect on uranium recovery and fission product removal. These variations included:

1) Use of three different halide salt compositions:
(a) 47.5 m/o CaCl_2 -47.5 m/o MgCl_2 -5 m/o CaF_2 , (b) 50 m/o CaCl_2 -50 m/o MgCl_2 , and (c) 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl .

2) Performance of the noble metal extraction step and reduction step at temperatures of 700 and 750°C for 1 to 2 hr with a mixing speed of 650 rpm, and performance of the uranium product dissolution step at 810°C for $1\frac{1}{2}$ to 2 hr with mixing speeds of 300 to 400 rpm.

Overall operating times for the completion of a run varied from 10.5 to 12 hr, of which 4 to 5 hr were required for bringing the furnace from room temperature to 700°C. To simulate plant operating conditions, successive runs were made without cleanup of the furnace and without removal of the product solution heel from the tungsten crucible between runs. The results of these runs are reported below.

Process Performance: Uranium Behavior. Uranium recoveries in these runs have averaged about 93%. The desired recovery is 95%. The smaller recovery was attributed to uranium losses in two wastes of the reduction step. These are the waste salt and 60 w/o Mg-Zn supernatant solution. The loss in the waste salt is attributed to incomplete reduction of the uranium oxide which resulted from a lack of sufficiently vigorous reaction conditions (mixing intensity, temperature and time). The loss in the 60 w/o Mg-Zn supernatant was somewhat higher than that which could be attributed to solubility (about 2% loss versus a solubility of 1.4% at the temperature of transfer, 700°C). The greater loss sustained may be the result of an insufficiently long settling period. Conditions in subsequent runs will be modified to overcome these difficulties.

Fission Product Behavior. Fission product removals in the initial series of runs may be summarized as follows: Removals of cerium, a representative rare earth, were consistently good (usually about 95%). The ruthenium removals were generally satisfactory but lower than

in pilot-plant runs. Molybdenum and zirconium removals were generally lower than desired. As is the case for uranium reduction, it is believed that the planned increases in mixing intensity will improve the removals of these elements.

Effect of Fluoride Ion on Process Performance. In three of the scouting runs, fluoride ion was omitted from the process salt. This change in procedure was prompted by a desire to avoid fluoride salt contamination of the final zinc-magnesium-uranium product. The fluoride salt was suspected of having a deleterious effect upon the BeO crucible in which the zinc-magnesium-uranium product is retorted.

In the absence of fluoride ion, the removal of molybdenum, ruthenium, and zirconium in the noble metal extraction step was significantly improved. However, the absence of fluoride resulted in high uranium losses (~14%) in the waste salt from the reduction step, indicating that fluoride ion is necessary for achieving high reduction of uranium oxide. The desirability of omitting fluoride salt from the noble metal extraction step and adding it just prior to the reduction step will be investigated in the next series of runs. Techniques will also be investigated for removing any residual flux that may accompany the zinc-magnesium-uranium solution during its transfer from the reduction furnace.

Mechanical Performance of Reduction Furnace and Auxiliary Equipment. The important components of and auxiliary equipment for the reduction furnace include: (1) a tungsten crucible (14-in. ID by $24\frac{1}{2}$ -in. inside height) where the reduction and purification steps are performed, (2) a mixer, (3) a transfer line, (4) a transfer receiver for collecting transferred molten materials, and (5) fume control equipment. A detailed description of this equipment was given in the preceding Highlights Report (ANL-7020, pp. 23-28). The furnace and auxiliary equipment operated very well. The associated operations of materials charging, heating, mixing, sampling, and transferring of waste and product solutions were carried out successfully.

The agitator shaft seal and the 4-bladed impeller of the mixer were described in the previous Highlights Report (ANL-7020, pp. 26-27). No leakage of fumes through the shaft seal has been apparent when the furnace has been pressurized during transfer operations. (The shaft seal assembly is purged by a small argon stream; thus, any leakage through the seal would be argon rather than furnace fumes.) No difficulty has been noted in the operation of the bearing and seal assembly.

The transfer line consisted of an inverted J-shaped molybdenum-30 w/o tungsten tube that was initially heated by seven heaters insulated with swaged magnesia (see ANL-7020, p. 27). In the course of the shakedown runs, the seven heaters were replaced with three lengths of

heater cable made of Chromel P heater wire insulated with braided silica and covered with a spiral-wound stainless steel strip. This change resulted in a significant improvement in temperature control. Since being rebuilt, the transfer line has been used successfully for 29 separate transfers of molten salts and metals.

The transfer receiver equipment and its operation were described previously in ANL-7020, pp. 28-29. In the simplified flowsheet now being used, purging of the transfer line has been eliminated as a process requirement. This eliminated the need for a gas-tight seal around the discharge end of the transfer line, and, therefore, the motorized equipment for raising and sealing the secondary waste container into position has been removed. The transfer receiver now serves to weigh materials being transferred and to confine the fumes that are generated at the discharge end.

In the course of a run, process reagents are added twice to the hot ($\sim 750^{\circ}\text{C}$) reduction furnace. During the shakedown runs, when the furnace was opened, considerable quantities of zinc fumes escaped from the furnace. Fuming also occurred, but to a lesser extent, during and following the transfers of molten metals and salts from the furnace. If the furnace were installed in the Fuel Cycle Facility without provision for fume control, fuming would cause in-cell atmosphere contamination and would create difficulties in viewing through the 5-ft thick shielding windows.

To overcome this problem, an exhaust manifold which fits around the furnace charging port was built and successfully tested. This manifold was connected by ductwork to a filter-exhauster assembly. AEC type high-temperature absolute filters were used in the assembly and reduced to a negligible value the fumes from the gas stream exhausted through the manifold. The same filter-exhauster assembly was also connected to the transfer receiver and satisfactorily prevented the escape of fumes during transfer operations.

To reduce further the fume load on the filter-exhauster system, the furnace charging equipment is being modified for use in the EBR-II Fuel Cycle Facility. The modification consists of incorporating a 4-in.-dia. ball valve as a closure at the bottom of the charging hopper; the valve will be opened only to charge process reagents. In this way, the length of time that the hot furnace is open will be reduced from almost an hour to about a minute for each run.

Physical Condition of Reduction Furnace after Ten Runs.

Following completion of the final run of the series, the inert atmosphere enclosure was returned to an air atmosphere to permit direct disassembly of the reduction furnace and examination of its interior and auxiliary parts.

The inner wall of the tungsten crucible was covered with an adherent, black pebbly mixture of metal and flux weighing about 2 kg.

The external surface of the crucible was clean, and no damage to the crucible itself was evident. There was no accumulation of material in the Hastelloy C furnace body, which also showed no evidence of corrosive attack by any of the process materials.

The major accumulation (~4 kg) of condensed zinc, magnesium and salt was on the heat shield assembly which rests on the tungsten crucible. This quantity is regarded as slight and did not interfere with the operation of the furnace.

The mixer assembly bearing and stuffing box were in good condition. The top mounted sealed ball bearing still contained adequate lubricant; the two graphite sleeve bearings showed little wear; and the seal packing was still resilient.

(2) Retorting Equipment

The final product solution transferred from the reduction furnace consists of about 8 liters of a Zn-12 w/o Mg-12 w/o U solution weighing approximately 36 kg and containing 4 to 4.5 kg of uranium. A plant-scale retorting furnace has been built and installed in the inert atmosphere enclosure for the recovery of uranium by the distillation of the volatile zinc and magnesium. Figure I-7 is a vertical section of the retorting apparatus; Fig. I-8 shows the heating assembly mounted on its base in the inert atmosphere enclosure; and Fig. I-9 shows the furnace with the sealed bell-jar cover in position.

Seven test runs have been completed in the plant-scale apparatus. Of these runs, two were for calibration purposes using uranium-free zinc-magnesium charges and five were made with uranium-bearing charges. All the runs were conducted in beryllia retorting crucibles at a nominal pressure of 10 torr. Beryllia crucibles instead of tungsten crucibles (see ANL-7020, p. 16) were used, since a study revealed that the hydriding of uranium, which is necessary for its removal from a tungsten crucible, was undesirable.

The bulk of the volatile zinc and magnesium metal present in the charge was distilled at temperatures between 650 and 750°C. Vaporization of the remaining volatile material and liquation of the uranium product were achieved by increasing the temperature to about 1150 to 1200°C for a period of 30 to 100 min. In the five runs with uranium-bearing charges, the distillation rates varied from 55 to 67 g/min. No difficulty was encountered in removing the consolidated uranium ingot from the beryllia retorting crucible.

The retorting furnace has operated without difficulty. Control of temperatures and pressures for proper operation has been readily achieved. A "bump-detector" employing a sensitive contact microphone

108-8736

✓ Fig. I-7. Plant-scale Magnesium-Zinc Distillation Apparatus. The product of the reduction furnace consists of about 8 liters of a Zn-12 w/o Mg-12 w/o U solution weighing approximately 36 kg and containing 4 to 4.5 kg of uranium. This material is charged as an ingot to the crucible. The charge is heated inductively under reduced pressure. The Zn-Mg vapors rise through the center tube to the condenser. The condensed liquid drains into the graphite distillate collector. The graphite felt and Fiberfrax insulators prevent loss of vapor during distillation and permit the collector to be separated from the secondary-container cover when the apparatus has cooled.

108-8727

Fig. I-8. Retorting Furnace Heating Assembly. Retorting furnace tests are being carried out in the large inert atmosphere enclosure shown here. The heating assembly for the retorting furnace is shown mounted on the furnace base. On this base is the large fusible metal seal trough which is used to make a leak-tight seal when the bell jar is in place (see Fig. I-9). The graphite condenser and distillate collector (see Fig. I-7) rest on top of the heating assembly during operation.

108-9181

Fig. I-9. Retorting Furnace with Bell Jar Enclosure in Place. The retorting furnace is shown with the bell jar sealed to the base. The cylindrical assembly in the foreground is a standard induction-power feedthrough of the type that is used in the Argon Cell of the Fuel Cycle Facility in Idaho. It is being tested here to establish optimum coupling conditions between the induction heating workstation and the induction heating coil of the furnace.

has been developed to serve as a reliable warning of excessive boilup rate, which can result in escape of zinc-magnesium vapors from the graphite distillate collector.

In the five runs made with uranium-bearing charges, 99% of the volatilized zinc and magnesium was found in the graphite distillate collector and graphite condenser. These components together with the condensed metals would be discarded to waste in plant operation in Idaho, but are reused in the demonstration work. About 1% of the volatilized material was found on the Fiberfrax insulating sleeve. An average of only

0.07% of the metal vaporized was unaccounted for. The apparatus could be readily disassembled, and no sticking of equipment components was encountered.

Further testing of the retorting furnace is planned with the uranium-zinc-magnesium products from the new series of reduction furnace runs referred to previously.

(3) Inert Atmosphere Enclosure

The reduction furnace, retorting furnace, and skull oxidation furnace⁸ for the skull reclamation process are located in the large (24 ft long by 12 ft wide by 14 ft high--volume, ~4000 cu ft) inert (argon) atmosphere enclosure (see ANL-7020, pp. 14-16 and ANL-7055, pp. 59-62). This equipment is being tested in an argon atmosphere to simulate its operation in the Argon Cell of the Fuel Cycle Facility and to expose problems which are unique to the operation of equipment in a dry argon environment (e.g., effect on lubricating and wetting properties of materials and on heat transfer rates for natural or forced convection). The concentrations of impurities in the enclosure atmosphere are being maintained at the same concentrations as in the Fuel Cycle Facility Argon Cell. These concentrations are as follows: nitrogen, about 5 v/o; oxygen or water, between 20 and 60 ppm each. The purification system has proved adequate to control oxygen and water contaminants at the desired level of 40 ± 20 ppm each and this has been accomplished by operating the system only part time and at a low circulation rate. The system requires a minimum of attention.

Since the initial filling of the enclosure with argon, the atmosphere has been returned to an air atmosphere twice to permit inspection and modification of process equipment. The atmosphere was subsequently reconverted to high-purity argon within 24 hr. Approximately 5000 cu ft of argon was required to displace ~99% of the air in the enclosure. Final cleanup was carried out with the purification system. The ability to change from an air atmosphere to an argon atmosphere quickly and economically makes it practical for personnel to enter the enclosure at reasonable intervals for the installation and modification of equipment under test.

In the inert atmosphere enclosure, a single one-ton bridge crane is used for transporting equipment and materials. Operations upon the equipment are performed with this crane and with special tongs and tools which are handled by the operating personnel working through the gloves in the enclosure windows. Considerable ingenuity has been required in the design and use of these tools. All normal process operations and equipment

⁸The skull oxidation furnace is used to oxidize uranium-fissium metal to prepare skull oxide for use in reduction furnace runs.

maintenance have been successfully performed in this manner. Only major changes and disassembly of large components have required direct personnel entry into the enclosure.

The excellent experience with the inert atmosphere enclosure demonstrates the feasibility of using large enclosures for operation and testing of equipment under controlled atmosphere conditions.

2. Removal of Nitrogen from Argon with Titanium Sponge

A method for removing nitrogen from argon by gettering the nitrogen with hot titanium metal sponge has been investigated. Although this method has general utility for purifying argon for such applications as glovebox atmospheres, the major incentive for its development has been a possible future need to remove nitrogen from the atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility. Two sets of experimental equipment were constructed for the nitrogen removal study: (1) equipment for determining the kinetics of nitrogen removal from argon on hot titanium sponge and (2) a pilot plant for obtaining overall process performance data and information on component reliability. Studies were conducted with argon containing nitrogen at concentrations between 100 and 50,000 ppm. The following sections present the major conclusions from these investigations, which have now been completed.

a. Kinetics of Nitrogen Removal from Argon with Titanium Sponge

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

Metallographic and X-ray diffraction studies were made in an effort to determine the probable controlling reaction mechanism. In most

reacted sponge particles, three phases were identifiable. These were identified by X-ray diffraction techniques as the TiN_x and $\epsilon\text{-TiN}$ phases^{9,10} and the solid solution of nitrogen in alpha titanium. These results are in general agreement with data presented in the literature.¹¹ Although all the phases in the titanium-nitrogen system have not yet been identified, it is known that at least two surface films, TiN_x and $\epsilon\text{-TiN}$, are present in the reacted particles. The controlling mechanism of the reaction appears to be a combination of the rate of growth of these two films and the diffusion of nitrogen across the two-film boundary.

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

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

where

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

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

t = time, hr.

Figure I-10 presents this correlation.

The above empirical relation adequately describes the rate of reaction of titanium metal sponge with nitrogen impurity (concentration range, 100 to 50,000 ppm) contained in argon at 900°C . Although this equation was developed utilizing titanium metal sponge with a surface area of about $800 \text{ cm}^2/\text{g}$, a moderate change in surface area should not affect the applicability of the equation. However, the gas phase should be relatively free of such impurities as oxygen and carbon dioxide which would interfere with the reaction. The applicability of this relation in cases of wide variation of conditions of temperature, titanium surface area, and gas phase impurities is unknown.

⁹Erhlich, P., Z. anorg. Chem. 259, 1 (1949).

¹⁰Brager, A., Acta Physicochim URSS 11, No. 4, 617 (1939).

¹¹Wasilewski, R. J., The Diffusion of Hydrogen, Nitrogen, and Oxygen in Titanium, Columbia University Doctoral Dissertation, University Microfilm, Ann Arbor, Michigan, Publication No. 8857, 1954.

Fig. I-10
 Kinetics of Nitrogen Removal from
 Argon by Titanium Sponge at 900°C

108-9306

b. Pilot Plant for the Removal of Nitrogen in Argon

As reported previously in ANL-7020, pp. 33-34, the pilot-plant, which was designed to demonstrate the removal of nitrogen impurity from argon on a large scale, was operated for a total of about 1800 hr. Since the pilot plant had fulfilled its purpose of providing information on the reliability of engineering-scale components, it was shut down and dismantled.

c. Conclusions and Recommendations

An evaluation of the operation of the pilot-plant unit and the small kinetics system has led to the following conclusions and recommendations on the gettering of nitrogen from argon on hot titanium sponge:

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

(2) The presence of oxidizing gases such as oxygen, water vapor, and carbon dioxide inhibits the titanium-nitrogen reaction. If a gas stream to be purified of nitrogen contains such impurities, they must be removed upstream from the titanium gettering system for optimum utilization of the titanium.

(3) If an oxygen getter such as copper at 600°C is used, this same vessel can serve as a gas preheater for the titanium system.

(4) In plant-scale operation, the cost of nitrogen removal by titanium sponge is estimated to be approximately \$12 per pound of nitrogen removed if a 40% conversion of the metal to the mononitride can be obtained. A conversion of this magnitude is considered feasible and has been demonstrated. This cost is about 75% of the cost for a similar calcium system and 8% of the cost for a uranium system, based on 50% conversions to Ca_3N_2 and UN_2 .

(5) A critical component in the purification system is the gas circulating blower. The blower must circulate gas at a discharge pressure of a few psig because of the pressure required to circulate the gas through the titanium bed. General leak-tightness of the blower or a leak-tight blower enclosure is also required to avoid air and water vapor contamination of the circulating gas. It is recommended that the system blower be located upstream from the water- and oxygen-removal components of the purification system so that any air contamination introduced into the circulating gas at the blower would be removed prior to reaction with titanium sponge.

(6) Periodic reversal of the direction of gas flow through the titanium bed has the desired effect of permitting a higher average conversion of the sponge before nitrogen breakthrough.

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

A final report on this project will be published as ANL-7128.

C. Supporting Chemical Investigations

1. Liquid Metal Solvent Studies

The liquid metal solvent systems of primary interest in pyrochemical processes are alloys of magnesium with zinc, cadmium, and, most recently, copper. To provide basic data for process development, information is required on phase diagrams, solubilities, interactions with container materials, and the thermodynamic properties of liquid metal solutions.

Solubility Measurements

Plutonium-Magnesium-Zinc and Plutonium-Magnesium-Copper Systems. Since plutonium is a fuel constituent of major importance, its solubility in various magnesium alloys is of interest. Previous work (ANL-7020, p. 66) had shown the existence of a liquid miscibility gap between about 600 and 1000°C in the binary system, plutonium-magnesium.

These solubility studies have been extended to the ternary systems, plutonium-magnesium-zinc, and plutonium-magnesium-copper, both of which are of particular importance in processes which utilize a molten salt as a transport medium (see Section A).

The liquid immiscibility region of the plutonium-magnesium system is observed in both the plutonium-magnesium-zinc and plutonium-magnesium-copper phase systems. In the plutonium-magnesium-zinc system, the maximum solubility of plutonium in the magnesium-rich liquid phase is very high, reaching about 70 w/o (27 a/o) at 800°C. A rapid decline of the plutonium solubility in the zinc-rich portion of the ternary system was observed and is attributed to the formation of plutonium-zinc intermetallic compounds.¹² However, no experimental data were obtained on the identity of the solid phases and the locations of the solidus lines.

In the plutonium-magnesium-copper system the solubility of plutonium is generally lower than that in the magnesium-zinc system. A maximum plutonium solubility of about 60 w/o at 800°C occurs at magnesium concentrations of approximately 10 to 20 w/o. Again, the compositions of the equilibrium solid phases were not determined, but it is known that plutonium forms intermetallic compounds with copper.¹³

These plutonium solubilities are sufficiently high that either of these solvents can be used in the salt transport processes.

Solubility of Uranium in Copper-Cadmium Alloy. Both copper-magnesium and cadmium-magnesium alloys are potential liquid metal solvents for pyrochemical processes. The ternary system, copper-cadmium-magnesium, may permit a compromise between the advantages of the two binary systems, that is, the high fission product separation factors avail-

able with the copper-magnesium system, and the low melting points of the cadmium-magnesium system. Since magnesium is expected to be present in small concentrations, a few measurements were made on the solubility of uranium in copper-cadmium alloys. The results are listed in Table I-1. At a nominal copper concentration of 15 w/o, the solubility of

TABLE I-1. Solubility of Uranium in Copper-Cadmium Alloys

Temperature (°C)	Copper Concentration (w/o)	Uranium Solubility (w/o)
556	14.8	1.80
562	16.0	1.76
660	15.5	1.90
565	35.6	0.131
600	31.8	0.506
646	32.8	0.628

uranium is about 1.8 w/o and shows essentially no temperature dependence. At the higher copper concentrations of 32 to 36 w/o, the solubility is considerably less.

¹²Johnson, I., and Chasanov, M. G., *J. Inorg. Nucl. Chem.* **26**, 2059 (1964).

¹³Schonfeld, F. W., *et al.*, in "Metallurgy and Fuels," *Progr. in Nuclear Energy, Series V, Vol. 2*, H. M. Finniston and J. P. Howe, Eds., Pergamon Press, New York, 1959, p. 596.

Solubility of Iron, Chromium, Zirconium, and Niobium in Zinc-Magnesium Alloy. Iron, chromium, niobium, and zirconium are all potential constituents of fuel cladding alloys. Data on the solubilities of these elements in liquid zinc-magnesium alloys at 800°C are summarized in Table I-2. These results are smoothed values derived from the experimental measurements and pertinent literature data.¹⁴⁻¹⁷ They indicate a marked decrease in solubility of these metals with increase in magnesium concentration.

TABLE I-2. Solubilities of Iron, Chromium, Zirconium, and Niobium in Liquid Zinc-Magnesium Alloys at 800°C

Mg Concn in Zn (w/o)	Solubility (w/o)			
	Fe	Cr	Zr	Nb
0	7.7 ⁽¹²⁾	1.54	12.0 ^a	0.29 ^a
10	1.7	0.49	2.9	0.13
20	0.70	0.23	1.8	0.054
30	0.40	0.14	1.4	0.023
40	0.26	0.10	1.1	0.010
50	0.20	0.084	0.94	0.0044
60	0.16	0.070	0.84	0.0018
70	0.13	0.062	0.76	0.00078
80	0.11	0.056	0.70	0.00033
90	0.087	-	0.66	0.00015
100	0.075 ⁽¹³⁾	-	0.64 ⁽¹⁵⁾	-

^aExtrapolated to 800°C from data in Ref. 14.

Solubility of Iron in Copper-Magnesium Alloy. Steels have been considered as potential container materials for liquid copper-magnesium alloys. To assist in corrosion evaluations (see Materials Testing section below), the solubility of iron in copper-magnesium alloys at magnesium concentrations of particular process interest was determined. The results, given in Table I-3, show that iron has a significant solubility in this system, especially at the higher temperatures.

¹⁴Truesdale, E. C., Wilcox, R. L., and Rodda, J. L., Trans. AIME 122, 198 (1963).

¹⁵Siebel, G., Z. Metallkunde 39, 22 (1948).

¹⁶Martin, A. E., Knighton, J. B., and Feder, H. M., J. Chem. Eng. Data 6(4), 596 (1961).

¹⁷Schaum, J. B., and Burnett, H. C., J. Research Nat. Bur. Standards 49, 155 (1952).

TABLE I-3. Solubilities of Iron in Copper-Magnesium Alloys

Temperature (°C)	Mg Conc'n in Cu (w/o)	Fe Solubility (w/o)
747	8.78	0.082
800	8.61	0.100
850	8.96	0.144
597	33.5	0.012
646	30.4	0.018
700	30.3	0.034
748	29.8	0.049
802	29.6	0.086
850	30.3	0.092
601	51.7	0.013
646	51.6	0.019
700	51.0	0.034
751	51.8	0.054
803	51.2	0.074
855	51.8	0.122

2. Molten Salt Chemistry

a. Cadmium (I) Chloride Studies

In processes that employ liquid cadmium alloys as a solvent, CdCl_2 in a molten salt phase is sometimes used as an oxidizing agent. It is known that CdCl_2 interacts with cadmium metal under these conditions to form a subhalide species.^{18,19} It has been inferred from magnetic, cryoscopic, and electrical measurements that the subhalide species is Cd_2^{+2} . It has also been suggested that polymeric species such as Cd_3Cl_4 or Cd_4Cl_6 are formed. Therefore the reaction

was investigated in order to determine the value of n . Spectrophotometric measurements, together with chemical analyses of molten chloride solutions, were made. The molten salt solvents used were: LiCl , 59 m/o LiCl -41 m/o KCl (eutectic), and 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl at 500 or 650°C. The results showed the predominant light-absorbing species resulting

¹⁸Bredig, M. A., in *Molten Salt Chemistry*, M. Blander, Ed., Interscience Publishers, Inc., New York, 1964, p. 415.

¹⁹Corbett, J. D., in *Fused Salts*, B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, 1964, p. 375.

from the reaction of cadmium metal with CdCl_2 in the above salts to be a Cd_3^{+4} compound ($n = 2$). The "solubility" of cadmium metal in the three solvents (containing equal concentrations of CdCl_2) decreases in the order $\text{MgCl}_2\text{-NaCl-KCl} > \text{LiCl} > \text{LiCl-KCl}$. The molar absorptivity of the subhalide species is estimated to be approximately 10^4 liters mole $^{-1}$ cm $^{-1}$, and the absorption maximum varies from 305 to 365 m μ , depending upon the solvent and the temperature.

To investigate the chemical feasibility of regenerating CdCl_2 by the direct chlorination of liquid cadmium metal in a process, laboratory-scale experiments were performed in which chlorine gas was passed through cadmium at about 500°C in the presence of a molten salt (50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl). The reaction proceeded smoothly and rapidly but, as expected, with considerable heat evolution ($\Delta H_f^\circ = -92.2$ kcal/mole for CdCl_2 at 800°K).²⁰ The characteristic red color of cadmium subchloride was evident until the reaction was complete. The resulting $\text{CdCl}_2\text{-MgCl}_2\text{-NaCl-KCl}$ salts were then used to oxidize uranium metal. The results indicated that UCl_3 concentrations up to 30 or 35 m/o can be accommodated in this salt at 600°C.

b. Liquidus of $\text{MgCl}_2\text{-MgBr}_2$ System

Since MgCl_2 has a relatively high melting point (716°C), a brief investigation was made to determine whether the addition of MgBr_2 (m.p., 711°C) would result in a low-melting eutectic while allowing the high magnesium ion concentration needed for certain process separations to be maintained. The $\text{MgCl}_2\text{-MgBr}_2$ system apparently forms solid solutions with a minimum liquidus temperature of about 700°C. Thus the binary system offers no significant advantage over MgCl_2 alone.

3. Separations Chemistry

a. Halide Slagging

In the preceding Highlights Report (ANL-7020, pp. 47-49), data were presented on a halide slagging procedure in which cerium was extracted from molten uranium-plutonium alloys by molten salts. This work was subsequently extended to the extraction of plutonium from molten uranium by liquid $\text{CaCl}_2\text{-UCl}_3$ mixtures:

Uranium containing 0.2 to 4.2 w/o plutonium was melted under molten CaCl_2 containing varying amounts of UCl_3 . In the various experiments, the system

²⁰Wicks, C. E., and Block, F. E., "Thermodynamic Properties of 65 Elements--Their Oxides, Halides, Carbides, and Nitrides," U. S. Bureau of Mines Bulletin 605 (1963).

was liquated in beryllia crucibles for 15 to 90 min at 1150 or 1200°C. After quenching, the uranium and plutonium concentrations in the salt phase and the plutonium concentration in the metal phase were determined by chemical analysis. Since the metal phase was nearly pure uranium, the uranium concentration in the metal phase was determined by difference.

The results are summarized in Table I-4. The first few experiments showed that a period of 15-45 min was required to attain equilibrium. Although a side reaction with the beryllia crucible resulted in an oxidic material containing up to about 11% of the plutonium, this solid material probably had little, if any effect on the equilibrium between the two liquid phases.

TABLE I-4. Extraction of Plutonium from Molten Uranium by $\text{CaCl}_2\text{-UCl}_3$ Salt Mixtures

<u>Charge</u>									
Uranium (g)	13.931	13.756	13.569	13.365	13.777	12.902	13.178	13.445	13.762
Plutonium (g)	0.268	0.256	0.266	0.245	0.034	0.568	0.246	0.263	0.269
CaCl_2 (g)	2.198	2.199	1.999	2.000	2.004	1.997	1.999	2.010	2.012
UCl_3 (g)	0.461	0.465	1.371	0.862	0.860	0.861	0.571	1.009	0.874
Temperature (°C)	1200	1200	1200	1200	1200	1200	1150	1150	1150
Time (min)	15	90	45	45	45	45	60	60	60
<u>Plutonium (%)</u>									
Metal Phase	36.3	28.7	10.2	21.7	8.3	25.3	16.8	12.6	12.6
Salt Phase	49.0	59.5	88.9	69.0	87.4	68.0	80.1	85.7	77.4
Crucible ^a	11.4	5.8	0.6	9.2	4.8	3.8	1.1	1.2	11.0
<u>Uranium (%)</u>									
Metal Phase	98.4	98.2	94.9	96.2	94.8	97.4	97.3	95.2	95.3
Salt Phase	1.1	0.9	4.9	2.6	3.4	1.8	1.9	4.0	3.5
Crucible ^a	0.5	0.8	0.7	0.7	1.0	0.6	0.02	0.6	0.7

^aA reaction layer adhered to the inner surface of the beryllia crucible after the ingot was removed.

Experimental equilibrium constants were obtained in terms of moles, i.e.,

$$K_{eq} = \frac{n_{\text{PuCl}_3} \cdot n_{\text{U}}}{n_{\text{UCl}_3} \cdot n_{\text{Pu}}} \quad (3)$$

Thermodynamic equilibrium constants could not be computed because of the lack of information on activity coefficients of uranium and plutonium chlorides in the salt phase. However, the experimental values of K_{eq} , which averaged 187 at 1200°C and 203 at 1150°C, are useful for process calculations. These results are in excellent agreement with the earlier data obtained by McKenzie *et al.*,²¹ who reported a value of 189 at 1200°C on the basis of experiments with only tracer-level concentrations of plutonium.

²¹McKenzie, D. E., Elsdon, W. L., and Fletcher, J. W., Can. J. Chem. 36, 1233 (1958).

The results of this study indicate that a $\text{CaCl}_2\text{-UCl}_3$ mixture could be used, for example, to extract bred plutonium from a metallic uranium blanket of a fast breeder reactor. Further work would be required, however, to find a satisfactory crucible material.

b. Distribution Coefficient Measurements

To devise process steps for the separation of uranium and plutonium from fission products, extensive data are needed on the distribution coefficients of the individual fuel constituents between liquid metal and molten salt solutions in contact with each other. For process calculations, it is convenient to define the distribution coefficient, K_d , of an element, M, on a weight basis:²²

$$K_d = \frac{w/o \text{ M in salt solution}}{w/o \text{ M in metal solution}} \quad (4)$$

The distribution coefficient involves the following equilibrium reaction:

Since the extent of reaction depends primarily upon the free energies of formation of the reactants and products, the distribution coefficients generally fall in the order of the electrochemical potentials of the chlorides involved. Among the major fission products, praseodymium is immediately above plutonium in the electrochemical series, and zirconium is immediately below uranium. Therefore, these two elements represent the most difficult fission product separations from uranium and plutonium and are of particular interest.

A conceptual process using cadmium-magnesium alloy as the metal phase and 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl as the salt was presented earlier (ANL-7020, pp. 39-40). Distribution coefficients at 600°C for uranium, plutonium, praseodymium, and zirconium in this salt-metal combination are shown in Fig. I-11 as a function of magnesium concentration in the metal phase. The differences in the distribution coefficients are sufficiently large that a good separation of fission product elements from uranium and plutonium can be effected by the use of multi-stage extraction equipment, such as a packed column. However, the maximum solubility for uranium in cadmium-magnesium alloys (about 1 w/o in Cd-3 w/o Mg at 600°C) is rather low, with the result that large volumes of liquid metal solution would be required for a process in which the uranium would all be in solution.

²²For theoretical purposes, the distribution coefficient is more conveniently defined as $D = \frac{m/o \text{ MCl}_x \text{ in salt solution}}{a/o \text{ M in metal solution}}$.

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Fig. I-11. Distribution of Praseodymium, Plutonium, Uranium, and Zirconium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Cadmium-Magnesium Alloy at 600°C

To reduce the required salt-metal operating ratio, it would be desirable to increase the distribution coefficients. The results in Table I-5 indicate that substitution of bromides for chlorides as the salt phase increases the distribution coefficients at 600°C. Thus a more practical salt-metal ratio is possible with this system; however, the resulting separation factor is somewhat decreased.

In two additional series of measurements, distribution coefficients of cerium, plutonium, and uranium between liquid MgCl_2 and solutions of zinc-magnesium and copper-magnesium alloys at 800°C were obtained (Fig. I-12). These data are of particular interest in salt transport processes, which are discussed in a preceding section. In general, the distribution coefficients are higher in the copper-magnesium system than in the zinc-magnesium system. Thus Cu-Mg is a good "source" or "donor" solvent and Zn-Mg is a good "sink" or "acceptor" solvent.

TABLE I-5. Distribution Coefficients and Separation Factors of Praseodymium, Plutonium, and Uranium between Chloride and Bromide Salt Mixtures and Cadmium-10 w/o Magnesium Alloy at 600°C

Element	Distribution Coefficient, K_d		$\frac{K_d \text{ (bromide)}}{K_d \text{ (chloride)}}$
	$\text{MgCl}_2\text{-NaCl-KCl}^a$	$\text{MgBr}_2\text{-NaBr-KBr}^a$	
Praseodymium	1.35	2.05	1.5
Plutonium	0.065	0.15	2.3
Uranium	0.0105	0.035	3.3

	Separation Factors	
	$\text{MgCl}_2\text{-NaCl-KCl}$	$\text{MgBr}_2\text{-NaBr-KBr}$
Pr from U	128.5	58.6
Pu from U	6.2	4.3

^a Atomic ratio of $\text{Mg}^{2+}:\text{Na}^+:\text{K}^+ = 0.5:0.3:0.2$.

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Fig. 1-12

Distribution of Cerium, Plutonium, and Uranium between MgCl_2 and Zinc-Magnesium Alloy and between MgCl_2 and Copper-Magnesium Alloy. Temperature: 800°C .

has potential application in several flowsheets, particularly for the separation of rare earths from plutonium.

Several preliminary extraction experiments were performed to evaluate the extraction kinetics between liquid metal-liquid salt phases in a packed column. The transient mass transfer of cerium and uranium from cadmium solutions to MgCl_2 -30 m/o NaCl -20 m/o KCl was investigated in small columns. Two different columns were employed, a 7/8-in. ID quartz tube with a 6-in. packed section and a 1.4-in. ID stainless steel pipe with a $12\frac{1}{2}$ -in. packed section. Both columns contained 1/4-in. OD by 1/4-in. lengths of tantalum tubing as packing. To make a run, a column was filled with molten salt to a level above the packed section, and the

A particularly interesting characteristic of the copper-magnesium system is the large difference in the distribution coefficients of cerium and plutonium at low magnesium concentrations in the metal phase. Because of this, a single-stage extraction may be adequate for the separation of rare earth fission products from plutonium.

D. Supporting Engineering Studies

Procedures and equipment for continuous and batch pyrochemical processes are being tested. The studies are directed to the fuel processing requirements of large power reactors and hence must provide for high processing rates and recovery of both plutonium and uranium from ceramic and metallic fuels. Because the advanced flowsheets are not clearly defined at this time, the objective of the engineering program is to develop equipment which is generally applicable to pyrochemical processes.

1. Countercurrent Liquid Metal-Liquid Salt Extraction Studies

One initial objective of the engineering program is the demonstration of countercurrent, liquid-liquid extraction between a liquid metal and a liquid chloride salt. This unit operation

metal alloy (e.g., Cd-11 w/o Zn-5 w/o Mg-1 w/o Ce) was allowed to flow through the column of salt. A run was terminated by quenching the column in a bath of low-melting metal at 100°C to freeze the contents and minimize further transfer of solute across the metal-salt interface at the tube bottom.

For the experiments with the quartz column, a relatively large flow of metal was employed. The metal-to-salt ratio was large so that little change in uranium concentration occurred in the metal phase during a run. In the steel column, the metal was introduced slowly and a relatively smaller amount was employed so that the concentration change in the salt phase was slight during a run.

The results of five runs in the quartz column, three with uranium and two with cerium as the transferring solute, indicate an equilibrium stage height of about 22 in. The results of two cerium runs in the steel column indicate an equilibrium stage height of about 10 in. The transient tests successfully fulfilled the objectives for which they were intended of indicating the order of magnitude of the transfer rates and of demonstrating the feasibility of countercurrent extractions in salt-metal systems.

Apparatus was then assembled for a countercurrent extraction experiment in which salt would flow upward through a packed column countercurrent to a falling metal phase. Sufficient capacity of both phases was provided to permit operation of the column for a long enough time to reach virtual steady state conditions. The column used in the first experiment was a 1.4-in. ID stainless steel pipe and contained a 36-in. packed section of 1/4-in. mild steel Raschig rings. The extraction of cerium from Cd-11 w/o Zn-5 w/o Mg-1 w/o Ce into MgCl_2 -30 m/o NaCl-20 m/o KCl was studied. Analysis of the results shows a height equivalent to a theoretical stage of 15 in., which is in excellent agreement with the transient experiments and with results obtained at Brookhaven National Laboratory for a bismuth-salt system.²³

Entrainment of metal with the effluent salt proved a problem in the operation of the column. Therefore, a new column has been designed with provisions to eliminate the metal entrainment. The countercurrent extraction experiments will be resumed after the new column has been constructed.

2. Purification of Chloride Salts

Advanced fuel recovery processes will require the use of relatively large quantities of purified chloride salts. Untreated salts containing MgCl_2 are extremely corrosive to all steels, contain large quantities of insolubles, and contain substances such as water that react with UCl_3 to form

²³Hill, F. B., and Kukacka, L. E., Axial Mixing and Mass Transfer in Fused Salt-Liquid Metal Extraction Columns, BNL-791, January 1963.

UO_2Cl_2 and UO_2 . An engineering-scale study is underway to develop a practical method for purifying the chloride salts used in these processes. The objectives of the study are (1) elimination of oxidizing substances which would attack structural materials, (2) removal of insoluble material that might interfere with the flow of fluids through equipment, and (3) removal of any substance that would form precipitates with uranium, plutonium, or rare earths.

Equipment has been assembled to purify large batches (up to 80 kg per batch) of impure MgCl_2 -base salts for use in engineering-scale experiments. Oxidizing constituents of the salt are reduced by contacting the molten salt with cadmium-30 w/o magnesium alloy at 600°C . Insoluble materials are then removed by settling and by passing the supernatant salt at 600°C through a stainless steel filter having $20\text{-}\mu$ pores into a receiver tank. Earlier small-scale experiments showed this method of treatment to be effective in producing a salt that is noncorrosive toward stainless steels and that contains small amounts of oxygen and insolubles. Five batches of 20 to 40 kg each (a total of 130 kg of usable salt) have been prepared. The equipment operated satisfactorily and, based on preliminary analyses, the product salt appeared to be of good quality. The residual oxygen content of the purified salt was in the range of 200 to 2000 ppm. The oxygen is thought to be present as magnesium oxide in finely divided form. The magnesium oxide, an insoluble, inert material, causes no difficulty in engineering experiments.

3. Materials Testing

A materials testing program is being conducted in support of the engineering development of pyrochemical processes. The object of this work is the selection of materials of construction for process applications. Emphasis is being placed on the choice of relatively inexpensive and readily available materials of construction whenever possible. Metal alloys, ceramics, and graphites are being tested under simulated process conditions to obtain corrosion rates and other information, such as the porosity of ceramics and graphites to process solutions and the most suitable method of manufacture of equipment items. Most testing is done in systems of zinc, copper, magnesium, and cadmium in contact with magnesium chloride-base salts. At the present time these solvents show the most promise for potential process use.

a. Tungsten Crucibles

The pressed-and-sintered tungsten crucibles used in the demonstrations of the skull reclamation process have continued to perform well under process conditions (see ANL-7020, p. 18). These crucibles are considered very reliable and entirely satisfactory for use in pyrochemical processes. No failure of any of these crucibles has occurred in the past year. However, such crucibles are fairly expensive, and because of the

thick walls required in their manufacture, are heavy and unwieldy. Alternative methods of fabrication, which may result in lighter or less expensive crucibles, are being investigated. Such manufacturing techniques as shear-forming, plasma-spraying, and vapor deposition have been investigated during the past year. Crucibles fabricated by plasma-spraying and shear-forming have been obtained commercially for testing.

A small plasma-sprayed tungsten crucible (4-in. OD by 6-in. high by $1/4$ -in. wall) was fabricated by spraying tungsten on a sacrificial mandrel, and the crucible was sintered in hydrogen at 2500°C for 1 hr. Failure of this crucible occurred after it had been used to contain zinc, zinc-magnesium, and cadmium-magnesium-zinc systems at temperatures between 600 and 850°C for a total exposure time of about 1000 hr. Failure was most probably caused by physical or thermal shock acting upon residual stresses left in the crucible after fabrication. The plasma-spraying technique of crucible fabrication is considered attractive since the size limitations imposed by most of the other methods of fabrication are not present. Plasma-spraying of tungsten coatings on suitable substrate materials is also feasible, and could produce a lighter, less expensive crucible.

A shear-formed tungsten crucible (18-in. high by 11-in. OD by 0.18-in. thick wall) was successfully fabricated by Metallwerk Plansee of Austria. A photograph of this crucible, one of the largest shear-formed crucibles ever produced, is shown in Fig. I-13 (left). The completed

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✓ Fig. I-13. Shear-formed Tungsten Crucible and Internal Baffle Assembly. Crucible Dimensions: 11.1-in. OD by 18.1-in. high by 0.18-in. wall thickness.

crucible is equipped with three full-length tungsten mixing baffles that are 1 in. wide and extend 1.2 in. into the crucible (see Fig. I-13, right). This crucible was first thermal cycled in an argon atmosphere for 15 cycles between 600 and 800°C with no noticeable deterioration. Now in service, its appearance is unchanged after having been used for 100 hr to contain zinc-magnesium-uranium/salt and copper-magnesium-uranium/salt systems. The shear-forming fabrication method is considered feasible for tungsten crucible fabrication, but the ultimate size of a crucible fabricated by this technique is limited by the availability of large tungsten starting blanks.

b. Testing of Tungsten Containing 0.1 w/o Nickel in Zinc/Chloride Salt System

A sample of pressed and sintered tungsten containing 0.1 w/o nickel was tested in a zinc/chloride salt system. At this concentration of nickel in tungsten, a solid solution is reported to be formed during sintering and results in a higher density product than is obtainable with pure tungsten. The sample was exposed as an agitator blade to a zinc/MgCl₂-30 m/o NaCl-20 m/o KCl system at 800°C for 200 hr. The quantity of the metal phase (~2 kg) was sufficient to allow for dissolution of all nickel contained in the agitator blade without saturating the solution with nickel.

The results obtained in this test were very encouraging. Metallographic examination of the agitator blade after exposure indicated no evidence of deterioration of the blade except for a slight surface roughening that measured about 0.1 mil deep. It is concluded that the small addition of nickel to the tungsten, potentially useful in producing denser tungsten crucibles, has little effect on the corrosion resistance properties of tungsten in the zinc/salt system.

c. Corrosion of Iron-Chromium Alloys by Liquid Cadmium Alloy/Salt Systems

One of the processes currently under development for advanced reactor fuels utilizes cadmium containing smaller amounts of zinc and magnesium as a solvent metal and a solution of MgCl₂-NaCl-KCl as a solvent salt. Results of previous tests (see ANL-7020, pp. 54-56) showed that Type 405 stainless steel possesses adequate corrosion resistance to this system. Because of success in the use of this chromium steel as a containment medium for this system, other, similar chromium steels that are more readily available or are better suited for welding than Type 405 are being tested.

Three alloys, Type 430 stainless steel, Type 1-JR steel (Type 410 stainless steel with 3% aluminum added), and Type 329 stainless steel, have been tested for corrosion resistance to an 81 w/o Cd-11 w/o Zn-6 w/o Mg-2 w/o U/chloride salt²⁴ system at 650°C. The zinc concentration

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

chosen is about the highest that can be tolerated in steel equipment and was employed to magnify differences in corrosion resistances. In short (24-hr) screening tests, Type 430 stainless steel appeared the most corrosion resistant of the three, with a maximum observed attack in the vapor phase to a depth of 0.5 mil. Type 430 stainless steel was then retested under similar conditions for a period of 400 hr. In this test the observed corrosion depths of the stainless steel were 4.5 mils in the metal phase, 2.5 mils in the salt phase, and less than 0.2 mil in the vapor phase. Inspection of the samples indicated that the primary mode of corrosion was probably surface dissolution or reactions resulting in nonadherent reaction products.

Although these corrosion rates are fairly high, steels offer considerable promise of being satisfactory for containment of less corrosive cadmium-magnesium-zinc alloys, i.e., those containing less zinc (the most corrosive constituent) and more magnesium (the least corrosive constituent).

d. Corrosion of Ferrous Alloys by Copper-Magnesium/Salt Systems

A program is also in progress to determine the corrosion resistance of ferrous alloys to copper-magnesium/chloride salt systems. In initial screening tests, four alloys, mild steel (AISI Type 1020), 1% Cr alloy steel (AISI Type 4130), Type 304 stainless steel, and Type 405 stainless steel, were tested at 600 and 800°C for 200 hr in 50 to 90 w/o Cu-Mg/MgCl₂-30 m/o NaCl-20 m/o KCl systems.

At 600°C the corrosion observed after 200 hr was minor, being 0.1 mil or less for all samples except the Type 4130 steel exposed to a 90 w/o copper-10 w/o magnesium/chloride salt system. The Type 4130 steel was corroded to a depth of 0.7 mil. An increase in temperature from 600 to 800°C significantly increased the corrosion rates of all these steel alloys. The corrosion observed at 800°C varied from less than 0.1 mil in 200 hr for Types 304 and 405 stainless steel in a 50 w/o Cu-50 w/o Mg system to about 1.5 mils for the same alloys in a 90 w/o Cu-10 w/o Mg system. The corrosion of the 4130 and 1020 steels changed from about 1.0 mil at the lower copper concentration to 1.7 and 0.8 mils, respectively, in the 90 w/o Cu-10 w/o Mg system. In nearly all instances the mode of attack appeared to be uniform surface removal in the molten metal-salt mixture, indicating a possible dissolution mechanism. The results are considered sufficiently promising to warrant more testing of these and similar alloys in order to obtain more accurate estimates of the corrosion rates that would be experienced in process applications.

e. Testing of Vitreous Carbon with Zn-Mg-U/Salt and Cu-Mg-U/Salt Systems

A new crucible material, vitreous carbon, is being tested for containment of zinc-magnesium-uranium/salt and copper-magnesium-uranium/salt systems. Vitreous carbon has characteristics similar to

glass, i.e., it is fragile, microscopically sealed, and impervious to gases. It possesses good resistance to thermal shock because of its good thermal conductivity. The material is obtained by carbonizing and heat treating organic materials having strong transverse molecular bonds to produce a coke having crystalline disorder and submicroscopic pores. Its maximum wall thickness is limited to about 0.1 inch. This material should be very useful for laboratory-scale applications and possibly for engineering-scale equipment if adequate support is provided.

In a preliminary test, a small ($1\frac{5}{8}$ -in. dia. by 1-in. high by 0.1-in. thick wall) vitreous carbon crucible material was not wet by a Zn-5 w/o Mg-10 w/o U/MgCl₂-30 m/o NaCl-20 m/o KCl solution after 24-hr exposure at 800°C. This material has now been exposed to zinc-magnesium-uranium/salt systems at 800°C for times up to 655 hr in approximately 200-hr increments.²⁵ None of the contact surface was wetted by a zinc-2 w/o uranium/salt system after 208 hr of exposure at 800°C, 10% appeared to be wetted after 209 additional hr (total of 417), and 50% after 238 additional hr (total of 655), but in none of these cases did the solidified content stick to the crucible. No wetting of the vitreous carbon occurred after 321 hr of exposure to a copper-10 w/o magnesium-2 w/o uranium system at 800°C. It is concluded that vitreous carbon has excellent potential as a container material for these systems.

4. Component Testing

A number of components, such as valves, pumps, flow meters, liquid level detectors, and pressure measuring devices, are required for liquid metal and liquid salt systems. The program for developing components is largely one of adapting the techniques and equipment developed elsewhere. A new test loop is being installed for the testing of such equipment. The loop is constructed of Type 304 stainless steel with welded joints. Provisions have been made to relieve expansion and contraction stresses in the loop during heating and cooling. The loop is intended for tests in which long-term circulation of salt is needed.

A pump, a bellows-sealed valve, a freeze valve, two types of pressure sensors, and an orifice flow meter have been installed in the new loop for an evaluation of their performance. The pump, a centrifugal sump type, was obtained from Oak Ridge National Laboratory where it had been used in the Molten Salt Reactor program. The bellows-sealed valve is similar to ones that are commercially available and which have given satisfactory service both in liquid metal and in liquid salt systems. Long-term testing of this valve is planned.

²⁵In the first 208 hr of exposure, the salt was MgCl₂-47 $\frac{1}{2}$ m/o CaCl₂-5 m/o MgF₂; in the remaining 447 hr of exposure, the salt was MgCl₂-30 m/o NaCl-20 m/o KCl.

Eddy-current liquid level probes of the design discussed in a previous report (ANL-7020, pp. 57-62) are proving to be useful and reliable for the measurement of liquid metal levels. Such a probe has been mounted in a feed vessel and used to determine flow rates in extraction experiments. An eddy-current detector is also employed in the new loop to detect the position of a float in a null-point pressure instrument.

Two major problems in the handling of liquid salts are: (1) extreme stresses on equipment as a result of freezing and remelting and (2) severe corrosion which can result if the salt becomes contaminated with oxygen or water vapor. Techniques and designs are being evolved to avoid the freezing of salts in the equipment and to make equipment less subject to stressing during the remelting of salts.

II. VOLATILITY AND FLUIDIZATION PROCESSES

The objective of the fluoride volatility program is to develop the technical data required for the design of an all-volatility commercial reprocessing plant for power reactor fuels. To achieve this aim, the program is directed toward the development of a fluid-bed volatility process applicable to a wide variety of fuels. Acceleration of activity in the fluoride volatility program has been prompted by the plan to construct a hot engineering-scale pilot plant at Oak Ridge National Laboratory. Argonne has the major responsibility of providing the data necessary for the establishment of the process flowsheet and the data necessary for the design of much of the equipment to be used in the facility.

The high level of interest in the fluoride volatility program is exemplified by public announcements made from industrial concerns of plans to employ fluoride volatility procedures in the reprocessing of reactor fuel materials. Currently, the industrial plans are for processes that combine aqueous separation methods with fluoride volatility techniques. The process concepts employ technology that has been fairly well proven. For example, separation of plutonium from uranium and fission products can be accomplished by conventional aqueous processing methods; final recovery and purification of uranium can then be effected in subsequent steps which involve calcination, fluorination of the uranium to UF_6 , and distillation-purification of the UF_6 product. Other processing schemes which combine aqueous and volatility separation methods are also under consideration. Most of the volatility technology for these process concepts was developed at Argonne and other AEC National Laboratories in earlier work. These combination schemes do not require the volatilization of plutonium; however, they retain some of the disadvantages of aqueous processes.

The current AEC program at Argonne and other laboratories is aimed toward the development of a more advanced process in which both uranium and plutonium are treated by volatility methods and no aqueous steps are required. Major attention in the development program is being directed toward the demonstration of the fluoride volatility process with low-enrichment UO_2 - PuO_2 fuel clad in Zircaloy. Two alternative process flowsheets for this type of fuel are being considered. In the first process (described in ANL-7020, pp. 100-101), the declad oxide fuel is reacted with oxygen and fluorine to form UF_6 and PuF_6 which are subsequently separated from each other and from associated volatile fission product fluorides. Major emphasis in the development program has been placed on demonstration of this flowsheet.

In the second process (interhalogen flowsheet, see Fig. II-1), the separation of uranium and plutonium is accomplished by selective fluorination

of uranium by bromine pentafluoride. The process involves two major steps. In the first step, the uranium in the de-clad fuel is oxidized to U_3O_8 by an oxygen-nitrogen mixture, and the U_3O_8 is fluorinated with BrF_5 gas to UF_6 . The UF_6 is volatilized from the vessel and collected in a condenser together with the excess BrF_5 and the reaction product BrF_3 . During the fluorination, plutonium reacts to form nonvolatile PuF_4 which remains in the primary reactor. The UF_6 is separated from the interhalogens and volatile fission product fluorides by fractional distillation. The BrF_3 in the bromine fluoride mixture is refluorinated to BrF_5 and the BrF_5 is recycled. In the second step, plutonium is recovered as PuF_6 by fluorination of the PuF_4 with fluorine gas. The volatile PuF_6 is collected in separate cold traps and then revaporized and passed into a heated vessel where it is thermally decomposed to a nonvolatile PuF_4 product.

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Fig. II-1. Fluid-bed Volatility Process Interhalogen Reference Flowsheet

It is intended that the processing schemes under development for low-enrichment fuels will also be capable, with minor modifications, of accommodating high enrichment uranium-235 fuels. Thus high enrichment fuels might be utilized as a feed to supplement the low enrichment fuels during the initial years of operation of a reprocessing plant. Development work on a fluid-bed volatility process for high-enrichment fuels was completed and reported in previous reports of the Chemical Engineering Division.

A. Laboratory Investigations

1. Oxidation and Fluorination of Simulated UO_2 - PuO_2 Fuels in Fluid Beds

Development studies are being conducted using a 2-in. dia. fluid-bed reactor to determine optimum fluorination conditions for simulated uranium dioxide power reactor fuel pellets. It is desired that a minimum of the uranium and plutonium be retained by the fluidized alumina bed. Currently, two fluorination agents are being considered: fluorine and bromine pentafluoride (BrF_5).

Fluorination with fluorine is carried out as part of a two-zone oxidation-fluorination process.¹ In this process, pulverization of the pellets and fluorination of the resulting fines are carried out simultaneously; a packed bed of pellets in the lower zone of the reactor is reacted with oxygen to form U_3O_8 fines which react with fluorine in the upper fluid-bed zone of the reactor. During the fluorination more than 99% of the uranium and about 75% of the plutonium are removed from the alumina bed as volatile hexafluoride products. The remainder of the plutonium and uranium is recovered in a subsequent step by recycle-fluorination with 90 v/o fluorine.

In the alternative fluorination process, the UO_2 - PuO_2 pellets are first pulverized to U_3O_8 - PuO_2 powder by reaction with oxygen. The powdered material is then reacted with BrF_5 , producing volatile UF_6 and nonvolatile PuF_4 . Plutonium is recovered as PuF_6 in a separate step by high temperature reaction with elemental fluorine. Work with the 2-in. dia. fluid-bed reactor is being directed mainly toward finding the recycle-fluorination conditions required for effective plutonium removal from alumina.

Mixtures of hydrogen fluoride and oxygen are of interest for the chemical decladding of fuel clad with stainless steel (ANL-7020, pp. 123-127) and for the pulverization of beds of fuel pellets. During the HF-O_2 decladding operation, both the cladding and the fuel pellets are disintegrated and dispersed throughout the alumina bed material; reaction of the pellets with the gas mixture results in the formation of UO_2F_2 , UF_4 , PuF_4 and fission product (F.P.) fluorides or oxides. Experiments with UO_2 pellets were performed to establish suitable reaction conditions for pulverization of the pellets with HF-O_2 mixtures and fluorination of the resulting fines with fluorine, such that recycle-fluorination could then be satisfactorily performed.

¹Anastasia L. J., and Mecham, W. J., Oxidation-Fluorination of Uranium Dioxide Pellets in a Fluidized Bed, Ind. Eng. Chem., Process Design Develop. 4(3), 338-344 (July 1965).

a. Equipment and Procedure

The major components in the experimental system (Fig. II-2) are the following: 2-in. dia. fluidized-bed reactor, hexafluoride collection system, thermal conductivity cell for continuous fluorine analysis, fluorine disposal system, hydrogen fluoride-bromine pentafluoride disposal system, and remote-head diaphragm pump. These components are contained in an alpha glovebox. A photograph of the fluidized-bed reactor is shown in Fig. II-3.

In most tests, approximately 650 g of 0.5-in. dia. by 0.5-in. thick UO_2 pellets (or a charge of UO_2 - PuO_2 pellets containing 2.8 g plutonium) were added to the reactor to form a packed bed 2 in. deep. The pellet bed was supported by a bed of 1/4-in. dia. nickel balls. Approximately 1100 g of inert alumina particles, -40+170 mesh, were added to the reactor to form a fluid bed 12 in. deep above the pellet bed.

During the pulverization of UO_2 - PuO_2 pellets by HF-oxygen mixtures, hydrogen fluoride is disposed of in a series of two soda lime traps, a water vapor condenser and an activated alumina trap. The hexafluoride products are collected in a series of cold traps and sodium fluoride traps (Fig. II-2). Fluorine concentrations in the range 5 to 20 v/o are used for fluorination when significant quantities of uranium are present in the reactor. A thermal conductivity cell is used during these periods to measure fluorine utilization by continuous fluorine analysis of effluent gas

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Fig. II-2. Schematic Diagram of Two-inch Diameter Fluidized-bed Reactor System

108-8144 A

Fig. II-3. Two-inch diameter Fluidized-bed Reactor

from the hexafluoride collection traps. Three activated alumina traps are used for disposal of excess fluorine. The thermal conductivity cell is not used when fluorination is carried out with a high concentration of fluorine (e.g., 90 v/o). In these periods, called recycle-fluorination periods, consumption of fluorine by reaction is small and the reactor effluent gases are recycled with the remote-head diaphragm pump to conserve the fluorine reagent.

During fluorination of oxide fuel material with BrF_5 , the unreacted BrF_5 , bromine fluoride reaction products, and the UF_6 product

are disposed of by reaction with soda lime. Collection of the UF_6 product in refrigerated traps would be impractical in an operation of this scale, since both BrF_5 and BrF_3 would also condense with the UF_6 .

During fluorination, samples of the fluidized alumina bed were taken through the bed sampler (see Fig. II-2) to determine the course of uranium and plutonium volatilization from the reactor. The sampler consists of a 1/4-in. OD tube which extends into the reactor such that the sampling point is 7 in. above the top of the bed support of nickel balls. In a typical sampling procedure, two bed samples are taken; the initial sample is taken to prevent cross-contamination from previous samples and is discarded, while the second sample is utilized for chemical analysis.

b. Reaction of UO_2 Pellets with HF-O_2 Mixtures

Several experiments were carried out to determine suitable reaction conditions for pulverization of the UO_2 pellets with HF-O_2 mixtures and for fluorination of the resulting fines with fluorine, such that the recycle-fluorination step, required in the processing of plutonium-containing pellets, could then be satisfactorily performed. Two-inch deep fluidized-packed beds (~660 g) of high-density UO_2 pellets were reacted with various HF-O_2 mixtures for 3 hr at temperatures from 400 to 550°C. After pulverization of the pellets, the uranium fines represented 40 w/o of the total fluidized bed material. The experimental conditions and the results are summarized in Table II-1.

Caking of the pellet bed was encountered in runs which used approximately 40 v/o HF in oxygen (runs 2, 5, and 7) at 400 or 550°C. In one case, run 5, the caking condition was successfully removed by continuing the exposure to the HF-O_2 mixture. In runs 1 and 9 the hydrogen fluoride concentration exceeded that of oxygen, and UF_4 formed on the pellet surfaces, inhibiting further reaction at both 400 and 550°C. (Visual examination of the pellets showed a thin layer of green material which covered the surface of the pellets; this material was believed to be uranium tetrafluoride.) Satisfactory conversion of the pellets to fine powder was demonstrated at 550°C in runs 3 and 4, for which the pellets were stacked vertically in open baskets, simulating the orientation of the pellets in the reactor during a de-cladding operation. Satisfactory reaction of the pellet bed was also obtained with 20 v/o HF-30 v/o O_2 in nitrogen at 450°C, as demonstrated in run 11.

The complete processing cycle, including 20 hr of recycle-fluorination at 450 to 550°C, was demonstrated in run 5; uranium removal from the alumina bed was greater than 99.95%. The operating procedure developed for fluorination of a fluidized bed containing 40 w/o uranium fines resulting from pulverization of pellets with HF-O_2 is outlined in Table II-2. This procedure was used for run 11. In this run, only the first 5 hr of recycle-fluorination were carried out since the entire scheme was adequately demonstrated in run 5.

TABLE II-1. Oxidation-Fluorination of UO_2 Pellets with HF-O_2 Mixtures

UO_2 pellets:	0.5-in. dia. by 0.5-in. right cylinders
Pellet bed depth:	2 in. (~660 g)
Bed support:	Nickel balls
Alumina fluid bed:	High-fired alumina
$\text{UO}_2/\text{Al}_2\text{O}_3$:	0.6 g/g
Superficial gas velocity in fluid bed at operating conditions:	0.7 to 1.0 ft/sec
Duration:	3 hr
Reactant gas diluent:	Nitrogen

Run	Temp. (°C)	Reactant Concentration to Pellet Bed		Comments
		HF (v/o)	O_2 (v/o)	
1	550	47	12	No reaction
2 ^a	550	42	58	Cake after 0.5-hr reaction
3	550	33	60	{ Pellets contained in basket-- satisfactory reaction
4	550	46	46	
5	400	40	60	Satisfactory reaction--partial cake during run
7 ^b	400	42	58	Cake after 2.4 hr of reaction
9	400	21	10	No reaction
10	400	19	28	Approximately 50% reaction
11	450	19	29	Satisfactory reaction

^aSuperficial gas velocity in the fluid bed at operating conditions was 1.4 to 1.7 ft/sec.

^bRun duration was 3.5 hr.

TABLE II-2. Conditions^a for Fluorination of Uranium Fines

UO_2 weight:	660 g
Alumina fluid bed:	1100 g
Temperature:	450°C

Uranium fines produced by reacting UO_2 pellets with a HF-O_2 mixture
(see Table II-1)

Cumulative Process Time (hr)	Fluorine		Gas Flow
	(v/o)	Inlet Location	
3.0- 4.0	10	Lower side ^b	Once-through
4.0- 4.5	3	Bottom	Once-through
4.5- 5.0	8	Bottom	Once-through
5.0- 6.0	15	Bottom	Once-through
6.0-11.0	80-95	Bottom	Recycle

^aFor other operating conditions, see Table II-1.

^bLower side inlet is 3 in. above the bed support of nickel balls.

c. Reaction of UO_2 - PuO_2 -Fission Product Pellets in Two-zone Oxidation-Fluorination Cycle and Bromine Pentafluoride-Fluorine Cycle

A series of tests was performed to establish processing conditions which result in high plutonium recoveries for both the two-zone oxidation-fluorination (O_2 - F_2) cycle and the bromine pentafluoride-fluorine (BrF_5 - F_2) cycle. The feed material for these tests was UO_2 - PuO_2 -fission product pellets, 0.5-in. dia. by 0.5-in. thick cylinders, which contained, nominally, 0.4 w/o plutonium, 86 w/o uranium, and 1 w/o fission products (F.P.) as oxides. The pellets, which simulated typical commercial nuclear fuels after discharge from power reactors, contained a mixture of 19 non-radioactive fission product oxides: Ag_2O , BaO , CdO , Ce_2O_3 , Eu_2O_3 , Gd_2O_3 , In_2O_3 , La_2O_3 , MoO_3 , Nb_2O_5 , Nd_2O_3 , PdO , Pr_6O_{11} , RhO_2 , RuO_2 , Sm_2O_3 , SrO , Y_2O_3 , ZrO_2 . Two types of pellets were used. Type I pellets were made from solid solution UO_2 - PuO_2 powder mixed with fission product oxides and sintered for 2 hr at 1600°C in nitrogen-6 v/o hydrogen to 92 to 94% theoretical density. Type II pellets were made from UO_2 and PuO_2 powders mixed with fission product oxides and sintered for 6 to 8 hr at 1700°C in nitrogen-6 v/o hydrogen to 86 to 88% theoretical density. Two-inch deep fluidized-packed beds of UO_2 - PuO_2 -F.P. pellets (650 g) were used in most experiments. The fluidized bed consisted of 1100 g of high-fired alumina (40 to 170 mesh) with a static bed depth of 12 in.

(1) Two-zone Oxidation-Fluorination Cycle

Two-zone oxidation-fluorination of the UO_2 - PuO_2 -F.P. pellets at 450°C , using 20 v/o oxygen in the lower zone and 10 v/o fluorine in the upper zone, proceeded smoothly in all runs. A higher concentration of oxygen (20 v/o) was required than in preliminary runs with pure UO_2 pellets (<10 v/o) to give equivalent reaction rates. The lower oxidation rates were attributed to the presence of fission products and plutonium dioxide in the pellets; similar effects have been observed by Schmets et al.² Approximately 80 to 90% of the pellet bed was reacted in 3 hr of two-zone oxidation-fluorination under these conditions. The remainder of the pellet bed was reacted by a single-zone fluorination procedure in which approximately 10 v/o fluorine in nitrogen was passed into the bottom of the reactor for about one hour.

Plutonium Removal during Recycle-fluorination. In six runs using Type I pellets, the effects of overall recycle-fluorination times

²Schmets, J., et al., Reprocessing of Nuclear Fuels by Volatilization, presented at the Third United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1964, Paper A/Conf. 28/P/771.

of 12 to 20 hr were investigated. In runs using a total recycle-fluorination time of 20 hr, the final uranium and plutonium concentrations in the fluidized beds of alumina were 0.004 and 0.007 w/o, respectively. These results are in good agreement with results of previous studies (ANL-6875, pp. 98-107). In each run, uranium removal from the alumina bed was >99.99% complete, while plutonium removal was 97% complete, for a single use of the alumina bed. The effective plutonium removal can be increased by the reuse of the alumina bed to process several batches of spent fuel (ANL-7020, pp. 103-105).

The course of uranium and plutonium removal from the alumina bed was determined from analyses of bed samples taken during the recycle-fluorination periods. The results indicated that the highest rates of plutonium removal occurred during the first few hours of recycle-fluorination at a given temperature and that the overall recycle-fluorination time could be reduced without adversely affecting the final plutonium retention on the alumina. Uranium and plutonium concentrations in the fluidized alumina bed are shown in Fig. II-4 for a 20-hr recycle-fluorination period and in Fig. II-5 for a 12-hr recycle-fluorination period. With a total recycle-fluorination time of 12 hr, consisting of 1 hr at 450°C, 3 hr at 500°C, and 8 hr at 550°C, the removal of uranium and plutonium was identical to that obtained with the longer recycle-fluorination periods.

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Fig. II-4. Uranium and Plutonium Concentrations in Fluidized Alumina Bed during 20-hr Recycle-fluorination

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Fig. II-5. Uranium and Plutonium Concentrations in Fluidized Alumina Bed during 12-hr Recycle-fluorination

Effect of Cesium Fluoride Addition and Use of Type II Pellets on Retention of Uranium and Plutonium on Alumina Beds. With the completion of the runs described above, the supply of Type I pellets was exhausted and subsequent runs were made using Type II pellets. Since cesium oxide is lost by volatilization during the pellet sintering step, cesium was not present in either Type I or Type II pellets. However, to simulate more closely the conditions which would exist in the reprocessing of irradiated fuel, cesium fluoride (CsF) was added to the alumina beds in most runs with Type II pellets.

Three runs were made to determine the reproducibility of the data obtained in these fluidized bed experiments using Type II pellets. In these runs, 2-in. deep fluidized-packed beds of pellets, with no cesium fluoride added to the alumina bed, were reacted in a sequence similar to that used previously. The results of these tests are compared in Table II-3 with an equivalent experiment using Type I pellets. The results of the replicate experiments indicate that adequate reproducibility can be achieved in these types of tests. It appears that differences between Type I and II pellets do not have a significant effect on plutonium retention in the alumina bed.

TABLE II-3. Effect of Cesium Fluoride Addition and Type of Fuel Pellets on Final Uranium and Plutonium Concentrations in Alumina Beds

Charge:

UO ₂ -PuO ₂ -F.P. pellets:	650 g
Alumina:	1100 g

Reaction Sequence:

Simultaneous oxidation-fluorination:	3.0 hr
Single-zone fluorination:	1.0-2.0 hr
Recycle-fluorination:	450°C, 1.0 hr
	500°C, 3.0-4.0 hr
	550°C, 8.0 hr

Pellets (Type)	CsF Addition	Final Alumina Bed	
		U (w/o)	Pu (w/o)
II	No	0.010	0.010
II	No	0.006	0.006
II	No	0.004	0.008
I	No	0.004	0.007
II	Yes	0.024	0.014

} Replicate
Experiments

Several runs were performed to evaluate the effect of the addition of cesium fluoride to the system on the removal of plutonium. In these runs, a 2-in. deep fluidized-packed bed of Type II pellets was reacted in a sequence involving two-zone oxidation-fluorination, single-zone fluorination at 450°C, followed by recycle-fluorination at 450, 500, and 550°C. Recycle-fluorination periods of up to 20 hr were employed. Since the residual plutonium concentrations in these runs were higher than achieved in previous runs employing two-zone simultaneous oxidation-fluorination in the absence of cesium, a new fluorination scheme was adopted in which the uranium oxide and plutonium oxide fines were first contacted with fluorine at low temperatures (300 to 400°C). This scheme was incorporated into a two-step separate oxidation-fluorination process. This process involves an initial step in which the fuel pellets are pulverized by reaction with oxygen followed by a fluorination step in which the oxide fines are converted to volatile fluorides by reaction with fluorine. Two runs were made using the two-step separate oxidation-fluorination process. In these runs, a 2-in. deep fluidized-packed bed of Type II pellets (650 g pellets, and 1100 g alumina containing 0.6 g CsF) was reacted according to the sequence: (1) pulverization of the pellets by oxidation with 20 v/o oxygen for 3 hr at 450°C, and (2) fluorination with 10 v/o fluorine for 2.5 hr at 300°C and 3 hr at 350°C, on a once-through basis, followed by recycle fluorination with 90 v/o fluorine for 3 hr at 350°C, for 6 hr while the bed temperature was increased from 350 to 550°C in increments of 5°C/9 min, and finally 3 hr at 550°C. In both runs the plutonium concentration in the final alumina beds was 0.009 w/o. These results indicate that the effect of the presence of cesium fluoride on plutonium removal becomes negligible when the initial fluorination is carried out at low temperatures.

Effect of Pellet/Alumina Ratio on Plutonium Retention.

A series of three runs was made to determine the effect of pellet/alumina charge weight ratio on plutonium volatilization from the alumina bed. In these runs, $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellet charges of 0.33, 0.65, and 1.32 kg were used with 1100 g of high-fired alumina, corresponding to pellet/alumina weight ratios of 0.3, 0.6, and 1.2, respectively. The corresponding pellet bed depths were 1, 2, and 4 in. In each run, an amount of cesium fluoride in proportion to the pellet charge was added to the alumina bed.

The processing sequence involved two-zone oxidation-fluorination and single-zone fluorination at 450°C, followed by recycle-fluorination for 1 hr at 450°C, 3 hr at 500°C, and 8 hr at 550°C. The total duration of the oxidation-fluorination and single-zone fluorination steps was 2 hr with the 1-in. bed of pellets, 4 hr with the 2-in. bed, and 6 hr with the 4-in. bed. The plutonium retention in the alumina bed did not increase proportionally with increases in the weight of the pellet charge, and the volatilization of plutonium from the alumina bed was improved by increasing the pellet/alumina weight ratio from 0.3 to 1.2.

(2) Oxidation-Fluorination: O_2 - BrF_5 - F_2 Cycle

A test was performed with a 1-in. bed of Type II pellets to demonstrate the use of BrF_5 as a selective fluorinating agent for the conversion of uranium to UF_6 . The pellets were initially pulverized with oxygen for 2 hr at 450°C in a bed to which CsF was added. The fines were then fluorinated for 3 hr at 400°C with 2 to 8 v/o BrF_5 to form volatile UF_6 and nonvolatile PuF_4 . After the reaction with BrF_5 had been completed, plutonium tetrafluoride was fluorinated to volatile PuF_6 by recycle-fluorination with 90 v/o fluorine for 1 hr at 450°C, 3 hr at 500°C, and 8 hr at 550°C. The course of uranium and plutonium removal during both fluorination steps, determined by analyses of samples from the fluidized alumina bed, is shown in Fig. II-6.

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Fig. II-6. Uranium and Plutonium Concentrations in Alumina Fluidized Bed. One-inch bed, Type II pellets, CsF added.

use of the alumina bed material. Data will be obtained to define more clearly the effects of cesium fluoride on plutonium retention. Experiments are also planned to investigate the effect of the temperature at which the BrF_5 fluorination is conducted on the extent of plutonium removal in the subsequent recycle-fluorination step.

Approximately 99% of the uranium was converted to UF_6 during the initial 1.75 hr of fluorination with BrF_5 . During the subsequent 1.25 hr of this fluorination step, the uranium concentration in the alumina bed decreased to 0.051 w/o, corresponding to conversion of 99.8% of the initial uranium to UF_6 . The concentration of both uranium and plutonium in the final alumina bed was 0.008 w/o. This compares favorably with the final concentrations of uranium and plutonium (0.010 w/o) obtained when a 1-in. bed of pellets was reacted by the O_2 - F_2 cycle. Analyses of the chemical traps used for disposal of the gaseous reagents indicated that no plutonium was volatilized during the fluorination with BrF_5 .

d. Future Work

Additional tests will be performed to optimize the conditions for the recycle-fluorination step and to investigate the re-

2. Reactions of BrF₅

A laboratory program on the reactions of uranium compounds and mixtures of uranium and plutonium compounds with BrF₅ has been started. The primary purpose of this work is to investigate the use of BrF₅ as a selective fluorinating agent for the fluid-bed fluorination of mixtures of uranium and plutonium compounds present in spent nuclear power reactor fuels. Since it is expected that BrF₅ will convert uranium compounds to volatile UF₆ while plutonium compounds are converted to nonvolatile PuF₄, this scheme should provide separation of uranium from plutonium in a single fluorinating step. A process based on the use of BrF₅ is being developed as an alternative method for reprocessing low-enrichment fuels.

A series of tests was performed to determine the optimum conditions for converting uranium compounds to UF₆ by reaction with BrF₅. These tests involved the fluorination of mixtures containing uranium compounds or mixtures of oxides of uranium, plutonium, aluminum, and non-radioactive fission product elements in a horizontal tubular reactor constructed of nickel. The BrF₅ flow was metered using a rotameter constructed of Fluorothene, a polymer of chlorotrifluoro-ethylene. Nitrogen used to dilute the BrF₅ was metered by a conventional glass rotameter. The apparatus is described further in ANL-7055, p. 115. In these tests, the total gas flow rate averaged about 500 ml/min over the temperature range 175 to 400°C at 1-atm pressure, corresponding to a linear velocity of about 0.04 ft/sec. The gas phase composition was 26 v/o BrF₅ and 74 v/o nitrogen.

In one set of experiments, the solid reaction mixture contained UO₂F₂, UF₄, fission products, and alumina (which would be present after a HF-promoted oxidative decladding step). In several experiments, stainless steel decladding product (mainly Fe₂O₃ and Cr₂O₃), or Zircaloy decladding product (ZrF₄), was added to the mixtures. In a second set of experiments, the solid reaction mixture contained U₃O₈, fission product oxides, alumina, and, in some cases, Zircaloy decladding product, to determine the effect of the solid diluents on the fluorination of U₃O₈ by BrF₅. A third series of experiments was performed using a solid reaction mixture containing U₃O₈, PuO₂, fission product oxides, and alumina.

In other work, reaction kinetics were determined for the UF₄-BrF₅ and UO₂F₂-BrF₅ reactions over the temperature range 175 to 300°C, and preliminary rate data were obtained for the U₃O₈-BrF₅, UO₂-BrF₅, and UO₃-BrF₅ reactions over the temperature range 250-400°C. The method used to correlate the rate data was based on the diminishing sphere model developed by Anderson.³ In this model, the reaction rate is related to the changing

³Anderson, J. S., Bull. Soc. Chim. 20, 781 (1953).

surface area, which decreases as the diameters of the reacting particles become smaller with time. The final equation is:

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

in which F is the fraction of the solid reacted in time t , and k' is a reaction rate constant.

a. Fluorination of UO_2F_2 - UF_4 -Alumina-Fission Product Oxide Mixtures

In these experiments, the solid reaction mixtures fluorinated with BrF_5 contained 10 g of type T-61 alumina, 4.2 g UO_2F_2 , 2.2 g UF_4 , and 0.07 g of fission product oxide mixture. The fission product oxide mixture contained Y_2O_3 , ZrO_2 , BaO , La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Gd_2O_3 , Sm_2O_3 , Eu_2O_3 , MoO_2 , SrF_2 , CsF , Nb_2O_5 , and RuO_2 . The alumina to uranium ratio in the solid reaction mixture was 2:1. In these and all the experiments described subsequently, the gaseous reaction products were passed through a trap containing soda lime to dispose of bromine fluorides and other reaction products.

Experiments were performed for 30-min reaction times over the temperature range 175 to 250°C. The values of the reaction rate constants, k' , varied from 0.0038 min^{-1} at 175°C to 0.017 min^{-1} at 250°C, corresponding to conversions of uranium to UF_6 of 30% and 88%, respectively. The temperature dependence of the reaction rate is shown in Fig. II-7. The

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Fig. II-7. Variation of Rate Constants for the Reaction between Mixtures of UF_4 and UO_2F_2 with BrF_5 over the Temperature Range 175-250°C

Arrhenius equation was fitted to the data and resulted in the equation $\log k' = 2.01969 - 1970/T$. From the slope of the plot, an activation energy of 9 kcal/mole was calculated. Also plotted on Fig. II-7 is a curve based on calculated rate data for a $2/3 \text{ UO}_2\text{F}_2 - 1/3 \text{ UF}_4$ mixture (the data for the UO_2F_2 - BrF_5 and UF_4 - BrF_5 reactions, reported in a following section, were used in these calculations); from the slope of this curve, an activation energy of 10 kcal/mole was calculated.

Based on the results reported above, experiments

were performed to determine the conditions necessary to convert 99% of the uranium in UO_2F_2 and UF_4 to UF_6 . A reaction time of 60 min and

temperatures of 250 and 300°C were used. Experiments were also performed to determine the effect of the addition of stainless steel or Zircaloy decladding product on the uranium conversion to UF_6 . The results, listed in Section A of Table II-4, show that a fluorination temperature of 300°C is necessary to convert more than 99% of the uranium to UF_6 . The results also indicate that the presence of decladding product does not reduce the extent of uranium conversion to UF_6 .

TABLE II-4. Effect of Temperature and the Presence of Stainless Steel or Zircaloy Decladding Product on the Reaction between BrF_5 and Uranium, Alumina, and Fission Product Mixtures

Reaction time:			60 min		
BrF ₅ flow rate:			0.5 g/min		
Total gas flow rate:			250 ml/min at 25°C (74 v/o N ₂ , 26 v/o BrF ₅)		
Linear velocity of gas at 300°C:			0.04 ft/sec		
Temp. (°C)	Additive	Uranium Volatilized ^a (%)	Temp. (°C)	Additive	Uranium Volatilized ^a (%)
A. UO_2F_2 - UF_4 -Alumina-F.P. Mixtures ^b			B. U_3O_8 -Alumina-F.P. Mixtures ^e		
250	none	98.2	350	none	97.6
300	none	99.8	400	none	99.8
300	S.S. ^c	99.6	400	S.S. ^c	99.8
300	Zirc. ^d	99.2	400	Zirc. ^d	99.6

^aBased on uranium analysis of residue and uranium content of original uranium compounds.

^bMixtures contained 4.2 g UO_2F_2 , 2.2 g UF_4 , 10 g alumina, and 0.07 g fission product oxides.

^cThe stainless steel decladding product was prepared by the HF-promoted oxidation of type 304 stainless steel and contained 47.6% Fe and 12.8% Cr; 0.89 g of the decladding product was added to the solid mixtures described in footnotes b and e.

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

^eMixtures contained 5.9 g U_3O_8 , 10 g alumina, and 0.07 g fission product oxides.

b. Fluorination of U_3O_8 -Alumina-Fission Product Mixtures

The solid reaction mixtures fluorinated with BrF_5 in some experiments contained 5.9 g U_3O_8 , 10 g alumina, and 0.07 g fission product oxide mixture. Preliminary experiments showed that a reaction temperature of 350 to 400°C was necessary to achieve uranium conversions to the extent obtained with mixtures of UO_2F_2 and UF_4 at 300°C. A series of experiments was performed with a reaction time of 60 min at 350 and 400°C. In other tests carried out under similar conditions, stainless steel decladding product or Zircaloy decladding product was added to the bed. The results obtained (Section B of Table II-4) show that a reaction temperature of 400°C is necessary to convert greater than 99% of the uranium to UF_6 , and that the presence of decladding product does not reduce the extent of uranium conversion to UF_6 .

c. Kinetics of the UF_4 - BrF_5 and UO_2F_2 - BrF_5 Reactions

The reaction rates were determined for the UF_4 - BrF_5 reaction over the temperature range 200 to 275°C and for the UO_2F_2 - BrF_5 reaction over the temperature range 175 to 300°C. For the UF_4 - BrF_5 reaction, the rate constant, k' , varied from 0.0024 min^{-1} at 200°C to 0.0331 min^{-1} at 275°C. For the UO_2F_2 - BrF_5 reaction, the rate constant varied from 0.004 min^{-1} at 175°C to 0.028 min^{-1} at 300°C. The temperature dependence of the rate for both reactions is shown in Fig. II-8. The

Fig. II-8

Variation of Rate Constant
for the UF_4 - BrF_5 and
 UO_2F_2 - BrF_5 Reactions over
the Temperature Range
175-300°C

Arrhenius equation was fitted to the rate data and resulted in the following equations.

$$\text{UF}_4\text{-BrF}_5: \log k' = 5.71942 - 3948/T$$

$$\text{UO}_2\text{F}_2\text{-BrF}_5: \log k' = 1.49312 - 1747/T.$$

From the equations, activation energies of 8 and 18 kcal/mole were calculated for the $\text{UO}_2\text{F}_2\text{-BrF}_5$ and $\text{UF}_4\text{-BrF}_5$ reactions, respectively.

d. Reaction Rates for the $\text{U}_3\text{O}_8\text{-BrF}_5$, $\text{UO}_2\text{-BrF}_5$, and $\text{UO}_3\text{-BrF}_5$ Reactions

A preliminary study was made of the reactions between BrF_5 and U_3O_8 , UO_2 , and UO_3 in the temperature range 250 to 400°C. In all of these reactions a change in the rate of the reaction was noted with increasing reaction time. This effect is illustrated by data obtained at 300°C in Fig. II-9, in which the function $(1-F)^{1/3}$ (F is the fraction of uranium

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Fig. II-9. Reactivity of U_3O_8 , UO_3 , UO_2 , UO_2F_2 , and UF_4 with BrF_5 at 275°C or 300°C

converted to UF_6) is plotted versus the reaction time, t , expressed in minutes. This change in rate with time can be attributed to the interaction between UF_6 and the uranium oxides as reported by Rampy.⁴ It was observed by Rampy that the interaction between UF_6 and uranium oxides produces a solid coating of UO_2F_2 and UF_4 on the surface of the uranium oxide particles. As a result of this reaction, a reduction in the volatilization of UF_6 and a corresponding reduction in the measured reaction rate is observed during the initial period of reaction. In the reaction between uranium oxides and BrF_5 at 300 to 400°C, it was observed that the coating layer contained primarily UO_2F_2 , since at 300°C the UF_4 formed is readily fluorinated by BrF_5 . After the UO_2F_2 layer reaches a thickness sufficient to inhibit further interaction of UF_6

⁴Rampy, G. A., USAEC report GAT-L-366 (1957); GAT-265 (1959).

UF₄ at 275°C. Comparison of the plots indicates that at 300°C the reactivity of these materials with BrF₅ decreases in the following order: UF₄, UO₂F₂, UO₂, UO₃, U₃O₈.

e. Fluorination of U₃O₈-PuO₂-Alumina-Fission Product Mixtures

Experiments were performed in which mixtures containing U₃O₈, PuO₂, alumina, and fission products were reacted with BrF₅ to determine whether PuO₂ is converted to a volatile fluoride during the BrF₅ fluorination. The reaction conditions used (reaction time of 60 min at 400°C at a gas flow rate of 250 ml/min) were those which resulted in the conversion of more than 99% of the uranium to UF₆. In each of two experiments, the solid reaction mixture contained 5.8 g U₃O₈, 0.2 g PuO₂, 10 g of alumina, and 0.07 g fission product oxides; in a third experiment, which was only carried through the BrF₅ step, the solid mixture contained only 2.0 g PuO₂ and 10 g of alumina. During the BrF₅ fluorination periods, the gas phase was passed through a trap containing 250 g of soda lime to convert the gaseous products and unreacted BrF₅ to nonvolatile compounds. After the reaction was completed, the contents of the trap were removed, ground, and analyzed for plutonium.

The plutonium analyses of the soda lime showed less than 10⁻³ mg of plutonium per gram of soda lime, which amount was accounted for as contamination from the sample grinding system. These results indicate that none of the plutonium was volatilized during the BrF₅ fluorination step.

After the BrF₅ fluorination step in the first two experiments, fluorination of the solid residues with 100% fluorine was performed at 550°C for 5 hr in one experiment and for 8 hr in the other. Fluorination resulted in removal of 97.8 and 99.5% of the plutonium in the 5- and 8-hr reaction periods, respectively.

3. Phase Studies

a. Liquid-Vapor Equilibria in the System PuF₆-UF₆

An experimental program is under way to determine the vapor-liquid phase equilibria for the system PuF₆-UF₆. Equilibrium data for this system are necessary for the design of a fractional distillation column for the separation of mixtures of PuF₆ and UF₆ produced in the fluid-bed fluoride volatility process. A description of the experimental apparatus used for the determinations appeared in ANL-6875, pp. 114-115.

Vapor-liquid equilibria for UF₆-rich mixtures of PuF₆-UF₆ were determined at 73, 81, and 89°C. The results of these determinations

are presented in Table II-5. A plot of total pressure of the mixtures as a function of composition is presented in Fig. II-10. The lines identified as Ideal Liquid Composition were obtained by a Raoult's law calculation. In several of the experiments as indicated in the table and on the graph, very small samples of the liquid phase were obtained. This was because of experimental difficulties--presumably partial plugging of the liquid sampling valve orifice with solid PuF_4 produced by the alpha radiation decomposition of PuF_6 (ANL-6875, pp. 108-111).

TABLE II-5. Vapor-Liquid Equilibria in the System PuF_6 - UF_6

Temp. (°C)	X_{UF_6}	Y_{UF_6}	Pressure (torr)	γ_{UF_6}	γ_{PuF_6}	Pressure (torr) Corrected ^a to 73, 81, 89°C
73.6	0.989	0.992	1527	1.00	0.97	1499
76.7	0.976	0.982	1732	1.04	1.09	1546
73.3	0.959	0.969	1529	1.02	1.10	1515
72.4 ^b	0.939	0.956	1538	1.06	1.07	1565
72.9 ^b	0.922	0.879	1556	0.99	2.26	1561
80.8 ^b	0.999	0.999	1849	0.98	1.38	1859
79.9	0.893	0.918	1855	1.04	1.09	1913
79.8 ^b	0.822	0.749	1764	0.88	1.90	1822
80.8 ^b	0.780	0.688	1736	0.81	1.83	1745
89.2	0.987	0.991	2398	1.01	1.00	2385
88.4 ^b	0.989	0.942	2332	0.96	7.17	2370
89.8	0.888	0.907	2179	0.97	1.13	2289
89.0 ^b	0.675	0.631	2138	0.85	1.44	2139
89.6 ^b	0.524	0.388	2058	0.64	1.52	2006

$$\gamma = \text{activity coefficient} = \frac{PY}{P^0X}$$

X = mole fraction in the liquid phase

Y = mole fraction in the vapor phase

P = total pressure

P^0 = vapor pressure of the pure component

$$\text{aCorrection: } \Delta P = (X_{\text{UF}_6})(\gamma_{\text{UF}_6})\left(\frac{dP^0}{dT}\right)_{\text{UF}_6} \Delta T + (1 - X_{\text{UF}_6})(\gamma_{\text{PuF}_6})\left(\frac{dP^0}{dT}\right)_{\text{PuF}_6} \Delta T$$

^bResults uncertain because of small liquid sample (see text).

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Fig. II-10. Pressure-Composition Diagram:
Plutonium Hexafluoride--Uranium
Hexafluoride

Activity coefficients calculated from the data are, in general, close to unity, indicating that only small deviations from ideality occur in the range of composition studied. Since continuous fractional distillation of PuF_6 - UF_6 mixtures in the fluid-bed fluoride volatility process would involve UF_6 -rich mixtures, a fractional distillation column could be designed on the basis that there is ideal behavior of the system in this range of composition. Extension of the determinations into PuF_6 -rich mixtures would increase the experimental problems already encountered as a result of PuF_4 deposition in the system. Since the fractional distillation behavior of the system can be predicted from the results obtained, the purposes of the investigation have been substantially realized and the investigation was therefore brought to a close.

b. Solid-Liquid Phase Equilibria in the System UF_6 - PuF_6

As a part of the program to gain information on the UF_6 - PuF_6 system, the solid-liquid phase equilibria were also investigated. Consequently, thermal analyses of PuF_6 - UF_6 mixtures were carried out to obtain a temperature-composition phase diagram.

Two determinations of the triple point of the sample of UF_6 used in this study yielded values of 64.1°C and 64.2°C. The best literature value⁵ for the triple point of UF_6 is 64.05°C.

⁵Weinstock, B., Weaver, E. E., and Malm, J. G., J. Inorg. Nucl. Chem. 11, 104-114 (1959).

The PuF_6 used in this work was prepared in this laboratory by fluorination of PuF_4 . Two determinations of the triple point of this PuF_6 yielded values of 51.5°C and 51.3°C . The best literature value⁵ for the triple point of pure PuF_6 is 51.59°C .

Thermal halts corresponding to solidus and liquidus points were obtained from heating curves only. Results obtained on cooling were not used because the mixtures underwent supercooling. Two to five curves were obtained for each mixture at heating rates ranging from 1°C per min to 0.3°C per min. The temperatures of all thermal halts were between the melting points of the two pure compounds; no maximum-melting or minimum-melting mixtures were observed. From this observation and from the shape of thermal analysis curves, it is concluded that solid phases involved in solid-liquid phase equilibria of UF_6 - PuF_6 mixtures are solid solutions.

Observed liquidus and solidus temperatures are plotted as a function of the mole fraction of UF_6 in Fig. II-11 where the resulting curves can be compared with the ideal solidus and liquidus curves calculated from the equations of Seltz⁶ using the physical properties of pure PuF_6 and pure UF_6 .

108-9426

Fig. II-11. Solid-Liquid Phase Equilibria in the System UF_6 - PuF_6

⁶Seltz, H., J. Am. Chem. Soc. 56, 307 (1934).

4. Chemistry of Neptunium Hexafluoride

a. The Absorption Spectrum of Neptunium Hexafluoride

Neptunium-237 is expected to be a significant contaminant in highly irradiated low-enrichment fuels. Little knowledge of the chemical properties of neptunium hexafluoride is available. This has prompted the development of nondestructive methods for the analysis of this volatile, reactive substance. In order to provide a satisfactory basis for the development of a quantitative analytical technique, the spectrum of gaseous neptunium hexafluoride was determined in the region 2000 to 20,000 Å.

Neptunium hexafluoride was prepared by the reaction of the dioxide of neptunium-237 and elemental fluorine at 500°C. The volatile product of this reaction was purified by trap-to-trap distillation until the vapor pressure measured at several temperatures agreed with data in the literature.⁵

The absorption spectrum of neptunium hexafluoride was determined using a Cary Model 14 recording spectrophotometer. The determination of the absorbance of gaseous neptunium hexafluoride resulted in the spectrum shown in Figs. II-12, II-13, and II-14, in which the molar absorptivities are plotted against wave numbers. In each instance, the indicated molar absorptivities were the result of at least three separate determinations. Peak positions and peak heights were usually determined from four or more separate determinations. Table II-6 lists the major peaks observed in the spectrum together with their molar absorptivities and also lists the calculated values for the oscillator strengths (g) as determined from the shape of the spectral peaks.

Several of the peaks observed for neptunium hexafluoride are useful for the quantitative analysis of this compound in hexafluoride mixtures; Beer's law plots for the peaks of pure neptunium hexafluoride at 12970 Å and 2210 Å show no significant deviation from linearity.

b. Fluorination Rate of Neptunium Tetrafluoride by Elemental Fluorine

A knowledge of the pertinent physical and chemical properties of neptunium hexafluoride is necessary in order to establish process conditions for achieving a complete separation of uranium and plutonium from neptunium by the fluoride volatility process. The work reported here concerns determining the rate of fluorination of neptunium tetrafluoride (NpF_4) by elemental fluorine in the temperature range 250 to 400°C.

Fig. II-12
Absorption Spectrum of
Gaseous Neptunium Hexa-
fluoride in the Near Infra-
red Region

108-8613

108-8615

Fig. II-13. Absorption Spectrum of Gaseous Neptunium Hexafluoride in the Visible Region

108-8611

Fig. II-14. Absorption Spectrum of Neptunium Hexafluoride in the Ultraviolet Region

TABLE II-6. Absorption Spectrum of Gaseous Neptunium Hexafluoride

(Principal peaks and shoulders)

Instrument: Cary Model 14
 Cell lengths: 10 cm, 1 cm
 Windows: quartz 3 mm thick
 Temperature: $22 \pm 1^\circ\text{C}$
 Pressure: 4-100 mm Hg

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\epsilon\left(\frac{\text{liter}}{\text{mole-cm}}\right)$	g^a	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\epsilon\left(\frac{\text{liter}}{\text{mole-cm}}\right)$	g^a
13520	7396	3.674 ± 0.035	3.634×10^{-6}	4400 ^c	22727	1.553 ± 0.103	-
13099 ^b	7634	4.488 ± 0.062	-	4175	23952	2.695 ± 0.093	-
13050 ^b	7663	4.823 ± 0.031	-	4065 ^b	24600	4.214 ± 0.058	-
12970	7710	5.877 ± 0.015	6.083×10^{-6}	3835 ^b	26075	9.607 ± 0.066	-
12540	7974	0.904 ± 0.064	-	3700 ^b	27027	12.863 ± 0.046	-
12040	8306	1.077 ± 0.058	0.693×10^{-6}	3615 ^b	27662	15.362 ± 0.045	-
10875	9195	3.726 ± 0.055	2.314×10^{-6}	3510 ^b	28490	18.505 ± 0.087	-
10665	9376	3.738 ± 0.046	1.290×10^{-6}	2575	38835	1675 ± 49	-
10495	9528	6.924 ± 0.049	4.141×10^{-6}	2210	45249	2360 ± 54	9.66×10^{-4}
10250	9756	0.379 ± 0.065	-				
9982	10018	0.359 ± 0.064	-				
9825	10178	0.267 ± 0.059	-				

^a $g = 4.60 \times 10^{-9} \cdot \epsilon_{\text{max}} \cdot \Delta\nu_{1/2}$ ^bShoulder.^cBroad; peak location estimated.

The NpF_4 used for this work was prepared by the reaction of NpO_2 with hydrogen fluoride-oxygen gas mixture at 500°C . X-ray analysis of the material produced by this reaction indicates the product to be NpF_4 , and weight gain data indicate better than 99% conversion of the starting NpO_2 to NpF_4 .

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

Reaction rates were measured for the $\text{NpF}_4\text{-F}_2$ reaction over the temperature range 250 to 400°C . The data were treated using the "diminishing sphere model." In this kinetic model, developed by Anderson³ the reaction between a gas and a solid is related to the solid presenting a spherical interface which continuously diminishes with reaction time.

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

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

From this equation an apparent activation energy, E , of 20 kcal/mole was calculated.

5. Corrosion in Fluid-bed Reactors

Two $1\frac{1}{2}$ -in. dia. nickel fluid-bed reactors which had been exposed to UF_6 , PuF_6 , and fluorine for periods of 442 hr and 658 hr and temperatures up to 550°C have been sectioned at the following locations in preparation for microscopic examination: (1) at a location that was above the fluid bed but in the heated zone during fluidization, (2) at a location 1 in. above the conical gas distributor and thus exposed to the fluid bed, and (3) a thermocouple well located within the fluid bed near the conical gas distributor. Two sections of the well were made: one at the welded tip and one immediately adjacent to the tip. Samples taken from the reactor wall were obtained from opposite sides of the reactor. The samples were mounted in plastic, etched, and examined for intergranular attack. This examination showed

that the reactor wall in the heated zone above the fluidized bed and the wall one inch above the conical gas distributor had intergranular penetrations up to 2.5 and 2.0 mils, respectively. The thermocouple well from the reactor which had been exposed for 442 hr had intergranular penetration of up to 2.5 mils at the tip and 1.5 mils at a location immediately below the tip, while the thermocouple from the reactor which was exposed for 658 hr showed an uneven penetration of up to 9 mils, both at the tip and immediately below the tip.

For the reactor that was exposed to the fluorides for a total of 442 hr, the intergranular penetration was quite uniform at all locations examined and averaged 1 to 2 mils in depth. However, the reactor that was exposed for 658 hr showed a wide variation in the depth of intergranular penetration that ranged from zero to 9 mils. This variation may have been caused by greater reaction of the metal at certain locations than others followed by spalling of the NiF_2 scale.

A program is underway to determine the corrosion of nickel and nickel-containing alloys by some of the volatile fission product fluorides either individually or in the presence of fluorine. The experiments are being performed in a static system at 500°C . Among the volatile fluorides being investigated are GeF_4 , AsF_5 , MoF_6 , SeF_6 , TeF_6 , and UF_6 .

B. Engineering-scale Investigations

1. Recovery of Uranium and Plutonium from Uranium Dioxide Fuels in the Engineering-Scale Alpha Facility

Development work was continued on a fluid-bed fluoride volatility process for the recovery of uranium and plutonium from spent ceramic oxide fuels. Representative of these fuels is the type used in commercial power reactors, namely, low-enrichment ceramic uranium dioxide (UO_2) pellets contained in Zircaloy or stainless steel tube clusters. The spent fuels contain sufficient plutonium to warrant its recovery.

The process flowsheet currently under development (see ANL-7020, pp. 100-101) includes the following basic steps:

- a. Removal of the Zircaloy cladding by reaction with hydrogen chloride,
- b. Fluorination of the fuel to uranium and plutonium hexafluorides, which volatilize and are collected in a separate vessel,
- c. Distillation of the hexafluoride mixture to concentrate the PuF_6 fraction and to purify the hexafluorides,

- d. Thermal decomposition of PuF_6 to PuF_4 as a means of separating the hexafluorides, and
- e. Conversion of UF_6 - PuF_6 mixtures to mixed dense oxide particles by reaction with steam and hydrogen.

Steps a, b, d, and e involve fluid-bed operations. Other alternative steps, such as chemical reduction as a means of separating PuF_6 from PuF_6 - UF_6 mixtures, are also under consideration.

All the steps in this process except decladding of the oxide fuel will be demonstrated with unirradiated UO_2 - PuO_2 materials in the engineering-scale alpha facility. The facility comprises two alpha boxes, the larger one containing the process equipment, and the smaller one containing off-gas scrubbers and other auxiliary equipment. Installed in the facility are a fluorination pilot plant (fluorinator) for processing batches of fuel to a mixed UF_6 - PuF_6 product and a converter. The converter produces a final stable product (mixed UO_2 - PuO_2 or PuF_4), thereby eliminating the need to store plutonium hexafluoride (which undergoes both alpha decomposition and thermal decomposition). A complete description of the alpha facility and the fluorinator and converter systems is given in a topical report.⁷

Distillation Apparatus. A distillation column for studies with UF_6 - PuF_6 mixtures has been fabricated. The unit is now installed in a mock-up area (see Fig. II-15) for preliminary testing. A schematic drawing of the column piping showing sampling points and the manifold for recycling vapor is given in Fig. II-16. The column will eventually be positioned in the facility adjacent to the converter as shown in the isometric drawing of the large alpha box (Fig. II-17). The unit will be introduced into the large box by a vertical bag-in technique that was developed in the course of the facility installation work.

Testing of Alpha Facility. The facility was given a final check after all windows were installed and sealed. Included was a test to determine the air leakage rates from the two alpha boxes. The boxes, which will be operating normally at 0.5-in. water negative pressure, were tested at a positive pressure of 2.5 in. water. Leaks were reduced to acceptable levels, ~0.11 cfm for the larger box and 0.06 cfm for the smaller box (0.42% and 0.7% of box volume per hour, respectively). A helium mass spectrometer leak detector was used extensively in this work. Final versions of standard operating procedures for the alpha facility were established during the shakedown tests.

⁷Vogel, G. J., Carls, E. L., and Mecham, W. J., Engineering Development of Fluid-Bed Fluoride Volatility Processes. Part 5. Description of a Pilot-Scale Facility for Uranium Dioxide-Plutonium Dioxide Processing Studies, ANL-6901.

108-8792A

Fig. II-15. Distillation Apparatus for UF_6 - PuF_6 Systems

Fig. II-16.

Distillation Apparatus
for UF_6 - PuF_6 Mixtures

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108-8791T

Fig. II-17. Large Alpha Box of Engineering-scale Alpha Facility

In the flowsheet under current investigation, the fluorination is carried out by the two-zone oxidation-fluorination method. The pellets in the form of right cylinders (0.5-in. dia. by 0.5 in. long) are added to the fluorinator to form a packed bed supported on a 3-in. deep bed of 1/4-in. dia. nickel balls. Sintered alumina is added to provide a fluidized-packed bed in the pellet zone and a 2-ft deep fluidized bed above the pellets (see Fig. II-18). In the two-zone oxidation-fluorination process, oxygen diluted with nitrogen is introduced into the bottom of the fluorinator. The oxygen reacts with the sintered pellets to form U_3O_8 and PuO_2 fines (generally less than 200 mesh) which are transported into the fluidized-bed zone where they are reacted with a separate fluorine stream, forming volatile UF_6 and PuF_6 . Four fluorine inlet ports are provided; as the pellet bed is consumed by reaction with oxygen, the position at which fluorine is introduced is successively lowered. After approximately 95% of the oxide has been converted to hexafluorides by fluorine introduced at side ports, the production of hexafluorides appears to cease as indicated by readings from the continuous-weigh scales on which the cold-traps are mounted. Thereafter, fluorine is introduced instead at the bottom of the reactor and the reaction is continued for a period of one or more hours, depending on the extent of production of additional hexafluoride. During this period, recycle of the fluorine off-gas is often employed as an economy measure. This single-zone reaction period is followed by a fluorine recycle (cleanup) period in which the remainder of the uranium and plutonium are recovered from the reactor. The cleanup period

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Fig. II-18. Fluorination Process Equipment

is characterized by the use of higher fluorine concentrations (90 v/o fluorine) and higher temperatures (550°C) than those used in either the two-zone reaction period or the single-zone fluorination period.

After fluorination, the mixed hexafluorides are vapor-transferred to a 4-in. dia. product receiver. This receiver serves as the feed pot for the conversion step or thermal decomposition step. It will also be used as a transfer vessel to charge the distillation column still pot.

During the report period, shakedown experiments were completed with uranium materials in the fluorinator and in the converter in its dual role (conversion and thermal decomposition). Following this shakedown period, work with plutonium-containing materials was initiated. The converter is being used initially for fluid-bed thermal decomposition studies with UF_6 - PuF_6 mixtures (step d) and will later be used to convert UF_6 - PuF_6 mixtures to mixed oxide particles (step c).

a. Fluorination of UO_2 and UO_2 - PuO_2 Charges

The conditions for three shakedown experiments with UO_2 pellet charges and the first experiment with a uranium-plutonium oxide charge are summarized in Table II-7. In each run about 8.8 kg of pellets and 6 to 7 kg of alumina (Alcoa, Tabular T-61, nominal 48 to 100 mesh) were used. One of the major objectives in runs 2, 3, and 4 was to establish processing conditions for the two-zone oxidation-fluorination step which would result in steady, high hexafluoride production at a maximum bed temperature of 450°C. The oxygen was fed at a relatively uniform rate during a given experiment and oxygen concentration ranged from ~11 v/o in run 2 to ~23 v/o in run Pu-1. Overall process control was maintained by regulating the input flowrate of fluorine; the fluorine concentration was generally below 15 v/o. With manual fluorine control, considerable fluctuation in the hexafluoride production rate was experienced. Automatic

TABLE II-7. Conditions and Results for Recent Fluorination Runs

Fuel charge: 8.8 kg of UO_2 pellets in runs 2, 3, and 4

1.8 kg UO_2 + 7.0 kg of 0.5 w/o PuO_2 - UO_2 pellets in run Pu-1

	Total Duration (hr)	Two-zone Reaction Period		Duration of Single-zone Fluorination Period ^b (hr)	Cleanup Period (Total Recycle)		Final Bed Analysis (w/o)	
		Duration (hr)	Average Hexafluoride Production Rate to 95% Collection Point ^a (kg/hr)		Duration (hr)	Maximum Temperature (°C)	U	Pu
Run 2	19.7	11.5	1.0	-	7.0	490	~0.07	-
Run 3	27.0	15.0	0.5	~50	8.0	500	0.046	-
Run 4	35.8	20.5	0.4	~50	5.3	500	0.025	-
Run Pu-1	20.5	8.0	1.0	~50	4.2	550	0.018 ^c	0.025 ^c

^aThis point coincides approximately with the end of the two-zone reaction period.

^bGas was fed either once-through or recycled in this period, depending on fluorine utilization.

^cAnalyses of sample of fluid bed taken at the end of run. Values do not represent the uranium and plutonium in the hold-up fines.

control of fluorine flowrate has shown promise and is undergoing further development. Operating conditions studied included the use of a vertical temperature gradient in the pellet bed as an aid in controlling the oxidation rate. A temperature gradient of 50°C from the top of the pellet bed to the bottom has been found to be satisfactory.

In the four experiments, periods of hexafluoride production to about 95% collection ranged from 8 hr to over 20 hr. The longer periods were used in evaluations of control systems. A detailed summary of the operating conditions for the first experiment with PuO_2 - UO_2 materials in the engineering-scale alpha facility is presented in Table II-8. Figure II-19 (prepared from computer analysis of the run data) shows the rate of UF_6 collection during the first two periods of run Pu-1. Of particular significance in this figure is the decrease in hexafluoride production rate which occurs after about 75 to 80% of the charge has been reacted. The peak occurring at 9.0 hr, after fluorine introduction at the bottom began, reflects the direct fluorination of the remaining charge. Average hexafluoride collection rates of 1.0 kg/hr [$\sim 43 \text{ lb}/(\text{hr})(\text{sq ft})$] have been obtained during the single-zone fluorination period. The recycle cleanup periods lasted 4 to 10 hr, with 8 hr being typical.

Analytical Results and Discussion. The extent of removal of uranium and plutonium from the alumina bed is a major factor in the evaluation of experiments. The values listed in Table II-7 for the uranium content of the final bed samples reflect, in general, the effect of length of cleanup period and maximum temperature employed in the cleanup period; longer times and higher temperatures gave lower final concentrations. The best uranium removal achieved to date was that obtained in run Pu-1. The final uranium and plutonium concentrations in the alumina bed in this

TABLE II-8. Operating Conditions for Processing UO_2 - PuO_2 Fuel (Run Pu-1)

Run Time, hr	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21							
Period	2-Zone Fluorination								1-Zone Fluorination				Plutonium Cleanup																
Gas Flow Path	Once Thru												Recycle																
Cumulative Hexafluoride Collection, % of Charge					39			75		80		95																	
Fluorine Addition Point	Side Inlet	+	Side Inlet	+	Side Inlet	+																Bottom Inlet							
Flowrate thru Fluorinator Bottom Inlet, cfm	~1.8								+	~2.0				+	~1.6														
Flowrate thru Fluorinator Side Inlet, cfm	~0.6								+					+	Side Inlet Closed														
Average Concentration, v/o Fluorine in Entering Gas, v/o°	~6	+	~11		+	~9		+	~6		+																		
Oxygen in Entering Gas, v/o°	~23	+	~13		+	~17		+	~22		+	O ₂ Off																	
Fluorine Concentration of Process Off-gas, v/o	Variable but below 10										+	Increasing 10 to ~90				+	~90												
Nominal Temperature, °C																													
→ Pellet Bed	Gradient 400-450		+	450						+	450				+	450		+	500		+	500		+	550		+	550	
→ Alumina Bed	450								+	500				+	500		+	550		+	550		+	550		+	550		

*Fluorine flowrate is divided by the sum of the side and bottom flow inputs to obtain this value.

**Oxygen flowrate in the bottom input stream is divided by the total flowrate into the bottom inlet to obtain this value.

108-9421

Fig. II-19. Uranium Hexafluoride Collection Rate and Fluorine Utilization Efficiency during Run Pu-1

run were each 0.02 w/o. For a single use of an alumina bed, these values correspond to removals of about 99.9% and 95% of the uranium and plutonium in the charge. Uranium material balances, available only for runs 2 to 4, were excellent; for example, in run 2 only 6 g out of an 11,478-g input (UF₆ equivalent of the UO₂ charge) was not accounted for.

The data in Fig. II-20 show the course of uranium and plutonium removal from the fluorinator alumina bed throughout the cleanup period of run Pu-1. The data were obtained from grab samples taken at approximately hourly intervals. Each temperature period is generally characterized by a period of high removal rate followed by a period in which the removal rate, for all practical purposes, diminishes to zero. The plutonium data show this trend rather well; the uranium data show considerable scatter, but the overall decrease in concentration is apparent.

When the alumina bed was removed from the reactor after run Pu-1, it was observed that a finely divided solid material containing plutonium had been held up on reactor surfaces above the fluid bed. The plutonium content of this material was equivalent to about 15% of the plutonium in the UO₂-PuO₂ charge. Several methods are being investigated to reduce this holdup of fines and to return the fines to the bed where they will be reacted during fluorination.

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Fig. II-20. Percent Uranium and Plutonium Removal from Fluorinator Alumina in Run Pu-1

b. Conversion and Thermal Decomposition Experiments

The converter system (Fig. II-17, this report; ANL-7020, pp. 121-122) has undergone shakedown tests in which UF_6 was reacted with steam to form UO_2 , and has also been used in an experiment to separate plutonium from UF_6 - PuF_6 by thermal decomposition of the PuF_6 to solid PuF_4 .

(1) Conversion

Shakedown tests on the conversion of UF_6 to UO_2 were completed using conditions established in earlier work with a 3-in. dia. fluid-bed reactor.⁸ In the current tests, UF_6 was fed at rates of 12, 16, and

⁸Knudsen, I., and Levitz, N. M., Engineering Development of Fluid-bed Fluoride Volatility Processes. Part 6. The Fluid-bed Conversion of Uranium Hexafluoride to High-density Uranium Dioxide, ANL-6902.

18 g/min into a bed of UO_2 maintained at 650°C . A mole ratio of steam to UF_6 of about 2 was used which favors production of high-density oxide particles. The total flow rate of the gas mixture, which included hydrogen, provided a superficial velocity of the fluidizing gas of about 1 ft/sec. The final bed of UO_2 from one run was used as the starting bed for the next run. The starting quantities of material in the two cases were 2.5 kg and 3.3 kg (static bed heights of 9 and 12 in.).

The conversion process involves a cyclic operation: a 30-min hexafluoride feed period followed by a 30-min fluoride cleanup period and then withdrawal of a portion of the bed as product. After the average bed particle size has grown (through deposition of newly formed oxide) to a desired value, an in situ oxidation-reduction treatment is used to reduce the particle size of the bed. Only a fraction of the oxygen needed to fully oxidize the bed to U_3O_8 has been found adequate for the oxidation phase of the size-reduction step.

The final shakedown experiment included two complete cycles of growth periods followed by an oxidation-reduction treatment for resizing the bed material. Particle size behavior during this run was as follows:

	Initial and Final Particle Sizes of UO_2 (μ)
UF_6 feed period (3.10 kg UF_6 was fed in 5 hr)	288 to 366
Oxidation-reduction treatment (0.13 equivalent of oxygen was fed in 9 min)	366 to 344
UF_6 feed period (2.38 kg UF_6 was fed in 2.5 hr)	344 to 392
Oxidation-reduction treatment (0.27 equivalent of oxygen was fed in 23 min)	392 to 140

The results of the particle breakup treatments indicate the effectiveness of the oxidation-reduction procedure and its limits. The average bulk density of the oxide product was essentially the same as the starting bed density (8.4 g/cc). The quantity of uranium detected in the off-gas scrubber represented less than 0.001 w/o of the quantity fed.

Conversion studies with mixed UF_6 - PuF_6 feeds are planned immediately after the current series of fluorination-thermal decomposition experiments are completed. The mixed UO_2 - PuO_2 product from these conversion tests may then be recycled as feed to the fluorinator.

(2) Thermal Decomposition

A 10.6-kg batch of mixed uranium-plutonium hexafluoride produced in the fluorination experiment (run Pu-1) was processed in 9.6 hr for thermal decomposition. The operating conditions for the thermal decomposition experiment were:

Bed temperature:	350°C
Starting bed material:	18-in. static bed depth of Alcoa alumina (2.4 kg; -100 mesh particle size)
Superficial fluidizing gas velocity:	0.15 ft/sec
Hexafluoride feed rate:	22 g/min
Inlet gas composition:	40 v/o hexafluoride in nitrogen

The relatively low gas velocity and relatively deep bed gave average gas residence times of 5 to 10 sec. Process regions other than the bed were maintained at 80°C. It is expected that the alumina particles would become coated with PuF_4 , and the bed would then more nearly simulate one in which the bed material would be PuF_4 .

Samples of the decomposer off-gas and samples of the bed taken periodically throughout the run have been submitted for analysis to determine the extent of plutonium removal from the mixed hexafluoride gas stream. The starting hexafluoride mixture and the hexafluoride collected in the cold traps also were sampled. An evaluation of this step will be possible upon completion of the three successive fluorination-thermal decomposition experiments.

Future Work. The first of three scheduled experiments with the fluorinator and thermal decomposer (converter) operated in tandem has been completed satisfactorily. Following the three experiments, a clean-up fluorination will be carried out to recover plutonium deposited in lines and equipment as a result of thermal and alpha decomposition of plutonium hexafluoride. Plutonium and uranium material balances will be made after the third experiment.

2. Process Development Studies for Uranium Dioxide Fuels

Uranium dioxide fuels of low enrichment are commonly clad with either Zircaloy-2 or stainless steel. The fuel material, either as discharged from the nuclear reactors or as scrap from fabrication facilities, requires

reprocessing to recover uranium and plutonium values. For this purpose, fluid-bed fluoride volatility processes are being developed. The initial two steps in these processes involve the separation of the cladding from the oxide fuels and the fluorination of the uranium and plutonium compounds to convert these materials to volatile hexafluorides. Development studies on these two processing steps are being conducted with uranium-bearing fuels rather than uranium-plutonium fuels because operations are simplified in the absence of plutonium.

a. Decladding of Zircaloy-2-clad Uranium Dioxide Fuels by Reaction with Hydrogen Chloride

Studies have been initiated to demonstrate the decladding of simulated Zircaloy-2-clad UO_2 fuel bundles by reaction of the cladding with hydrogen chloride to form volatile ZrCl_4 , which is removed from the reactor in the process gas stream. The studies were carried out in the pilot-scale facility previously used to demonstrate the reprocessing of enriched uranium alloy fuels by the fluid-bed fluoride volatility process (see ANL-7020, pp. 137-141). The main components of this facility are a 6-in. dia. halogenation reactor, a 9-in. dia. down-flow packed-bed filter, and a 6-in. dia. pyrohydrolysis reactor for the conversion of volatile chlorides to solid oxides.

A series of runs was performed to determine: (1) the progress of hydrochlorination of Zircaloy-2-clad UO_2 fuel bundles, (2) the effect of small concentrations of oxygen in the decladding reagents on oxidation and thus pulverization of the oxide fuel, (3) the efficiency of packed beds of alumina in filtering, from the off-gas stream, U_3O_8 fines generated by the reaction between oxygen (in small concentrations) and the UO_2 fuel, (4) the performance of the equipment components during the decladding operation, and (5) the distribution of chloride in the filter bed at the end of the decladding step.

Zircaloy-2-clad UO_2 rods in the form of 28-in. long fuel bundles, simulating those used in the Dresden reactor, as well as unclad UO_2 pellets were hydrochlorinated in fluid beds of alumina. In general, the operating conditions used in the runs were similar.

A fuel bundle consisted of 25 Zircaloy-2 tubes, 28-in. long, loaded with a total of 15.8 kg of UO_2 pellets, and held in a square array with 0.14-in. spacing between tubes. The wall thickness of the Zircaloy-2 tubes was 0.030 in. The fuel bundle array was immersed in a fluid bed of refractory alumina particles and contacted with 40 to 85 v/o HCl in nitrogen at a bed temperature of 395°C . The off-gas from the fluid-bed reactor was filtered through an 11.5-in. deep packed bed (14.7 kg) of 14 to 48 mesh alumina particles. Progress of the decladding reaction was continuously monitored by hydrogen analyses of the off-gas stream and by gamma-ray photography of the tube bundle.

In all of the runs, the halogenation reactor, the packed-bed filter, and the pyrohydrolysis reactor operated smoothly during the entire period of decladding. The fuel bundle reacted gradually from the bottom to the top and, as the reaction progressed, the fuel bundle gradually immersed itself deeper into the fluid bed (see Fig. II-21). Both off-gas analysis and gamma-ray photography indicated that the decladding step was complete in 4.4 hr. The average reaction rate was 0.9 kg Zircaloy-2/hr, while the HCl utilization efficiency averaged 17%. The uranium loss owing to transport with the off-gas stream exiting from the filter was $<0.004\%$ of the uranium charged to the halogenation reactor. Although oxygen in small concentrations in the feed gas (0.04 to 2.5 v/o) reacted with UO_2 pellets, less than 5 w/o of the UO_2 charged to the fluid-bed reactor was converted to U_3O_8 fines and these fines were satisfactorily retained by the packed-bed filter. Analyses of the packed-bed filter indicated that uranium and chloride were not distributed uniformly throughout the filter. Uranium and chloride contents of the upper surface of the filter were 1.9 and 6.1 w/o, respectively, while the respective concentrations of these materials in the bottom layer of the filter were 0.003 and 0.02 w/o. No significant changes in appearance of the UO_2 pellets were observed after the decladding step.

108-9015

Fig. II-21. Decladding of Zircaloy-2-clad UO_2 Fuel Bundle in a Fluid-bed Reactor

b. Processing of Declad Uranium Dioxide

After decladding of Zircaloy-clad UO_2 fuel elements by the high-temperature reaction of the cladding with gaseous HCl , uranium and plutonium may be recovered as hexafluorides from the declad fuel by a two-zone simultaneous oxidation-fluorination technique (see ANL-6875, pp. 88 to 93). In this method, the UO_2 fuel pellets are oxidized in the lower part of the fluidized bed forming U_3O_8 fines which are transported to the upper portion of the bed and fluorinated to the hexafluoride.

In order to provide versatility in the fluid-bed fluoride volatility process, alternative schemes for processing UO_2 fuels are being studied. The alternative schemes are: two-step separate oxidation-fluorination, three-step oxidation-hydrofluorination-fluorination, and fluorination of U_3O_8 fines with BrF_5 instead of fluorine. These alternative processes may offer several advantages over the two-zone simultaneous oxidation-fluorination process: (1) sampling of the input feed material is facilitated after the oxidation step, (2) the alternative processes avoid large variations in rate of fluorination, which are caused by variations in the rate of transport of U_3O_8 fines from the lower to the upper zone of the bed in the two-zone process, and (3) the alternative techniques appear to be readily adaptable to the processing of fuel materials which are already in the form of powders. Eight runs were made to explore the feasibility of processing large quantities of fines in fluid beds. These runs were directed toward optimizing the fluid-bed temperatures, reactant concentrations, and gas velocities, and toward determining the proper ratio of coarse to fine particles which would result in satisfactory fluidization behavior.

Two tests were performed to determine if a sample of the fluid-bed material, taken after conversion of UO_2 pellets to fines, would satisfactorily represent the composition of the original oxide fuel charge. Uranium dioxide pellets of two enrichments were employed in the two tests with a 3-in. dia. pilot-scale reactor. The ^{235}U fraction served as a stand-in for the plutonium fraction. A 6-in. deep bed of UO_2 pellets, consisting of alternate 1-in. thick layers of depleted (0.2198% ^{235}U) and normal (0.7218% ^{235}U) UO_2 pellets, was charged to the reactor for each test. Equal quantities of the two enrichment types were used, the total being 4.4 kg. Sintered alumina, -100 mesh size with an average particle diameter of $84\ \mu$, was used as the fluid-bed material. The fluidizing gas, 13 v/o oxygen in nitrogen, was fed at a superficial velocity of 1.5 ft/sec. The oxidation was conducted at fluid-bed temperatures of 450 to 500°C.

A series of radiographs taken during the oxidation period are shown in Fig. II-22. The overall white appearance of the bed after $5\frac{1}{2}$ hr shows that oxidation was essentially complete.

108-8813

Fig. II-22. Gamma-ray Radiographs of Oxidation of Uranium Dioxide Pellets

Temperature: 450°C
 Initial charge: 4.4 kg of UO_2 pellets;
 6-in. deep bed
 Oxygen in feed: 13 v/o

Bed samples were taken at the end of the oxidation from sampling points 8, 28, and 38 in. above the bottom of the fluid bed. The uranium in the samples contained 0.4645, 0.4650, and 0.4714% ^{235}U ,

respectively, thus indicating that the ^{235}U concentration in the uranium was uniform throughout the bed. These values differ by only about 1% from the average input ^{235}U concentration of 0.4708%. Total uranium contents of samples taken at these three levels were 28.3, 31.5, and 32.3 w/o, as compared with 32.2 w/o (based on the uranium recovered from all process streams) and with 33.6 w/o (based on the uranium in the charge). These results suggest that a fluid bed of alumina containing large quantities of fines can be sampled representatively for accountability purposes.

The study of the fluorination step of the two-step process is under way.

Conversion of UO_2 to UF_6 by the Three step Scheme. The alternative three-step (oxidation-hydrofluorination-fluorination) scheme was successfully demonstrated in a test with a 2.2-kg charge of UO_2 pellets. The pellets were immersed in a 3.4-kg bed of alumina particles. The processing conditions were:

	<u>Oxidation</u>	<u>Hydrofluorination</u>	<u>Fluorination</u>
Temperature ($^{\circ}\text{C}$)	450	450	450 to 500
Time (hr)	4	3.5	4
Gas velocity (ft/sec)	1.5 to 1.8	0.9	0.8 to 1.1
Reactant concentration in feed (v/o)	5 to 25	4 to 44	5 to ~90

The progress of the oxidation reaction was monitored by continuous oxygen analysis of the off-gas stream and by periodic gamma-ray photographs of the pellet bed. The course of the hydrofluorination step was monitored by continuous analysis of the moisture content in the off-gas stream. High UF_6 production rates of 55 to 65 lb/(hr) (sq ft of reactor cross section) were achieved during the initial 1.5 hr of the fluorination step. The production rate data indicated that the fluorination of uranium fines proceeds initially at a constant rate, followed by a period in which the reaction rate slowly diminishes.

c. Alternative Method of Processing of Zircaloy-2-clad UO_2 Fuels

Although current plans are to declad Zircaloy-2-clad UO_2 fuels by treatment with HCl to form volatile ZrCl_4 , an alternative method is being studied for possible advantages. In the alternative method, a destructive oxidation of the Zircaloy-2-clad fuel is carried out with an HF -oxygen mixture. This treatment converts the zirconium alloy to flakes containing ZrO_2 and ZrOF_2 , while the UO_2 pellets are converted to UO_2F_2 and UF_4 powder. Two bench-scale tests were made to determine the destructive oxidation rates for Zircaloy-2, and a pilot-scale run was made to demonstrate both the destructive oxidation method and the uranium oxide fluorination step.

In the two bench-scale tests, Zircaloy-2 specimens, immersed in a fluidized bed of alumina, were contacted with a 40 v/o HF-40 v/o oxygen-20 v/o nitrogen mixture for 3 hr at 550°C. The penetration rates ranged from 12 to 18 mils/hr, suggesting that Zircaloy-2-clad fuel bundles may be declad satisfactorily under these conditions. To determine if selective volatilization of any of the constituents of Zircaloy-2 occurred during oxidation, the relative concentrations of zirconium, tin, iron, and chromium in the scaly oxide product and in the parent metal were measured with an electron probe microanalyzer. Since the relative concentrations of all constituents were the same in both the oxide product and the parent metal, it is believed that no selective volatilization of any constituent occurred during the destructive oxidation of Zircaloy-2.

In the pilot-scale run, the decladding-fluorination process was demonstrated using a fuel charge consisting of six 2-ft-long Zircaloy-2 tubes packed with cylindrical UO_2 pellets (0.43 by 0.43 in.). The total charge contained 3.2 kg UO_2 and 0.92 kg Zircaloy-2. The inert fluid-bed material was 5.5 kg of -40+170 mesh alumina particles.

The decladding conditions employed in this pilot-scale run were similar to those used in the bench-scale tests. Decladding was conducted for $6\frac{1}{2}$ hr at a nominal temperature of 550°C. Operation during the initial 3 hr proceeded smoothly. However, during the final $3\frac{1}{2}$ hr, the bed temperature decreased to 300°C. This is attributed to the formation of flakes during the disintegration of the Zircaloy tubing, which, in turn, caused a marked reduction in heat transfer from the reactor wall to the bed.

The HF-oxygen procedure for processing Zircaloy-2-clad fuel appears to be satisfactory; however, some difficulties were encountered during the tests. High UF_6 production rates [50 lb/(hr)(sq ft)] were achieved during the initial 2 hr of fluorination. This fluorination rate, however, was not sustained throughout the runs, owing to unsatisfactory fluidization properties of the bed.

No additional work on this method for decladding Zircaloy-2-clad fuel will be carried out at Argonne.

d. Processing of Uranium Dioxide-Stainless Steel Cermet Fuel

An exploratory test was made in the bench-scale fluid-bed reactor to determine the feasibility of reprocessing UO_2 -stainless steel cermet fuel material by the HF-oxygen, fluorine cycle. The initial process step, in which the uranium was separated from the cladding and matrix material, was carried out at 550°C with a gaseous mixture of 40 v/o HF, 40 v/o O_2 , and 20 v/o N_2 . During this step, the stainless steel was converted to oxide, which was in the form of a scaly material. The uranium appeared

as a powdered mixture of UO_2F_2 and UF_4 . The decladding step was followed by a three-step fluorination procedure: 3.3 hr at 250°C while the fluorine concentration in the feed gas was increased from 5 to 90 v/o; 4 hr with 90 v/o fluorine in nitrogen while the bed temperature was increased from 250 to 550°C ; and 1.0 hr at 550°C using 95 v/o fluorine.

The behavior of iron and chromium was observed during both the decladding and fluorination steps. Electron probe microanalyses of the scaly material produced in the decladding step and of the parent metal indicated that no volatilization of iron or chromium occurred during the decladding step. Approximately 45% of the chromium in the cermet fuel volatilized during the fluorination, whereas the iron was totally retained in the fluid-bed reactor. The chromium that had not volatilized and the iron were converted to very fine particulate fluorides during the fluorination step. The course of uranium and chromium volatilization during the three-step fluorination procedure was monitored by measuring the quantity of the volatile materials recovered in refrigerated condensers during each step. The data are shown in Table II-9. During the fluorination, 99.4% of the uranium in the fuel charge was recovered as UF_6 in the condensers. It is expected that separation of chromium from the UF_6 product can be performed without difficulty.

TABLE II-9. Course of Uranium and Chromium Volatilization during Fluorination of UO_2 -Stainless Steel Cermet Fuel

Duration of Fluorination Step (hr)	Temperature ($^\circ\text{C}$)	Fluorine Concentration (v/o)	Uranium Recovered (% of total recovered)	Chromium Recovered (% of total recovered)
3.3	250	5-90	89	21
4.0	250-550	90	10	52
1.0	550	95	1	27

During the study of stainless steel oxidation by HF-oxygen mixtures, preliminary data were obtained on the corrosion of nickel-200 (a proposed material of construction for fluid-bed reactors) in gaseous mixtures of HF, oxygen, and nitrogen. Corrosion rate data were based on measurements of weight gains of specimens suspended in the fluid-bed reactor. The specimens, 1-in. long sections of 1/4-in. dia. nickel-200 tubing, were exposed to 40 v/o HF, 40 v/o O_2 , and 20 v/o N_2 for 21 hr at temperatures between 500 and 600°C . During the testing period the specimens were thermally cycled several times between room temperature and processing temperature. The average corrosion rates were 8.8 mils/yr for specimens immersed in the fluidized bed of alumina particles. These data indicate that nickel-200 is a likely candidate for use in HF- O_2 environments.

A topical report⁹ has been issued summarizing engineering development of the fluid-bed fluoride volatility process for the stainless steel-uranium dioxide cermet fuel.

3. Cleanup of Cell Exhaust Air Contaminated with Plutonium Hexafluoride

Owing to the high volatility of PuF_6 (b.p. 62°C) and the extreme toxicity of plutonium (permissible concentration in air, $3 \times 10^{-8} \text{ mg } ^{239}\text{Pu}/\text{m}^3$),¹⁰ it is necessary that highly efficient cleaning systems be used for treating environmental air in fluoride volatility processing facilities such as gloveboxes in which plutonium is present. The gas cleanup systems utilize the reaction of hexafluoride with moisture in the glovebox air to produce a solid reaction product which is removed from the exhaust air as it passes through high-efficiency filters in the exhaust system. Two of the types of accidental releases of PuF_6 and UF_6 from equipment into an enclosure are being considered: an instantaneous release, in which most of the material is released into the enclosure in less than a minute, and a continuous release, in which the release once started continues at a relatively constant rate. The current investigation has been directed toward obtaining information needed for the design of high-efficiency cleaning systems for accommodating both types of releases of hexafluorides by simulating these releases in small-scale equipment.

In an accidental release of the hexafluorides, the concentration of the hexafluorides in the released gas may be very high (maximum 100%), such as from a storage cylinder, or very low (~ 0.01 ppm), such as from a process off-gas line. Previous experiments in this program (ANL-6800, pp. 245-252) indicated that the release of pure undiluted PuF_6 (or UF_6) into an atmosphere containing moisture resulted in an instantaneous reaction, which is as follows:

This reaction is completed in the gas phase and results in the production of a fume of plutonyl fluoride (PuO_2F_2) with a particle size of $< 0.1 \mu$. When the gas stream containing PuO_2F_2 was passed through two AEC-type filters

⁹Ramaswami, D., Levitz, N. M., and Jonke, A. A., Engineering Development of Fluid-bed Fluoride Volatility Processes. Part 2. Bench-scale Investigation of a Process for Aluminum-Uranium Alloy and Stainless Steel-Cermet Fuels, ANL-6830.

¹⁰U. S. Department of Commerce National Bureau of Standards Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure," Washington, D. C., 1959, p. 87.

in series at 40% of rated flow (i.e., at 1 cm/sec), the plutonium concentration of the fume in the gas stream was reduced by 10^{-6} to 10^{-9} . Studies of the hydrolysis and filtration of dilute PuF_6 and UF_6 indicated that the reaction does not proceed at a detectable rate in the gas phase, but occurs on any solid surface exposed to the reactants. The rate of hydrolysis for dilute UF_6 has been measured on packed beds of glass spheres (ANL-7020, pp. 129-134).

The data obtained to date on the hydrolysis of PuF_6 when it is released in concentrated or dilute form and on filtration of the hydrolyzed product have been summarized in a topical report.¹¹

a. Hydrolysis Rates of Dilute Hexafluorides in Small-scale Experiments

A series of ten experiments simulating a type of continuous release were performed to determine the hydrolysis rates of plutonium hexafluoride in dilute gas streams and the hydrolysis rates of dilute mixtures of uranium and plutonium hexafluorides. These experiments were performed in equipment similar to that used with UF_6 . Briefly, the equipment, which has been described in detail previously (ANL-7020, p. 132), consisted of a magnetically coupled stirrer for mixing the air-diluted PuF_6 and moist air streams. The mixed gases were passed through a packed bed of glass spheres which were 3.2 mm in diameter. The bed was 1.5 in. in diameter and was divided into 1/2- and 1-in. segments by stainless steel screens so that each of the segments could be removed separately. The gases leaving the packed bed were filtered by three AEC type filter media disks, 1.5 in. in diameter, mounted in series. The filters could be removed from the apparatus separately.

After each experimental run, the plutonium that had been deposited on the bed segments, filters, mixer, and other solid surfaces was dissolved by submerging each of the separated units in a measured volume of 10% nitric acid plus 0.01% wetting agent (Aerosol) for 24 hr. The solution was then mixed and sampled for analysis of plutonium or uranium.

The average hydrolysis rates of plutonium hexafluoride in the dilute gas stream, computed from the data on the individual bed segments, ranged from 4×10^{-7} to 1×10^{-1} mg plutonium/(cm²)(hr). These data were treated by the same computer program that had been used for calculating the constants in the rate equation for the UF_6 hydrolysis (ANL-7020, p. 129). The best rate equation for the PuF_6 hydrolysis was found to be:

$$r = \frac{53.5 p_{\text{PuF}_6} p_{\text{H}_2\text{O}}}{1 + 142 p_{\text{PuF}_6} + 1.9 p_{\text{HF}}}$$

¹¹ Kessie, R., and Ramaswami, D., Removal of Plutonium Hexafluoride from Cell Exhaust Air by Hydrolysis and Filtration, ANL-7066.

where r = reaction rate, $\text{mg Pu}/(\text{cm}^2)(\text{hr})$

p = partial pressure of subscripted component at the solid surface, mm Hg .

The relative error between the rates from the correlation and the measured rates was $\pm 81\%$. This form of the rate equation does not correlate the PuF_6 data as well as it did the UF_6 data but, considering the wide range of the partial pressures (0.06 to 5.6 mm Hg for water vapor, and 0.00001 to 0.02 mm Hg for PuF_6) used in the experimental program, the equation is regarded as a reasonable empirical correlation. The ratio of PuF_6 to UF_6 reaction rates at similar concentrations of reactants, as indicated by the correlations, ranges from 0.28 to 2.4. The extent of departure of this ratio from unity is not highly significant when one considers the relative error between the rates from the correlation and the observed rates.

The results from experiments involving hydrolysis of mixed hexafluorides showed that the rates of hydrolysis of the component hexafluorides in the mixture differed from the rates obtained when the hexafluorides were individually hydrolyzed. In experiments in which air of low moisture content was used, the hydrolysis rates for PuF_6 in the mixture were markedly higher than rates obtained when PuF_6 alone was hydrolyzed. On the other hand, hydrolysis rates for UF_6 in the mixture were lower than rates obtained with UF_6 alone. In the mixed gas, the hydrolysis rates for PuF_6 were always higher than the hydrolysis rates for UF_6 . The data indicate that the hydrolysis mechanism for mixed hexafluorides is more complex than that expected on the basis of mechanisms for individual hexafluoride species.

The hydrolysis rates of dilute plutonium and uranium hexafluorides suggest that, in a release of dilute PuF_6 alone or of a mixture of PuF_6 and UF_6 into a glovebox atmosphere, the quantity of plutonium passing through a series of filters will be less than the quantity of uranium from a UF_6 release under similar conditions.

b. Comparison of Results from Small-scale Experiments and a Large-scale Release

On March 12, 1965, a $3/4$ -in. dia. fluorethene tube containing 5.7 g of PuF_6 burst and the entire content of the tube was released into a ventilated glovebox. The release of PuF_6 to the glovebox atmosphere was rapid, occurring over a time interval much less than the air-residence time in the box (5.8 min). Therefore, the occurrence was considered to be an instantaneous release. Although the release was accidental, it provided an excellent opportunity to study the containment of PuF_6 in an alpha enclosure, especially since the glovebox and the glovebox filters had not been previously

exposed to plutonium. Complete details of the analysis of the release and the findings have been presented in a topical report.¹²

The ventilation air leaving the glovebox in which the release occurred was filtered by two banks of filters in parallel; each filter bank contained two AEC filters in series. The filtered air passed through a scrubber and then through the stack filter, which also contained two AEC filters in parallel, before discharge to the building exhaust system. After the gas passed through the stack filters, a portion of the gas stream was sampled by a stack monitor containing an alpha counter which measured the activity of material deposited on an integral filter. Following the release, a direct alpha count of the filter media indicated that the plutonium concentration in the exhaust gas had averaged 300 MPC (maximum permissible concentration) during the short period (7 min) of discharge. The total quantity of plutonium discharged from the stack was estimated to be $2.5 \mu\text{g}$. All attempts to detect plutonium at monitoring stations downwind from the release stack failed to show any plutonium above normal background levels.

The plutonium distribution throughout the filtering system was determined in order to evaluate the performance of the air-cleanup system and to compare the performance with the results of small-scale release experiments which had been designed to simulate large-scale releases.

The fraction of released plutonium which penetrated the AEC filters was within the range expected on the basis of results from the small-scale release experiments (see Table II-10). Comparison of these data indicates that the results obtained from the small-scale experiments can be used reliably to predict the behavior of large-scale releases.

TABLE II-10. Performance of AEC Filters during PuF_6 -release Accident and Small-scale Experiments

	Accidental Release	Small-scale Experiments
PuF_6 released (mg)	5700	1.5 to 25
$\text{PuF}_6/\text{H}_2\text{O}^a$	0.006	0.022 to 3.32
% of Pu penetrating the 1st filter	0.0031	0.0005 to 0.0016 ^b
Pu penetrating the 2nd filter (%) ^c	2 to 20	2 to 45 ^b
Fraction of released Pu which was discharged from last filter	6.7×10^{-7}	10^{-6} to 10^{-9b}

^aAverage mole ratio in release enclosure; source of water was moisture content of the contained air.

^bData for experiments where $\text{PuF}_6/\text{H}_2\text{O} < 0.1$.

^cBasis: Quantity of plutonium penetrating the first filter.

¹²Trevorrow, L. E., Kessie, R. W., and Steindler, M. J., Laboratory Investigations in Support of Fluid-bed Fluoride Volatility Processes. Part VIII. Analysis of an Accidental Multigram Release of Plutonium Hexafluoride in a Glovebox, ANL-7068.

4. Bench-scale Studies with Irradiated Fuels

A program demonstrating the fluid-bed volatility process with irradiated fuel materials is in progress. Experiments are being conducted in a $1\frac{1}{2}$ -in. dia. reactor installed in the Senior Cave Facility of the Chemical Engineering Division. Irradiated fuels of various types including high-enrichment uranium-Zircaloy (U-Zr) and uranium-aluminum (U-Al) alloys, low-enrichment uranium oxide and mixed uranium-plutonium oxides have been processed. The aims of the program are to obtain information regarding (1) the distribution of fission products (F.P.) during the various process steps, (2) decontamination factors that may be realized, and (3) the effects, if any, of irradiation and the presence of fission products on uranium recovery. Preliminary results from six runs using irradiated U-Zr and U-Al alloy fuel materials are presented below.

a. Experimental Procedure and Equipment Specifications

Two basic steps are involved in the processing of U-Zr and U-Al alloy fuels. In the first step, the fuel is reacted with hydrogen chloride gas to form volatile chlorides of zirconium or aluminum which separate from nonvolatile uranium chloride (UCl_3). In the next step, uranium is removed from the reactor as UF_6 by fluorination and is collected on sodium fluoride pellets. Further purification of the collected UF_6 may be achieved by desorption and collection of the UF_6 in cold traps.

In this facility, the volatile ZrCl_4 (or AlCl_3) generated in the first step is collected as a solid in a condenser.¹³ The noncondensables pass through a glass wool filter, which removes entrained particulate fines, and then into the scrubber wherein HCl in the process gas stream is removed by contact with the water-wetted packing. Any entrained water is collected in a de-entrainment trap before exhausting the process off-gas to the cave stack.

Fluorination of the UCl_3 in the reactor and packed-bed filter (see Fig. II-23) is carried out with a mixture of fluorine and nitrogen. The UF_6 produced passes through a packed-bed filter, then through trap NaF-1, which is maintained at 400°C to remove fission products, and is sorbed on NaF pellets in trap NaF-3 at 100 to 150°C . Residual UF_6 in the gas stream from trap NaF-3 is sorbed in trap NaF-4, which is maintained at room temperature. Fluorine in the gas stream is reacted with activated alumina. Remaining gases are discharged to the cave exhaust system.

¹³For plant applications the condenser would be replaced by a pyrohydrolysis reactor to convert the metal chlorides to oxides and to regenerate HCl for recycle to the first process step. The oxide waste produced is suitable for long-term storage.

Samples of the alumina in the reactor and packed-bed filter, the NaF traps, and fluorine trap are obtained for analysis by subdividing each bed to about a 20-g sample using a Riffle Sampler.¹⁴ The sample is then ground or milled to a fine powder. A few grams of the final material are submitted for analysis.

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✓ Fig. II-23. The Distribution of Uranium and Fission Products Following Fluid-bed Volatility Processing of Irradiated 5-yr Cooled Uranium-Zircaloy Alloy

(The values are the averages for runs SCAZ-1 and -2 and are in percent of the total activity charged to the reactor.)

¹⁴Conforming to ASTM-D271.

The equipment size and loading specifications are given in Table II-11.

TABLE II-11. Equipment Size and Loading Specifications

Component	Size		Charge Materials	
	ID (in.)	Length (in.)	Description	Weight or Volume
Fluid-bed reactor	1.5	14	Alcoa T-61 alumina (nominal 28 to 100 mesh)	700 g
Disengaging chamber	4.5	12	-	-
Packed-bed filter section	2.5	6.5	Alcoa T-61 alumina (nominal 14 to 48 mesh)	900 g
Metal chloride condenser	5.0	16	-	-
Scrubber	4.0	5 ft	3-ft depth, 1/2-in. Raschig rings	20 liters (reservoir capacity)
NaF-1 and NaF-2 traps	2.5	26	1/8-in. NaF pellets	1000 g
NaF-3 and NaF-4 traps	2.5	14	1/8-in. NaF pellets	500 g
F ₂ absorption tower (three sections in series)	3.0	12/section	1/4-in. dia. activated alumina pellets	1000 g/section
Glass wool filter section	3.0	3	Pyrex wool filtering fiber (Owens-Corning No. 3950)	22 g

(1) Uranium-Zircaloy Fuels

Descriptions of the fuel and operating conditions for two experiments with U-Zr fuel cooled 5 years are given in Table II-12. The distribution of uranium and fission products for these runs is shown in Fig. II-23. It should be noted that for these two runs a UF₆ desorption step was not employed and that the product was collected in the NaF-3 trap, which contained NaF pellets at 100°C.

(2) Uranium-Aluminum Fuels

The operating conditions and descriptions of the fuel material for four runs with uranium-aluminum alloy are given in Table II-13. The results obtained for these experiments with relatively short-cooled fuel are given in Figs. II-24, II-25, and II-26. A desorption step was not employed in the first run (SCAA-1); however, this step was used in the other three runs (SCAA-2, -3, and -4).

TABLE II-12. Operating Conditions and Charge Specifications for Fluid-bed Volatility Processing of Irradiated Uranium-Zircaloy Alloy
(Runs SCAZ-1 and -2)

Charge Data					
Uranium-Zircaloy-2 alloy weighed 270 g, cooled 5 years, contained 4.9 g uranium and 3.3 g fission products. Original uranium enrichment, 93%.					
Hydrochlorination Step					
Reactor bed temp:	400°C	Superficial gas velocity:	0.54 ft/sec		
Packed-bed filter temp:	350°C		(at process conditions)		
HCl concentration (av.):	40 v/o	Total gas flow:	5 liters NTP/min		
Fluorination Step					
Time (hr)	F ₂ Conc (v/o)	Reactor Temp. (°C)	Packed-bed Filter Temp. (°C)	Total Gas Flow (liters NTP/min)	Reactor Bed Condition
0-1½	8	250-475	270-425	5.5	Fluidized
1½-2	8-75	475-500	425-460	5.5	Fluidized
2-4	75	500	460-485	1.0	Static

TABLE II-13. Operating Conditions and Charge Specification for Fluid-bed Volatility Processing of Irradiated Uranium-Aluminum Alloy

<u>Charge Data</u>					
Runs SCAA-1 and -2. Uranium-aluminum alloy weighed about 107 g, cooled 7 months, contained about 4.3 g uranium and 4.3 g fission products. Original uranium enrichment 93%.					
Runs SCAA-3 and -4. Both irradiated and nonirradiated uranium-aluminum alloy charged. The irradiated alloy weighed about 37 g, cooled 3 months, and contained about 1.7 g uranium and 1.7 g fission products. The nonirradiated alloy weighed about 60 g and contained 2.2 g uranium.					
<u>Hydrochlorination Step</u>					
<u>Runs SCAA-1, -2, -3, and -4</u>					
Reactor bed temperature range:	220-250°C				
Packed-bed filter temperature range:	180-250°C				
Average HCl Concentration:	20 v/o				
Total gas flow:	7.1 liters NTP/min				
<u>Fluorination Step</u>					
<u>Runs SCAA-1, -2, -3, and -4</u>					
Time (hr)	Reactor Bed Temp. (°C)	Filter Bed Temp. (°C)	F ₂ Conc (v/o)	Total Gas Flow (liters NTP/min)	Reactor Bed Condition
0-1	260	250	5	6	Fluidized
1-2	260-505	250-485	10	6	Fluidized
2-4	505-520	485-505	75	1	Static
<u>Desorption Step</u>					
<u>Runs SCAA-2, -3, and -4</u>					
Uranium Holdup Traps NaF-2 or NaF-3		Cold Traps	F ₂ Conc	Gas Rate	
25 → 400°C		-70°C	75 v/o	2 liters NTP/min

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Fig. II-24. The Distribution of Uranium and Fission Products Following Fluid-bed Volatility Processing of Irradiated, 7 mo Cooled Uranium-Aluminum Alloy, Run SCAA-1. (Values are given as percent of the total activity charged to the reactor.)

108-9481

Fig. II-25. The Distribution of Uranium and Fission Products Following Fluid-bed Volatility Processing of Irradiated, 7 mo Cooled Uranium-Aluminum Alloy, Run SCAA-2. (Values are given as percent of the total activity in the fuel alloy charged to the reactor.)

108-9483

Fig. II-26. The Distribution of Activities Following Fluid-bed Volatility Processing of Irradiated, 3-mo Cooled Uranium-Aluminum Alloy, Runs SCAA-3 and -4. (Values given are the averages for two runs and are in percent of the total activity charged to the reactor.)

b. Discussion of Results and Conclusions

The removal of uranium from the reactor and filter beds for all runs with irradiated uranium-Zircaloy and uranium-aluminum alloys was similar to that found in processing nonirradiated fuel alloys. Apparently, the results obtained for removal and recovery of uranium in the bench-scale and pilot-plant work with nonirradiated alloy fuel materials can be validly applied to irradiated fuels.

It was observed that during the hydrochlorination step the fission products cerium, cesium, strontium, and ruthenium were essentially nonvolatile under the conditions employed. The elements that exhibited slight volatility (<10%) were antimony, tellurium, and technetium. The predominantly volatile species (>50%) were zirconium, niobium, and krypton. Krypton was monitored in the cave stack with a beta counter calibrated for

⁸⁵Kr. The observed amount of krypton released in the process off gas agreed fairly closely with the calculated krypton input to the reactor, indicating that the bulk of the krypton was released to the stack during hydrochlorination. Iodine was found to volatilize completely during the hydrochlorination step. A caustic scrubber was successful in effecting the removal of iodine from the process off-gas stream.

The distribution of the fission product elements following the fluorination step showed that cerium, cesium, and strontium are essentially nonvolatile and are retained on the reactor and filter beds. Ruthenium was also nonvolatile; less than 1% volatilized and collected in the fission product trap. The fission products which were found to be predominantly volatile (>50%) were molybdenum, technetium, and tellurium. The complete removal of tellurium from the process off-gas during the fluorination step was effected by the use of an activated alumina trap. Sufficient analyses were not performed to establish the complete behavior of neptunium; however, 21% of the neptunium in the charge was found with the uranium product. The use of a MgF_2 -containing trap (runs SCAA-3 and -4) was not successful in removing volatile neptunium or technetium from the UF_6 stream.

There is reason to believe that the reported cesium and gross gamma content of the alumina bed material may be low owing to losses during analysis. Therefore, the material balances for fission products may be higher than reported.

The uranium decontamination factors observed in the six runs are compared in Table II-14. It can be seen that the addition of a UF_6 desorption step, in general, increases the decontamination factors by one or two orders of magnitude. The removal of technetium from the UF_6 product, however, is not improved by this technique. The increase in the decontamination factor for molybdenum from 5 (run SCAA-1) to 44.6 (run SCAA-2) is due to increasing the temperature of the sodium fluoride product trap (NaF -3) from 100 to 150°C. By increasing the temperature of the trap, most of the molybdenum hexafluoride passes through the trap while UF_6 is sorbed. This technique for separating MoF_6 from UF_6 has been employed at ORNL.¹⁵

Gamma spectrometric analyses of the uranium product from the last two runs (SCAA-3 and -4) showed that the preponderant gamma activity in the uranium product was due to the uranium isotope ²³⁷U. This indicates that by the use of sorption-desorption techniques a uranium product with high decontamination levels can be achieved in the processing of alloy fuels by the fluoride volatility process.

¹⁵Chemical Technology Division Annual Progress Report for the Period Ending May 31, 1964, USAEC Report ORNL-3627, p. 32, 1964.

TABLE II-14. Uranium Decontamination Factors (DF) Obtained by Fluid-bed Volatility Processing of Irradiated High-enriched Alloy Fuels

Activity	Decontamination Factor ^a					
	DF Based upon U and FP Collected on NaF in Trap III			DF Based upon U and FP Collected in the Cold Traps		
	Fuel Cooled 5 yrs		Fuel Cooled 7 mo		Fuel Cooled 3 mo	
	SCAZ-1	SCAZ-2	SCAA-1	SCAA-2	SCAA-3	SCAA-4
Gross γ	5×10^4	2×10^4	5×10^3	2×10^5	2×10^7	3×10^7
Gross β	4×10^4	6×10^3	3×10^4	2×10^5	2×10^6	1×10^6
Ce			7×10^4	3×10^6	3.5×10^7	7×10^6
Sr			9.5×10^3	5×10^6	1×10^7	1×10^7
Cs	5×10^4	2×10^4	3×10^4	3×10^6	4×10^6	4×10^6
Ru	2×10^4	8×10^3	2×10^4	5×10^3	7×10^5	5×10^5
Sb	3×10^3	2×10^4	1×10^3	4×10^5	3.5×10^5	7.5×10^5
Zr			5×10^3	4×10^6	1×10^8	3.5×10^7
Nb			3×10^3	1×10^6	7×10^7	1×10^7
Tc			1.5	3	2	0.5
Mo	4	8	5	45		
Te	1.3	1.3	7×10^2	6×10^4		
Np					3.5	1.3
Pu					6×10^4	3×10^4

^aDecontamination factor = $\frac{\text{activity per gram U in the fuel charge}}{\text{activity per gram U in the product trap}}$.

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

Fluidization of fine particles, which is utilized in the fluorination of $\text{PuO}_2\text{-U}_3\text{O}_8$ fines and in the preparation of particulate nuclear fuel, continues to be studied. Previous studies (ANL-7020, p. 148) established that, by the addition of coarse particles to a bed of fine particles, fluidization of fine particles was improved. It was also observed that better heat transfer may be achieved by adding coarse particles to a bed of fines.¹⁶ However, in fluid beds with large differences in particle size and density, particles tend to segregate and the fine particles are readily elutriated from the fluidized bed since the fluidizing gas velocity exceeds their free fall velocities. A research program is under way to investigate the behavior of fine particles in fluidized-bed systems. Included in this program are studies concerning the distribution of fines in fluidized beds, the effect of the presence of fines on bed expansion, the rate of elutriation of

¹⁶Baerns, Manfred G., The Effect of Interparticle Forces on the Fluidization of Fine Particles, ANL-7086, August 1965.

fines from fluidized beds, and methods for removing fines from the gas stream and returning them to the fluidized bed.

Also in progress is an investigation of the mechanisms of heat and mass transfer in fluidized beds. Fundamental to eliciting these mechanisms is the residence time of particles at the transferring surfaces in the fluid bed, such as walls and particles undergoing reaction. Theoretical and experimental investigations have continued in order to determine the statistical distribution of particle residence times at walls in contact with a gas-fluidized bed.

1. Segregation Studies

Fluidized beds of particles with large differences in particle size and in density tend to segregate; the ease with which the materials segregate depends on factors such as particle size, shape, density, size range, and cohesiveness. On the other hand, particles having similar physical properties and irregular shapes may show little tendency to segregate. Since the particles of uranium and plutonium compounds processed by fluid-bed fluoride volatility techniques are fines and usually have physical properties that differ from those of alumina used as the inert fluid-bed material, a series of tests were made to determine the manner in which uranium fines are vertically distributed in a fluidized bed of alumina.

The uranium fines segregation tests were made in a 2-in. ID, 6-ft long Lucite column with sampling ports at 4-in. intervals. The fluidizing gas was humidified nitrogen, and the superficial gas velocity was 1.0 ft/sec. A porous metal plate served as the gas distributor and fluid-bed support. The fine particles used in these studies were -325 mesh particles of U_3O_8 which contained a small quantity of UO_2F_2 . A weighed portion of the fine particles was thoroughly blended with nominal 48 to 100 mesh alumina bed material prior to the test to give a mixture containing 40 w/o U_3O_8 fines. The static height of the bed was about 22 in. The bed was fluidized, and bed samples were taken from ports at various elevations after 5, 10, 15, and 60 min of fluidization. The samples were analyzed by leaching the uranium fines from a weighed sample with nitric acid and weighing the dried alumina residue.

The results of the tests revealed no distinct separation of the uranium fines and coarser alumina, although there was a variation in fines concentration with height. Fine particles were more concentrated at the top and bottom portions of the bed than at the center. These tests indicate that, under the conditions of the tests, a satisfactory distribution of fine particles for fluorination reactions would exist in the bed, and that if a portion of the bed became depleted of uranium by fluorination, fines would be transported into the depleted portion.

2. Bed Expansion Studies

The effect of the addition of fine particles to a bed of coarser particles on the expansion of a fluidized bed was studied in the 2-in. ID Lucite column. Accurate knowledge of this property of the fluidized bed is of practical interest, since in process applications it is required that the fluidized bed be confined to the reaction zone and not be expanded into the disengaging chamber, which is a larger diameter section at the top of the reaction zone.

Three tests were performed to measure bed expansion, using the fine and coarse particles employed in the studies on particle segregation. The tests involved measurements on (1) alumina alone, (2) alumina mixed with uranium fines, and (3) alumina in which UO_2 pellets were immersed. The tests consisted of measuring bed heights of the three different types of beds at various gas flow rates. Bed expansion as a function of gas velocity is shown in Fig. II-27. The bed expansion was represented fairly well by straight lines within the range of data obtained, although bed expansion is not generally considered a linear function of gas velocity. The data indicate that in all three cases the bed expansion increases uniformly in a linear manner from the point of incipient fluidization (minimum fluidization velocities, v_{mf} , are shown in the figure). The static height (16 in.) of the mixture

of uranium fines and alumina was less than the additive static heights (total of 19.2 in.) of the separate fines and alumina fractions because the small particles filled the void spaces in the bed of the coarser alumina particles. This effect continued over the range of gas velocities used, as evidenced by the parallel curves for the cases of alumina with and without fines.

Fig. II-27. The Effects on Fluidized Bed Expansion of Addition of U_3O_8 Fines and UO_2 Pellets to Alumina. Fluid-bed column: 2-in. ID Lucite column.

Another result of process interest is the lowering of minimum fluidization velocity from 0.18 ft/sec with alumina alone to 0.09 ft/sec in the presence of UO_2 pellets and to 0.06 ft/sec in the presence of uranium fines.

3. Elutriation and Filter Blowback Studies

In the fluid-bed fluoride volatility processing of UO_2 fuels, several operations are performed in fluid-bed equipment wherein fine particles (<200 mesh) are produced. The

production of a large quantity of this fine material greatly affects the behavior of the fluidized bed. During the processing steps a fraction of this fine material is elutriated from the fluid bed and collected on filters located in a cooler zone above the fluid bed. During fluorination it is highly desirable to have a maximum amount of the uranium-plutonium fines in the fluid bed. This may be achieved by reducing the rate of elutriation and by frequent blowback of the filter by a reverse flow of gas (nitrogen) through the filters.

Recent elutriation studies have been aimed at the determination of the optimum size distribution of coarse alumina particles which, when mixed with fine particles, would maximize the residence time of the fine particles in the fluidized bed and would, also, provide high rates of heat and mass transfer. Tests were made to determine the effect on the rate of elutriation of (1) concentration of nickel fines (stand-in for uranium fines) and (2) particle size distribution of alumina in the fluidized bed. These tests were performed in a 3-in. ID brass column, 6 ft long. To minimize effects of static electricity, the fluidizing gas, air or nitrogen, was humidified and the brass column grounded. The fluidizing gas was distributed by a porous metal plate at the bottom of the column. The elutriated fines were filtered from the off-gas and collected in a separate chamber adjacent to the fluid-bed column. A 9-in. long, $1\frac{3}{4}$ -in. wide bayonet filter of sintered Inconel was located in the chamber. Elutriation rates were calculated from the weights of particles collected in the filter chamber during periodic time intervals (5 min).

The superficial velocity of the fluidizing gas in these studies was 1.5 ft/sec (25°C, 1 atm). The initial concentrations of nickel fines (average particle diameter of $22\ \mu$) in the alumina beds ranged from 4.1 to 50 w/o. Alumina (Type T-61 tabular alumina, manufactured by Alcoa) with two size distributions, nominal 48 to 100 mesh (average particle diameter of $165\ \mu$) and -80+170 mesh (average particle diameter of $130\ \mu$), was used in the various tests. The static bed height was ~13.5 in. for each test.

The elutriation rate, defined as the rate of change of the ratio of the concentration of fines at any time to the concentration of fines initially present, decreased with increase in initial fines concentration in the bed (see Fig. II-28). This behavior was similar for both sizes of alumina used as the fluidized-bed material. The rates of fines elutriation from the 130- μ dia. alumina were lower than from the 165- μ dia. alumina.

Size distributions of samples of elutriated fines, taken after various times of elutriation for the run with an initial fines concentration of 8.3 w/o in the 165- μ dia. alumina, were determined by Coulter Counter analysis. The average particle diameter of the elutriated fines increased with time. Description of the elutriated fines by the logarithmic normal

distribution (i.e., the logarithm of the particle diameter is normally distributed) appears to be a useful means for characterizing the size distribution of these fines in development of the process kinetics.

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Fig. II-28. Effect of Initial Fines Concentration in a Fluid Bed on Rate of Elutriation. Air Velocity: 1.5 ft/sec; 3-in. ID brass column; 48 to 100 mesh alumina; and 22- μ dia. nickel fines. Curve labels indicate initial concentrations of fines.

A mathematical model was derived for determining the average concentration of fines in the fluid bed as a function of blowback frequency and elutriation rate. Knowledge of this relationship will be useful when deciding blowback frequencies for fluidized beds. It was assumed that elutriation can be described by a first order rate law, and that all elutriated fines are collected on the filter and, after a blowback, returned to the bed. Depletion of fines by chemical reaction was neglected. From the first order rate law, the change in fines concentration with time, t , in the bed is described by:

$$\frac{dC}{dt} = -kC \quad (1)$$

where C is the concentration of fines in the fluid bed and k is the elutriation rate constant, min^{-1} .

Integrating with the boundary condition of $C = C_0$ at $t = 0$ yields:

$$\frac{C}{C_0} = e^{-kt} \quad (2)$$

During this period the average fines concentration, $\bar{C}$, in the bed is found from

$$\bar{C} = \frac{\int_0^t C dt}{\int_0^t dt} = \frac{\int_0^t C_0 e^{-kt} dt}{t} = \frac{C_0}{kt} [1 - e^{-kt}] \quad (3)$$

This model predicts that, for U_3O_8 fines with an elutriation rate constant, k , of $\sim 0.03 \text{ min}^{-1}$, blowback frequencies of one every 4 and 8 min result in average concentrations of 96 and 87% of the original amount of fines in the bed, respectively. More frequent blowback of the filters would assure higher fines concentration in the bed, but this operation would significantly dilute the process gas with nitrogen during periods of recycle fluorination.

4. Particle Residence Times at Surfaces in Gas-fluidized Beds

Better understanding of the heat and mass transfer mechanisms in fluidized beds is needed for accurate design of processing systems. Of fundamental importance to the understanding of these mechanisms is knowledge of the residence times of particles at the transferring surfaces in the bed, such as walls and particles undergoing reaction.

Theoretical and experimental investigations have been continued to measure the statistical distribution of particle residence times at walls in contact with a gas-fluidized bed. The residence time distribution, $f(\theta)$, is defined so that $f(\theta)d\theta$ is the fraction of those particles which reside at the surface for a time between θ and $\theta + d\theta$.

As a result of the current theoretical studies, a formula has been derived relating the residence time distribution directly to the autocorrelation of the frame-to-frame statistical fluctuations in total counts of tagged (black) particles at a repeatedly photographed test surface. This formula has been used to estimate average residence times and average Nusselt numbers (a function of heat transfer properties) in two systems.

In the first system, particle residence times were obtained from a known, theoretical distribution which was simulated on a digital computer. The computer then determined a sequence of particle counts from these residence times, and the derived formula was applied to back-estimate properties of the theoretical distribution. In the second system, the particle residence times were determined experimentally using a 4-in. dia. gas-fluidized bed and were compared with residence times estimated by the autocorrelation method. The fluid-bed particles were 1/8-in. dia. cellulose acetate spheres, of which approximately 5% were black, and the remainder white. A test area on a flat, Lucite window was photographed at 20 frames per second. The average residence time of the black particles was found, by direct analyses of the frames, to be between 2.9 and 3.5 sec, while the autocorrelation method estimated 3 to 3.25 sec. Only ranges may be given in this case because of the small total number of particles involved; a significant increase in the number of particles analyzed was not feasible owing to the excessive man-hour requirement for the direct analyses. In addition, the average Nusselt numbers computed for the directly observed distribution and for the autocorrelations agreed within 10%.

On the basis of these results, it is concluded that the autocorrelation technique is sufficiently accurate for the desired prediction of heat transfer coefficients, as well as for other possible applications not yet recognized.

The next phase of the project will be devoted to the construction of a system in which both the residence times, via the autocorrelation method, and the heat transfer coefficients can be measured at the same surface. It is hoped that the data from this project will result in an accurate correlation for prediction of heat transfer coefficients from surfaces in fluidized beds.

III. STUDIES AND EVALUATIONS

The studies and evaluations done within the Chemical Engineering Division are concerned with the feasibility and costs of projected applications of current research and developmental work. Such studies may show which step of a process should be modified in order that the process as a whole may be more economical. Or they may show that some particular step or technique has an economic advantage and that new ways of incorporating this step in other process applications should be sought. The scope and specific objectives of these studies and evaluations vary with the interests of the Division.

An analysis¹ was made of cost differentials among alternative cases in the processing of fast reactor fuels in conceptual facilities to be operated in about 1980. The conceptual plant components on which the processing costs were based comprised the processing plant, ultimate waste disposal, analytical laboratory, and auxiliary facilities. Flowsheets and plant designs were specified for each of three fuel types (metal, oxide, and carbide) and estimates made of capital and operating costs for each of three alternative types of processes: aqueous solvent extraction, fluid-bed volatility, and pyrochemical. For each of the above cases, three sizes of processing plant were considered: a close-coupled plant serving a 1000 MW(e) fast reactor, a close-coupled plant serving three 1000 MW(e) reactors, and a central processing plant serving ten 1000 MW(e) reactors in a radius of 1000 miles. The analysis included other fuel cycle costs in addition to those directly associated with processing: out-of-reactor fuel inventory and (in the case of central processing plants) shipping charges for spent fuel. A common set of technical and economic ground rules was adopted for the calculation of costs for the several cases.

A. Processing Requirements and Technical Ground Rules

1. A common fuel processing load was adopted as a reference specification for all cases (three fuels and three processes). This reference processing load is stated in Table III-1 in terms of average mass rate of fuel discharged from the reactor per day of full power operation. The specifications in the table were selected as typical ones, in the light of recent conceptual designs of 1000 MW(e) ceramic- and metal-fueled fast reactors.^{2,3} The average burnup of core fuel was specified as 10%, the

¹The full report of this study is to be published as Comparative Cost Study of the Processing of Metal, Oxide, and Carbide Fast Breeder Reactor Fuels by Aqueous, Volatility, and Pyrochemical Methods, ANL-7137.

²An Evaluation of Four Design Studies of a 1000 MW(e) Ceramic Fueled Fast Breeder Reactor. AEC Chicago Operations Office, COO-279, December 1, 1964.

³Link, L. E., Ayer, J. E., Hub, K. A., Mecham, W. J., Trice, V. G., Jr., and Weils, J. T., A Large Metal-Fueled Reactor Study. Part II. Core Design and Fuel Cycle. Presented at the Conference on Safety Fuels and Core Design in Large Fast Power Reactors, October 11-14, 1965, at Argonne National Laboratory.

reference value which may be achievable in practice in 1980. (At present, no clear superiority with respect to burnup for the three types of fuels has been established; burnups of at least 6% appear to have been achieved for all three types of fuels in irradiation tests.)

TABLE III-1. Specifications of the Reference 1000 MW(e) Fast Reactor
All Quantities Stated as Weight of Elements

Total Thermal Power, MW(e)	2500
Net Electrical Power, MW(e)	1000
Fraction of Total Power Generated in Core	0.85
Total Breeding Ratio	1.4

Initial Composition of Fuel, weight percent on metal basis:

Core

Depleted Uranium	78.0
Plutonium (239, 241)	15.0
Plutonium (238, 240, 242)	7.0

Blanket

Depleted Uranium	100.0
Core Fuel Burnup, Percent of Actinides	10.0
Blanket Fuel Burnup, Percent of Actinides	0.71
Plant Factor, Percent	80

Average Daily Rate of Fuel Discharge, kg per full power day:

Core

Depleted Uranium	15.66
Plutonium (239, 241)	2.91
Plutonium (238, 240, 242)	1.56
Fission Products	2.24

Blanket

Depleted Uranium	53.90
Plutonium (239)	1.053
Plutonium (240)	0.058
Fission Products	0.39

Other Constituents

18-8 SS Clad for Oxide and Carbide Fuel	12.0
V-20% Ti Clad for Metal Fuel	12.0
1.78% Ti as Alloy Constituent of Metal Core Fuel	0.405
Bond Sodium in Metal Core and Blanket	0.95

2. A plant factor of 80% was adopted as the reference value for both reactor and processing plant operation. This is in keeping with the usual commercial standards and with AEC guidelines.⁴

3. The product of the processes was the substance (oxide, carbide, metal) of the reactor core or blanket in a form suitable as feed for fabrication operations without further chemical conversions.

4. In the reference processes, fission product decontaminations were higher for the products of aqueous and volatility processing than for pyrochemical processing. In all processes, refabrication of the core fuel requires at least semiremote techniques because of the hard radiation from the fuel actinides themselves. Although an estimate of the costs of refabrication is beyond the scope of this study, a preliminary analysis of possible cost penalties for low-decontamination blanket processing is included in the complete report.¹

5. Cladding was removed by either chop-leach or by chemical de-cladding, depending upon which of these was most favorable to the respective reference processes.

6. The ultimate disposal of high-level-radioactive waste as solids was taken as the reference method. However, because of present uncertainty as to the cost of solidification of aqueous waste, its disposal costs were calculated on the basis of perpetual on-site storage of concentrated waste solutions, with the expectation that technical developments in aqueous waste disposal would ultimately permit solid storage at an equal cost.

7. As a preliminary assumption, a 1% processing loss was assumed for all cases.

8. Two cost elements of processing were omitted from this study, namely, site acquisition and development costs and liability insurance. The magnitude of associated costs was expected to be of the order of only a few percent of the total cost and these cost items were assumed to be matters of economic indifference in the comparison of costs.

B. Chemical Flowsheets

Conceptual flowsheets adopted in this study as a basis for developing cost estimates are considered representative of advanced aqueous, volatility, and pyrochemical processes that could be expected to be operational by about 1980. While each flowsheet is an assemblage of individual steps believed to be feasible in the light of laboratory and pilot plant data, none of the processes has been fully demonstrated with high-enrichment, high-burnup fuel.

⁴AEC Guide to Nuclear Power Cost Evaluation, TID-7025, Kaiser Engineers, 1962.

The aqueous processes adopted in this study are of the generic type referred to as a chop-leach solvent extraction method. However, many simplifications and optimistic assumptions were incorporated in this aqueous plant design compared to what is done in presently operating plants, particularly as regards the plutonium handling steps. An analysis of the process feasibility is included in the complete study.¹ The basic features of the aqueous processes are shown in Fig. III-1. The uranium and plutonium outputs from the solvent extraction system were converted to oxide in fluid bed denitration and reduction units. For metal and carbide fuel, tail-end process steps were added as shown in Fig. III-2.

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Fig. III-1. Principal Steps in the Advanced Aqueous Process for Oxide, Carbide, and Metal Fuels

108-9439

Fig. III-2. Pyrochemical Process for the Conversion of Oxide to Metal and Fluid-bed Synthesis of Carbide

The pyrochemical processes for metal and ceramic fuels are illustrated in Figs. III-3 and III-4. These processes were adapted from the melt refining and skull reclamation processes developed for the EBR-II fuel cycle facility at Idaho. (A newer process concept, originally developed for oxide fuel, termed the salt transport process, holds promise for further cost reductions for all fuels. However, this concept was not developed sufficiently to be selected as the reference process for the cost estimates in the present study.)

Fig. III-3

Principal Steps in the
Advanced Pyrochemical
Processes for Metal Fuel

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108-9339

Fig. III-4. Principal Steps in the First Generation Pyrochemical Processes for Oxide and Carbide Fuels

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Fig. III-7. Simplified Flow Diagram for Fluid-bed Fluoride Volatility Processing of Carbide Core and Blanket Fuel from a Fast Reactor

C. Plant Designs and Cost Sources

The plant design concept and cost sources for aqueous processing was mainly derived from the Idaho small-plant concept presented by Schneider⁵ et al. It is considered that this process concept offers the lowest costs of aqueous plants for comparison with advanced nonaqueous processes. The concept was modified to accommodate maintenance of the hot portion of the plant while retaining the requirement of an 80% plant factor.

The plant design concept and cost sources for the pyrochemical process was mainly derived from the EBR-II fuel cycle facility now operating at Idaho.⁶

The volatility equipment design concepts and cost sources were derived from ANL pilot plant experience. Plant concepts were selected to conform to those for the aqueous or the pyrochemical plants as far as was appropriate.

Models relating costs to complexity and size were employed to estimate costs for the processing plant and its auxiliaries for the several cases (stated earlier) in a consistent manner. The chief models and factors of estimation were based on methods developed by Stockdale,⁷ Zevnik and Buchanan,⁸ and Bauman.⁹

⁵Schneider, H., et al., A Study of the Feasibility of a Small-Scale Reprocessing Plant for the Dresden Nuclear Power Station, IDO-14521, April 1961.

⁶Hesson, J. C., Feldman, M. J., and Burris, L., Description and Proposed Operation of the Fuel Cycle Facility for the Second Experimental Breeder Reactor (EBR-II), ANL-6605, April 1963.

⁷Stockdale, W. B., Estimating Costs for Radiochemical Plants, in Cost Engineering in the Process Industries, edited by C. H. Chilton, McGraw-Hill Book Company, Inc., New York, p. 304 (1960).

⁸Zevnik, F. C., and Buchanan, R. L., Generalized Correlation of Process Investment, Chem. Eng. Progress 59, No. 2, 70 (1963).

⁹Bauman, H. C., Fundamentals of Cost Engineering in the Chemical Industry, Reinhold Publishing Corp., New York, 1964.

The basic design concepts and cost sources for interim storage of high-activity-level solid waste was taken from Blomeke et al.¹⁰ The shipping charge for the cooled waste was based on the study by Perona et al.,¹¹ and the charges for final burial on the study by Bradshaw et al.¹²

The provisional cost estimate of aqueous waste disposal by perpetual liquid care was patterned after the study by Stoller.¹³

In the cases of the central processing plants, out-of-reactor inventory and shipping charges for spent fuel were based on a study by Nelson.¹⁴ Because longer cooling of spent fuel increases inventory costs but lowers shipping costs, optimum cooling times were found for which the sum of inventory and shipping charges were a minimum.

Auxiliary facilities for which cost estimates were made in this study included "hot" and "cold" maintenance shops, warehouse, offices, and personnel convenience areas.

D. Economic Ground Rules

1. For each case of fuel type, process type, and plant size, estimates were prepared of the investment in process equipment and building and in auxiliary facilities and spare equipment based on requirements established for the flowsheets and processing specifications.

a. Twenty-five percent of the above investments in process plant and auxiliaries was added for construction overhead, including engineering. This overhead factor is based on the assumption that the plants as built are not the first of their type.

b. A one-time charge associated with plant startup was added in an amount equal to 25% of the total annual operating cost.

c. Working capital was added to the total investment as a non-depreciating item. It was charged as 5% of process building and equipment (including auxiliary facilities) plus 20% of the total annual operating cost.

¹⁰Blomeke, J. O., Perona, J. J., Weeren, H. O., and Bradshaw, R. L., Evaluation of Ultimate Disposal Methods for Liquid and Solid Radioactive Wastes. Part III. Interim Storage of Solidified Wastes, ORNL-3335, October 21, 1963.

¹¹Perona, J. J., Bradshaw, R. L., Blomeke, J. O., and Roberts, J. T., Evaluation of Ultimate Waste Disposal Methods for Liquid and Solid Radioactive Wastes. Shipment of Calcined Solids, ORNL-3356, October 18, 1962.

¹²Bradshaw, R. L., Boegly, W. J., Jr., Empson, F. M., Kubata, H., Parker, F. L., Perona, J. J., and Struxness, E. G., Ultimate Storage of High-Level Waste Solids and Liquids in Salt Formations, pp. 153-175, in Proceedings of the Symposium on Treatment and Storage of High-Level Radioactive Wastes held by the IAEA in Vienna, October 1962. International Atomic Energy Agency, Vienna, 1963.

¹³S. M. Stoller Associates, The Perpetual Care of High-Level Radioactive Wastes in New York State, NP-12486, October 12, 1962.

¹⁴Chemical Engineering Division Semiannual Report, July-December 1964, ANL-6925, pp. 261-263, May 1965.

d. Annual charges on capital were calculated as the sum of two components, the return on capital and the repayment of capital. The return of capital was calculated as 13% of the total capital investment. The fixed charge rate of 13%/year applied to the nondepreciated portions of the capital investment was taken from the AEC Guide to Nuclear Power Cost Evaluation⁴ and is based on the practices of investor-owned electric utilities. The components are as follows:

Minimum Return	6.75
Property Insurance	0.40
Federal Income Taxes	3.40
State and Local Taxes	2.45
	<hr/>
	13.0%/year

e. The out-of-reactor fuel inventory was charged as a separate nondepreciating item at the 13%/year rate. The fuel values employed were \$10/g for plutonium isotopes 239 and 241; no value was assigned to other actinides.

f. The other component of capital cost, the repayment of capital, was calculated as the sum of annual charges on sinking funds at the 6.75%/year interest rate to recover the original amounts of depreciating capital items over their respective economic lifetimes. The economic lifetimes were assigned as follows:

- 1) Process equipment operating in radioactive areas and for which decontamination was not considered practical: 2 years.
- 2) Process equipment and mechanical equipment in radioactive areas maintained fully remotely or for which decontamination was practical: 5 years.
- 3) Chemical and mechanical equipment in nonradioactive areas, including laboratory, office items, and mobile equipment: 15 years.
- 4) Major building structures (including shielding windows in remote cells): 30 years.
- 5) One-time charges associated with startup and construction overhead: 30 years.
- 6) Spare processing equipment: 30 years.

Capital items not included in the above capital repayment assignment are plant working capital and out-of-reactor fuel inventory, which are nondepreciating items.

g. Estimates were made of the annual operating costs of direct labor, indirect labor for maintenance and analytical laboratory operations, and materials (including reagents and utilities) based on specific plant requirements. The above labor requirements were first established in man-hours per operating day. This man-hour requirement was then multiplied by 1.4 to obtain the quantity of man-hours per day for the actual payroll, which includes allowance for such benefits as vacations and sick leave. An average annual payroll cost per man of \$12,000 was used, which includes fringe benefits.

h. Supervision and indirect labor (other than that specified above) was taken as 25% of direct labor.

i. Maintenance materials cost was taken as 20% of the sum of (a) total labor costs and (b) the annual charge for capital replacement for process equipment and building items.

j. An annual overhead charge for administration was taken as 15% of the sum of all the operating costs above.

E. Summary of Cost Results

Total annual costs were calculated for each alternative case as the sum of: (a) the total annual operating cost, (b) the annual amount for capital repayment, and (c) the annual return on capital investment. The electrical unit costs in mills/kW(e)-hr of fuel processed were calculated from the total annual costs for the annual electric energy production at 80% plant factor for the reference reactor power. The electrical unit costs are the measures of comparative cost and are summarized in Table III-2.

TABLE III-2. Unit Cost Summary

Fuel Type	Cost Component	Close-coupled 1000 MW(e) Plants			Close-coupled 3000 MW(e) Plants			Central 10,000 MW(e) Plants		
		Aqueous	Volatility	Pyrochemical	Aqueous	Volatility	Pyrochemical	Aqueous	Volatility	Pyrochemical
Metal	Processing	0.59	0.39	0.29	0.32	0.24	0.17	0.18	0.15	0.12
	Waste Disposal	0.15	0.09	0.06	0.12	0.08	0.05	0.10	0.08	0.05
	Inventory	0.17	0.12	0.12	0.11	0.06	0.06	0.109	0.079	0.079
	Shipping	-	-	-	-	-	-	0.055	0.071	0.071
	1% Loss	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>
	Total	0.93	0.62	0.49	0.59	0.40	0.30	0.46	0.40	0.34
Oxide	Processing	0.53	0.35	0.44	0.29	0.21	0.25	0.16	0.14	0.18
	Waste Disposal	0.15	0.09	0.09	0.12	0.08	0.08	0.10	0.08	0.07
	Inventory	0.17	0.12	0.12	0.11	0.06	0.06	0.109	0.079	0.079
	Shipping	-	-	-	-	-	-	0.055	0.071	0.071
	1% Loss	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>
	Total	0.87	0.58	0.67	0.54	0.37	0.41	0.44	0.39	0.42
Carbide	Processing	0.62	0.43	0.46	0.33	0.26	0.26	0.19	0.17	0.19
	Waste Disposal	0.15	0.09	0.09	0.12	0.08	0.08	0.10	0.08	0.07
	Inventory	0.17	0.12	0.12	0.11	0.06	0.06	0.109	0.079	0.079
	Shipping	-	-	-	-	-	-	0.055	0.071	0.071
	1% Loss	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>	<u>0.016</u>
	Total	0.96	0.66	0.69	0.58	0.42	0.42	0.47	0.42	0.43

The estimates of unit costs shown in Table III-2 for processing waste disposal, inventory, and for shipping of spent fuel, are those made in this study. The cost associated with the assumed 1% plutonium lost is shown to indicate its relative magnitude. No attempt is made in this study to make a cost evaluation of the three alternative fuel types. Such a comparison would necessarily have to include differences in reactor performance and in fuel fabrication techniques. For example, if credits for bred plutonium were assigned to each fuel specifically, they would not be equal, but a somewhat higher credit would accrue to metal fuel because of the higher breeding potential.

Because this study had the objective of elucidating cost differences and not predicting actual costs, the chief result is the quantitative estimate of the cost differences as provided by Table III-3, wherein the differences of the sums of the cost of processing, waste disposal, and out-of-reactor fuel inventory are presented in mills/kW(e)-hr with an estimate of the uncertainty of the unit cost differences. This uncertainty was derived from an assumption that the precision of estimates of processing equipment and building costs in this study would be within $\pm 15\%$ of a mean of all estimates of the same type. This assumption is consistent with the evaluation by Nichols¹⁵ of the variances associated with various types of cost estimation categorized according to differing degrees of detail in the designs and estimates. An accuracy of $\pm 15\%$ is not claimed for any of the cases as an estimate of an actual plant cost, but only for the purposes of cost comparisons made in this study. The estimated uncertainties were used as a test of the significance of the cost differences for the various cases of comparison.

TABLE III-3. Summary of Unit Cost Differences (mills/kW-hr) for Alternative Processes

Fuel Type	Process Pairs Evaluated		Unit Cost Difference ^a for the Sums of Processing and Waste Disposal and Inventory, mills/kW-hr ^b		
			Close-coupled One Reactor 1000 MW(e)	Close-coupled Three Reactors 3000 MW(e)	Central Plant ^c Ten Reactors 10,000 MW(e)
Metal	Aqueous	Volatility	0.319 $\pm$ 0.133	0.174 $\pm$ 0.082	0.067 $\pm$ 0.055
	Aqueous	Pyrochemical	0.446 $\pm$ 0.124	0.271 $\pm$ 0.074	0.123 $\pm$ 0.050
	Volatility	Pyrochemical	0.125 $\pm$ 0.090	0.097 $\pm$ 0.059	0.056 $\pm$ 0.043
Oxide	Aqueous	Volatility	0.304 $\pm$ 0.121	0.169 $\pm$ 0.075	0.066 $\pm$ 0.051
	Aqueous	Pyrochemical	0.206 $\pm$ 0.130	0.129 $\pm$ 0.079	-d
	Pyrochemical	Volatility	-d	-d	-d
Carbide	Aqueous	Volatility	0.310 $\pm$ 0.139	0.166 $\pm$ 0.086	0.0611 $\pm$ 0.057
	Aqueous	Pyrochemical	0.279 $\pm$ 0.141	0.167 $\pm$ 0.085	-d
	Pyrochemical	Volatility	-d	-d	-d

^aUnit cost of Process A minus unit cost of Process B.

^bTo convert estimates to \$/kg multiply by 308.

^cDifference presented includes shipping costs for central plant only.

^dThe cost difference was judged to be not significant.

¹⁵Nichols, W. T., Capital Cost Estimating, Ind. Eng. Chem. 43(10): 2295-9 (1951).

From the differences of costs associated with processing in Table III-3, it is concluded that both the pyrochemical and volatility processing are significantly more economical than the aqueous processing for all fuel types for the two sizes of close-coupled processing plants. For the large central plant, the cost estimates also showed that the non-aqueous processes were more economical than aqueous processes for all fuels, but the cost differences were smaller and in some cases not significant by the test of significance applied in this study.

For oxide and carbide fuel, the cost differentials indicated that both volatility and pyrochemical processing were more economical than aqueous processing for the close-coupled plants. For the large central plant, volatility showed a significant cost advantage over aqueous processing. The cost differences between volatility and pyrochemical processing were not significant for the ceramic fuels.

For metal fuels, the greatest cost advantage was shown by pyrochemical processing for all three sizes of plants. This cost difference of pyrochemical processing with respect to both aqueous and volatility was significant for all plant sizes. Volatility processing was significantly more economical than aqueous processing for plants of all sizes.

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Fig. III-8. Sum of Estimated Unit Costs for Processing, Waste Disposal, and Out-of-reactor Fuel Inventory, and Shipping of Spent Fuel for Facilities Serving One, Three and Ten 1000 MW(e) Fast Reactors. Costs for shipping of spent fuel are included in the ten-reactor case only.

In Fig. III-8 is shown, for each fuel type and process, the combined unit cost for processing, waste disposal, out-of-reactor fuel inventory, and shipping of spent fuel as a function of the number of reactors served. The shipping charge is applied to the central plant but not to the close-coupled plants, and therefore the cost comparisons in this figure do not show an effect of scale only.

In the cases shown in Fig. III-8, a reduction of about 40% of unit costs was found for the increase of size from the case of one close-coupled reactor to the case of three close-coupled reactors. This result appeared for all types of processing and for all fuels. For the further increase in size accompanying the transition to the case of the central, ten-reactor plant, the unit costs of the aqueous plant incurred a reduction of about 40%, a proportional reduction similar to that in the previous threefold increase in size for the close-coupled reactors. For the sum of cost components shown in the figure, the volatility and pyrochemical plants showed

no decrease or, in some cases, an increase in unit costs for the transition from the three- to ten-reactor plants. This result for the nonaqueous plants was due to the higher costs of shipping of shorter-cooled spent fuel. The shipping charges for all cases included estimates of property and liability insurance.¹ However, no attempt was made to evaluate the effects upon costs of possibly more stringent future shipping regulations.

For each fuel type shown in Fig. III-8, the results indicate a comparison between close-coupled and central processing plants, as follows:

1. Aqueous processing is not competitive with volatility or pyrochemical processing for close-coupled plants of the sizes considered in this study. If aqueous processing were chosen, the promising application would be only for quite large central plants.

2. Economic incentives are small for building a large central plant, since nonaqueous processing plants of about one-fourth the size offer the same unit costs for a much lower required investment.

The proper effect of throughput on processing and waste disposal costs--in the absence of inventory and shipping charges--can be seen in Figs. III-9, III-10, and III-11, in which processing (only) and waste disposal costs are presented separately for the three fuel types.

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Fig. III-9. Estimated Unit Costs for Processing Metal Fuel as a Function of Plant Throughput from One to Ten 1000 MW(e) Fast Reactors

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Fig. III-10. Estimated Unit Costs for Processing Oxide Fuel as a Function of Plant Throughput from One to Ten 1000 MW(e) Fast Reactors

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Fig. III-11. Estimated Unit Costs for Processing Carbide Fuel as a Function of Plant Throughput from One to Ten 1000 MW(e) Fast Reactors

For the unit costs of processing (only) shown in Figs. III-9, III-10, and III-11, the economics of scale are generally similar for the three processes. However, the reference pyrochemical process employs strictly batch operations for all process steps and shows a lower economy of scale for the large central processing than either aqueous or volatility, which processes employ continuous or semicontinuous process steps for major portions of their flowsheet operations. In Fig. III-10, the indicated cost differential shown between aqueous and pyrochemical processing for the 10-reactor case is not significant by the test of significance adopted in this study.

For the waste disposal unit costs shown in Figs. III-8, III-9, and III-10, there is in all cases only a small economy of scale because costs correlate closely

with the quantity of fission products. The somewhat greater economy of scale shown for the aqueous process is due to the component of cost for waste solution evaporators.

The cost estimates were made in sufficient detail that the sources of the cost differentials could be identified for the alternative processes. The basic source of cost advantage of the nonaqueous processes was due to the fewer process operations and the more compact processing equipment. This effect had several sources: (1) the much smaller amount or absence of diluents in fuel processing, (2) the simpler accommodation of fuel of high fissionable content and high burnup owing to the absence of reagents offering neutron moderation and suffering irradiation damage, and (3) the direct process yield of solid actinide products and of concentrated solid radioactive waste. Substantial savings in the cost of shielded process cells and buildings as well as in process equipment accrued to the more compact equipment.

Significant savings were also found for the nonaqueous processes in the charges for out-of-reactor inventory. For the purely batch operations that are characteristic of the pyrochemical process, the low inventory costs were due to the short cooling time and overall rapid processing schedule. For the volatility process, the short cooling time and the relatively small processing equipment allowed similarly low inventory charges.

Relative process costs are compared in Table III-4, where the sums of unit costs for processing, waste disposal, inventory, and shipping are shown as ratios for the cases of this study.

TABLE III-4. Estimated Cost of Nonaqueous Processing Relative to Those for Aqueous Processing^a

Fuel Type	Identification of Process Ratios	Ratios of Unit Costs		
		Close-coupled One Reactor 1000 MW(c)	Close-coupled Three Reactors Totalling 3000 MW(e)	Central Plant Ten Reactors Totalling 10,000 MW(e)
Metal	Volatility/Aqueous	0.65	0.69	0.88
	Pyrochemical/Aqueous	0.52	0.51	0.73
Oxide	Volatility/Aqueous	0.64	0.68	0.84
	Pyrochemical/Aqueous	0.76	0.75	0.95
Carbide	Volatility/Aqueous	0.67	0.71	0.90
	Pyrochemical/Aqueous	0.70	0.71	0.95

^aThe estimated cost considered in this table is the sum of the unit costs for processing, waste disposal, inventory, and shipping.

IV. MATERIALS CHEMISTRY AND THERMODYNAMICS

A. High Temperature Materials Development

This program is directed toward the development of nuclear reactor materials for use at high temperatures (1500 to 3000°C). Its objective is to collect basic data on the vaporization and chemical stability of potential fuels, i.e., the oxides, carbides, phosphides, sulfides, arsenides, and nitrides of uranium, plutonium, and thorium, and their solid solutions; and on the reactions of these materials with other substances. The collected data will be useful for selecting materials and should lead to a better understanding of nonstoichiometry in solids, an important high-temperature phenomenon. Experimentation is carried out quantitatively so as to yield thermodynamic and phase-diagram information by several methods of investigation which are mutually supporting.

During the past year, emphasis has been placed on determination of the phase diagram of the condensed uranium-urania system, the equilibria between the vapor and condensed phases of this system, and the oxidation-reduction equilibria of urania.¹ The specific objective of these studies is to obtain comprehensive thermodynamic data for compositions ranging from nearly pure uranium to slightly hyperstoichiometric urania. Some exploratory work to evaluate the effect of tungsten on the uranium-urania system was also carried out. A survey and evaluation of the pertinent literature on the urania-plutonia system have been initiated preparatory to experimental study of this system.

The principal experimental results obtained during this report period are presented below.

1. Uranium-Urania Phase Diagram

Determination of the phase diagram of the condensed uranium-urania system was obviously required to guide and interpret the thermodynamic experimentation. Prior to this work, the limited information^{2,3} available was quite contradictory. The present work yielded the diagram

¹The term urania will be used in Section IV-A to denote a solid phase of fluorite structure with composition unspecified; the symbol UO_2 will be used to denote stoichiometric uranium dioxide. The terms hypostoichiometric and hyperstoichiometric refer to the oxygen in urania; the symbols UO_{2-x} and UO_{2+x} denote hypostoichiometric and hyperstoichiometric urania, respectively.

²Blum, P. L., Guinet, P., and Vaugoyeau, H., *Compt. Rend.* 257, 3401 (1963).

³Cleaves, H. E., Cron, M. M., and Sterling, J. T., in "Progress Report for December 1944," CT-2618, February 1945, pp. 5-11.

shown in Fig. IV-1. This is qualitatively the same phase diagram presented previously,^{4,5} but is refined as to quantitative detail. The essential features are summarized below.

108-8842

✓ Fig. IV-1. Uranium-Urania Phase Diagram at Elevated Temperatures

A wide liquid miscibility gap exists at temperatures above $2470 \pm 25^\circ\text{C}$, the monotectic temperature in the system. At the monotectic temperature, the compositions in O/U atom ratio units of the three condensed phases in mutual equilibrium are: liquid uranium, 0.05 ± 0.01 ; monotectic liquid, 1.30 ± 0.10 , and hypostoichiometric urania, 1.61 ± 0.02 .

The combined results of oxide growth experiments⁶ (and a few isopiestic equilibrations in helium) show that between 1600 and 2470°C the hypostoichiometric urania phase boundary compositions can be expressed by the equation

$$\log X_U = 1.335 - 5608/T \quad (1)$$

in which X_U is the mole fraction of uranium dissolved in UO_2 at saturation and T is temperature in degrees Kelvin. (Note that $2X_U$ is equal to the oxygen deficiency, x , in the formula UO_{2-x} .) Equation 1 reproduces the experimental values for X_U to within 8.6% (standard deviation). From Eq. 1, the heat of solution of uranium in the saturated solid is 26.5 kcal/mole. The preliminary studies^{4,5a} of this system had indicated a strong upturn of the hypostoichiometric phase boundary between 2300 and 2500°C . This upturn (and the implication⁷ of phase transformations in this region) no longer appears valid within experimental uncertainty.

The liquidus data obtained between 1790 and 2436°C yields the equation

$$\log X_O = 6.267 - 2.820 \times \frac{10^4}{T} + 0.2021 \times \frac{10^8}{T^2} \quad (2)$$

⁴ANL-7020, p. 151, Fig. III-1.

⁵(a) A preliminary disclosure of the uranium-urania phase diagram was published in J. Phys. Chem. 69, 1788 (1965). (b) Also, a paper on this work was presented at the Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids, IAEA, Vienna, Austria, July 22-27, 1965, SM-66/81.

⁶ANL-7020, p. 161; ANL-6925, p. 171.

⁷ANL-7055, pp. 163-164.

in which X_O is the mole fraction of oxygen in oxygen-saturated liquid uranium. Equation 2 is in good agreement with the data obtained by Cleaves et al.³ at 1810, 1900, and 2000°C, and its extrapolation gives fair agreement with their data at lower temperatures, 1400 to 1720°C. From Eq. 2, the composition of the uranium-rich liquid (L_1) at the monotectic temperature, 2470°C, is given by $X_O = 0.047$ or O/U atom ratio = 0.049.

The melting temperatures of urania that are indicated in Fig. IV-1 are based on recent literature data. The melting point at the stoichiometric composition has been drawn to agree with the value $2805 \pm 15^\circ\text{C}$ obtained by

H. Hausner.⁸ Within experimental error, this is equivalent to the value $2790 \pm 20^\circ\text{C}$ reported by J. A. Christensen.⁹ However, the maximum melting point of urania is shown at 2850°C at a slightly hypostoichiometric composition to conform with the indications of two recent studies.^{10,11}

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Fig. IV-2. Total Vapor Pressure over the Uranium-Urania Two-phase System. (Five series of measurements of the equilibrium $U(l, \text{sat'd with } UO_{2-x}) + UO_{2-x}(s, \text{sat'd with } U) \rightleftharpoons U(g), UO(g), UO_2(g)$; total pressure calculated assumes a mean molecular weight corresponding to that for UO .)

2. Knudsen Effusion Vapor Pressure Measurements in the Uranium-Urania Two-phase System¹²

Knudsen effusion measurements of total vapor pressure for the two-phase region indicated as $L_1 + UO_{2-x}$ in Fig. IV-1 have been completed. The data shown in Fig. IV-2, are expressible by the least-squares equation

$$\log P(\text{atm}) = (7.250 \pm 0.146) - (27,024 \pm 255)/T \quad (3)$$

The total vapor pressure data together with the phase boundary compositions established in Part I can

⁸Hausner, H., J. Nucl. Mater. **15**, 179 (1965).

⁹Christensen, J. A., "Irradiation Effects on Uranium Dioxide Melting," HW-69234, March 1962, p. 7.

¹⁰Bates, J. L., in "Ceramics Research and Development Operation Quarterly Report, October-December 1964," HW-81603, 1965, p. 2.21.

¹¹Duncan, R. N., and Ferrari, H. M., Trans. Am. Nucl. Soc. **6**, 154 (1963).

¹²This work was carried out with interdivisional collaboration and is described in "A Thermodynamic Study of the Urania-Uranium System," by R. J. Ackermann, E. G. Rauh, and M. S. Chandrasekharaiah, ANL-7048, July 1965.

now be correlated with the transpiration measurements for single-phase urania (see Part 4, below).

3. Mass Spectrometric, Effusion Studies in the Uranium-Urania Two-phase System¹²

Mass spectrometric, effusion studies of the two-phase system yielded data which, when coupled to Eq. 3, lead to the following partial pressure equations¹³ for the primary vaporizing species U(g), UO(g), and UO₂(g):

$$\log P_U(\text{atm}) = (5.194 \pm 0.140) - (25,620 \pm 300)/T; \quad (4)$$

$$\log P_{UO}(\text{atm}) = (7.109 \pm 0.140) - (26,870 \pm 300)/T; \quad (5)$$

$$\log P_{UO_2}(\text{atm}) = (7.728 \pm 0.140) - (30,165 \pm 300)/T. \quad (6)$$

Equations 3, 4, 5, and 6 are plotted in Fig. IV-3 and illustrate that UO is the predominant gaseous species over the two-phase system.

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Fig. IV-3. Partial Vapor Pressures over the Uranium-Urania Two-phase System. (For the equilibrium $U(l, \text{sat'd with } UO_{2-x}) + UO_{2-x}(s, \text{sat'd with } U) \rightleftharpoons U(g), UO(g), UO_2(g)$; assumes relative ionization cross sections and multiplier efficiencies equal for all vaporizing species.)

¹³These equations have been substantiated within the indicated uncertainty by mass spectrometric, effusion measurements made in the Chemical Engineering Division (by J. W. Reishus).

4. Transpiration Measurements of Total Vapor Pressure of Uranium-bearing Species and of Oxygen Partial Pressure over Urania

Transpiration measurements of total pressure of uranium-bearing species and (simultaneously) of oxygen partial pressure over urania have progressed very satisfactorily. The measurements were conducted with H_2 - H_2O buffering carrier gas mixtures which served to fix the oxygen partial pressures and thereby control the composition of the solid urania. The accumulated data obtained between 2080 and 2705°K are presented in Figs. IV-4 and IV-5.

Fig. IV-4

Total Pressure of Uranium-bearing Species as a Function of Urania Composition

Fig. IV-5
Monatomic Oxygen Partial Pressure as a Function of Urania Composition

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The isotherms of total pressure of uranium-bearing species given in Fig. IV-4 are effectively total pressure curves since the contribution from the species $O(g)$ and $O_2(g)$ is negligible. The triangular end-points represent conditions at the hypostoichiometric urania phase boundary and were calculated by means of Eqs. 1 and 3. The filled circles are extrapolations of the effusion data obtained by Ackermann, Gilles, and Thorn¹⁴ for stoichiometric urania. Linear extrapolations of their low-temperature vapor pressures were used rather than their experimental values, because the evaporating solid urania probably became hypostoichiometric at the higher temperatures. Figure IV-4 indicates that the results obtained by the transpiration and two effusion studies are consistent. The isotherms have been extended into the hyperstoichiometric urania region, and it is of interest to note that minima occur close to the stoichiometric composition. It will be recalled from Part 3 that UO is the predominant gaseous species in the far hypostoichiometric region, and that its partial pressure decreases rapidly as the oxygen content of the solid increases. Conversely, the partial pressure of UO_3 increases as the oxygen content of the solid increases; UO_3 becomes the predominant gaseous species in the far hyperstoichiometric region. The minimum in the total pressure curves near $O/U = 2.00$ is in accord with the expectation¹⁵ that equilibrium congruent vaporization occurs near the stoichiometric composition.

The measured oxygen partial pressures in Fig. IV-5 (open points) were computed from the moisture content of the exit carrier gas streams. The computations are based on the equation

$$\log P_O(\text{atm}) = \frac{-26,240}{T} + \log \left(\frac{P_{H_2O}}{P_{H_2}} \right) + 6.38 \quad (7)$$

which is derivable from well-known equilibrium equations^{16,17} involving $H_2O(g)$, $H_2(g)$, $O_2(g)$, and $O(g)$. The filled points in Fig. IV-5, representative of conditions at the hypostoichiometric urania phase boundary, were calculated by means of Eq. 1 and the following equation¹² derived in the mass spectroscopic, effusion study of the uranium-uranium two-phase system (see Part 3, above):

$$\log P_O(\text{atm}) = 7.59 - 40,980/T. \quad (8)$$

¹⁴Ackermann, R. J., Gilles, P. W., and Thorn, R. J., *J. Chem. Phys.* **25**, 1089 (1956).

¹⁵ANL-7020, p. 154.

¹⁶Kubaschewski, O., and Evans, E. LL., "Metallurgical Thermochemistry," Pergamon Press, New York, N. Y., 1958, p. 339.

¹⁷Stull, D. R., and Sinke, G. C., "Thermodynamic Properties of the Elements," *Advances in Chemistry Series*, No. 18, American Chemical Society, Washington, D. C., 1956, p. 144.

The isotherms of monatomic oxygen partial pressure smoothly interconnect the single-phase transpiration work with the two-phase effusion work. Of considerable interest is the fact that the isotherms rise less steeply at the stoichiometric composition as temperature increases. This behavior has important consequences for defect model theories¹⁸ and implies that stoichiometric urania is intrinsically disordered, with equal numbers of vacancies and interstitials.

One may use the data of Fig. IV-5 to obtain a preliminary value of ~ -45 eu for the relative partial molar entropy of solution of diatomic oxygen in stoichiometric urania. The experimental values obtained by other workers in the range 900 to 1400°C have been summarized by Hagemark;¹⁹ they seem to fall in the range -7 to 20 eu. The value of -45 eu is in good accord with estimates²⁰ based on defect theory.

The transpiration work has been so productive that a second transpiration apparatus is being set up. The components are being assembled and will be used for studying the Pu-O and/or Pu-U-O systems.

5. The Congruently Vaporizing Composition of Urania

An investigation of the congruently vaporizing composition(s) of urania has been initiated to clarify certain discrepancies in the literature concerning the vapor pressure of UO_2 . The usual methods for the experimental determination of vapor pressure require that the composition of the condensed phase attains some fixed value and remains there during the course of the measurement. However, residual gases in a vacuum system (or, in the case of transpiration measurements, contaminants in the inert carrier gas) can be oxidizing or reducing, depending on temperature, and can affect the solid composition. On cooling the residual solid prior to analysis, the composition may change and thus differ from that of the evaporating solid. To avoid some of these difficulties, an extremely clean system is being used for the effusion measurements now in progress. The residual gases ($<10^{-9}$ torr at temperature) are being monitored by a quadrupole-type analyzer to assure that they are safely below values which could affect the composition of the residual solid. A single experiment that can be reported at this time yielded the congruently vaporizing (effusion) composition $\text{UO}_{1.997 \pm 0.003}$ at 2185°C.

There are certain consequences associated with a knowledge of the true value of the congruent composition. For example, if the true value of the O/U atom ratio were 2.000, it would mean that, aside from a slight

¹⁸Anderson, J. S., "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, Ch. 1, p. 6.

¹⁹Hagemark, K., KR-67, Institutt for Atomenergi, Kjeller Research Establishment, Kjeller, Norway, February 1964.

²⁰Thorn, R. J., and Winslow, G., Argonne National Laboratory, private communication.

correction for effusion conditions, the partial pressures of UO and UO_3 are exactly equal. This equality would permit calibration of mass-spectrometric ion intensities for these species in terms of absolute ratios of pressure. (At present, the conversion of ion intensity ratios to partial pressure ratios is somewhat uncertain because of assumptions concerning ionization cross sections and multiplier efficiencies.) Also, if the partial pressures of UO and UO_3 were equal at all temperatures, one could conclude that the enthalpies of vaporization are the same. Further measurements up to 2400°C will be performed to elucidate this matter.

6. Uranium-Urania-Tungsten Phase Diagram

Some exploratory work was carried out with the uranium-uranium-tungsten ternary system because tungsten has been suggested as a cladding for high-temperature uranium fuels and is used as a container or support material in experimentation. No evidence was found for the existence of intermediate phases. The general form reported²¹ for the binary W-U system, namely, that of a simple eutectic system, was confirmed. The binary W- UO_2 system appears to be the same type, with the eutectic close to the composition UO_2 . The liquid miscibility gap that was found to exist in the uranium-uranium system above 2470°C (see Fig. IV-1) was found to extend into the ternary system as well. The distribution of tungsten between the two immiscible liquids is strongly in favor of the metallic phase. The solubility of tungsten in solid uranium appears to be quite low; for example, at 2300°C the solubility in uranium of O/U atom ratio ≈ 1.75 is less than 0.5 w/o. The solubility of tungsten in liquid UO_2 is also reported²² to be low, about 0.5 w/o at 2900°C .

Further study of this ternary system is not planned in view of the very limited solubility of tungsten in uranium.

B. Preparation of Reactor Materials

1. Ceramic Fuels

Refractory compounds of uranium and plutonium, such as carbides, nitrides, and sulfides, show promise as fast reactor fuels capable of withstanding high temperatures and high burnups. Methods are being investigated for the preparation of these fuel materials, and the more promising methods are being used to provide materials for fabricability evaluations and irradiation testing.

Various fluidized-bed processes are currently under study for synthesizing these fuel materials. These processes employ a reagent in the

²¹Schramm, C. H., Gordon, P., and Kaufman, A. R., Trans. AIME 188, 195 (1950).

²²Weidenbaum, B., and Hausner, H., A.N.S. Trans. 8(1), 32 (1965).

fluidizing gas which reacts with finely divided uranium or plutonium to yield the desired product. An example of such a process is the fluidized-bed carburization of hydrided uranium or hydrided uranium-plutonium alloy with hydrocarbon-hydrogen gas mixtures to form UC or (U,Pu)C, respectively. The preparation of UC in a fluidized bed has been described previously (ANL-7020, p. 88). The present report discusses thermodynamic principles and processing techniques for the fluidized-bed method for preparing UC and (U,Pu)C; data on kinetics and product characteristics for these processes are also reported.

In the planning stage, and therefore not discussed in detail herein, are various other fluidized-bed processes for preparing UN, UC-UN, and UC-US from hydrided uranium and fluidizing gases containing nitrogen, methane, or H₂S or combinations of these reagent gases.

a. Thermodynamic and Rate Considerations in Carbide Synthesis by the Metal-Hydrocarbon Reaction

The objectives in current work to produce UC or (U,Pu)C are to obtain (1) a satisfactory reaction rate and (2) a stoichiometric product. The first objective is partially met by hydriding the metal or alloy to obtain a fine powder which will react rapidly at carburizing temperatures of 600 to 900°C. A satisfactory reaction rate, such that the reaction will be complete in about 5 hr, can then be obtained in a fluidized bed if the hydrocarbon partial pressure is high enough at the maximum fluidizing gas velocity to provide an adequate supply of carbon. Experience has shown that the maximum fluidizing gas velocity for hydrided uranium is about 0.5 ft/sec; above this velocity, loss of fines from the bed is excessive.

The minimum partial pressure of hydrocarbon gas for reaction of the gas with uranium metal is very low ($\sim 10^{-6}$ atm of methane at 1 atm hydrogen pressure and 800°C) and thus does not pose a problem. However, if the partial pressure of hydrocarbon gas is too high, UC₂ or carbon are formed under equilibrium conditions by the reactions

In the case of U-Pu carbides, the sesquicarbide is formed by the reaction

Equilibrium ratios of methane to hydrogen can be calculated from data on the free energies of formation of methane and the carbides. However, the free energy of formation of UC and UC₂ are known

only to about ± 1 and ± 2 kcal/mole,²² respectively, which results in a severalfold uncertainty in the equilibrium methane-to-hydrogen ratio. In addition, the free energy of formation of the mixed carbides is even in greater doubt. It is apparent, from the chemical equations, however, that the use of high pressures would have a beneficial effect in allowing higher methane concentrations without resulting in deposition of free carbon or formation of higher carbides. At feasible operating temperatures and pressures, the allowable methane partial pressure is approximately proportional to the square of the total pressure.

At a given temperature and a given fluidizing velocity (conditions which cannot be widely varied), the methane throughput in a fluidized-bed reactor would be proportional to the partial pressure of methane. By operating at 800°C, 10 atm total pressure, 0.4 atm methane partial pressure, and 50% methane utilization efficiency (which has been attained in fluidized-bed experiments), a carbide production rate of about 10 kg/hr could be attained in an 8-in. dia. reactor. Under the above operating conditions the product expected should be stoichiometric monocarbide.

Even if small amounts of higher carbides are formed during carburization because of a high methane-to-hydrogen ratio, these could be reduced to the monocarbide by a final hydrogen treatment in the fluidized bed. Such a reaction has been shown by Harden et al.²³ to proceed rapidly at 850°C and 1 atm hydrogen pressure.

In summary, thermodynamic and rate calculations indicate that stoichiometric UC and (U,Pu)C powders can be produced at high rates by the metal-hydrocarbon reaction in a fluidized bed.

b. Thermobalance Experiments

Thermobalance experiments are being conducted in order to obtain preliminary data on the kinetics of the reactions of hydrocarbon gases with uranium and uranium-plutonium alloys. Another objective is to determine whether these reactions can be limited to formation of the monocarbides by the use of the proper gas composition, as expected from the thermodynamic calculations discussed above.

A schematic diagram of the equipment is shown in Fig. IV-6. An Ainsworth recording thermobalance installed in a plutonium facility is being utilized for the study. A length of fine platinum wire, fastened to the

²²"The Uranium-Carbon and Plutonium-Carbon Systems," A Thermochemical Assessment, Technical Report Series No. 14, International Atomic Energy Agency, Vienna, 1963.

²³Harden, B. R., Read, J., and Sowden, R. G., The Reduction and Sintering of Hyperstoichiometric Carbides in Hydrogen, J. Nucl. Mater. 17(3), 203, (1965).

left-hand balance pan, suspends a platinum dish that holds the metallic sample in a quartz furnace tube. The furnace is a $2\frac{1}{2}$ -in. dia. split Hevi-Duty furnace with a capacity of 1400 watts.

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Fig. IV-6. Schematic of Thermobalance and Equipment for Preparation of (U, Pu)C

The procedure consists of reacting about 3 g of metal with hydrogen at about 250°C in the thermobalance to yield finely divided hydride, and then reacting the hydride at 650 to 750°C with a hydrogen-hydrocarbon mixture. The carburizing gas flow is begun as soon as hydriding is complete in order to prevent sintering as the temperature is raised. The change in weight of the sample is recorded as a function of time.

Experiments have been performed in which uranium-20 w/o plutonium alloy samples were reacted with propane-hydrogen or methane-hydrogen gas mixtures. The operating conditions and the composition of the products resulting from a number of these runs are shown in Table IV-1.

TABLE IV-1. Thermobalance Experiments on Preparation of Uranium-Plutonium Carbide by the Metal-Hydrocarbon Reaction

Conditions: Approximately 3 g of U-20 w/o Pu alloy hydrided and then reacted with hydrocarbon-hydrogen mixtures at the temperatures indicated below, a gas flow rate of 1.4 to 3.1 liters/min, and 1 atm pressure

Run No.	Reaction Conditions				Product Compositions			
	Temp (°C)	Reagent Gas ^a	Reaction Time (min)		Weight Gain (% of Theor ^c)	X-ray Analysis		Carbon ^d (w/o)
			To Completion ^b	Total		Major	Minor	
18	650	100 v/o C ₃ H ₈	100	100	140	XC ^e	-	5.68
24	670	1.6 v/o C ₃ H ₈	200	200	105	XC	-	4.72
23	700	3.2 v/o C ₃ H ₈	120	120	91	XC	-	4.80
21	700	4.2 v/o C ₃ H ₈	100	100	-	XC	-	4.62
42	750	1.0 v/o C ₃ H ₈	125	270	113	XC	X ₂ C ₃	4.69
29	750	1.5 v/o C ₃ H ₈	52 ^f	90	98	XC	-	4.07
30	750	1.5 v/o C ₃ H ₈	210	400	107	XC	X ₂ C ₃	4.88
36	750	1.5 v/o C ₃ H ₈	-	215	102	XC	X ₂ C ₃ , XO ₂	4.26
48	750	1.0 v/o CH ₄	180	370	108	XC	X ₂ C ₃ , XO ₂	4.17
46	750	2.0 v/o CH ₄	85	290	114	XC	X ₂ C ₃	5.04

^aThe balance is hydrogen.

^bEstimated time for completion of reaction measured from the time temperature reached 500°C until the rate of change of weight became very low.

^cBased on formation of pure (U, Pu)C.

^dCarbon content of stoichiometric (U, Pu)C is 4.80 w/o.

^eFace-centered cubic structure with lattice parameter of about 4.96 Å, a value which is within the range that might be expected for a uranium-plutonium monocarbide solid solution.

^fA second hydriding was performed, thereby reducing the particle size and resulting in a faster carburizing rate.

The differences in reaction rate as a result of variation of temperature and gas composition were not large as compared to random variations in the reactivity of the hydrided alloy. However, increasing the hydrocarbon concentration did appear to increase the reaction rate slightly. In the experiment in which 100% propane was used (run 18), the carbon content of the product was high, as would be expected from thermodynamic analysis. This was probably due to the deposition of free carbon on the (U,Pu)C particles, since dissolution of these products in nitric acid resulted in a residue (probably carbon) and X-ray diffraction patterns gave no indication of the presence of higher carbides. Most of the runs were conducted with a gas composition which would be expected to be in equilibrium with carbon or the sesquicarbide. However, only small amounts of sesquicarbide were formed in runs that were continued several hours beyond the completion of the formation of UC. The low rate of formation of (U,Pu)₂C₃ in the temperature range of interest is probably caused by a low rate of diffusion of carbon through the (U,Pu)₂C₃ reaction layer. This view is supported by the work of Takeuchi et al.²⁴ on the reaction of uranium with graphite. In their studies, the authors found that the low rate of formation of UC₂ was due to the low rate of diffusion of carbon through a UC₂ reaction layer.

It should be noted that small amounts of the sesquicarbide were formed, even with 1 v/o methane (the lowest hydrocarbon concentration used), when the experiments were continued beyond the time required to complete the monocarbide reaction. The formation of the sesquicarbide indicates that a methane concentration of 1 v/o is too high for equilibrium of the gas phase for the reaction:

Another experiment with the thermobalance was devised to determine whether (U,Pu)₂C₃ which was formed during carbiding could, subsequently, be reduced to the monocarbide with pure hydrogen. In this experiment U-20 w/o Pu was carbided with a 1 v/o methane-hydrogen mixture at a temperature of 750°C to the point where the rate of change of weight had been very low for several hours. The methane flow was then terminated, but the hydrogen flow was continued. The response was a continuing decrease in the sample weight indicating reaction of sesquicarbide with hydrogen to form methane.

Further experiments of this type are planned which should aid in determining the methane-hydrogen equilibrium concentrations for uranium-plutonium carbide mixtures.

Information on the comparative reaction rates of uranium, plutonium, and U-Pu alloy with methane and propane was also obtained in

²⁴Takeuchi, S., Honma, T., and Satow, T., The Reaction of Uranium with Graphite at High Temperatures, Trans. Japan Inst. Metals 5(2), 111-115 (April 1964).

thermobalance experiments. Although data obtained in a fluidized-bed reactor would be more pertinent, the relative rates obtained in the thermobalance are of interest until facilities for preparing (U,Pu)C in a fluidized-bed reactor are ready for operation.

The relative rates of reaction of the metals with propane-hydrogen and methane-hydrogen gas mixtures were evaluated from the initial rate of weight change in the carbiding portion of the experiments. The data are summarized in Table IV-2. The alloy apparently reacts more rapidly than unalloyed uranium or plutonium.

TABLE IV-2. Rates of Reaction of Actinide Metals with Hydrocarbon-Hydrogen Gas Mixtures

The samples were hydrided before beginning the carbiding reaction

Temperature: 750°C
Sample weight: 3 to 3.5 g

Reactant Gas			Initial Rate of Reaction [mg/(g)(min)]		
Hydrocarbon	v/o	C:H Atom Ratio	Uranium	Plutonium	U-20 w/o Pu
Propane	1.5	0.0215	-	-	0.57
Propane	1.0	0.0147	0.22	-	0.52
Methane	2.0	0.0098	0.56	0.28	0.81
Methane	1.0	0.0050	0.27	-	0.30

c. Preparation of Carbides in Fluidized Beds

The experimental program on preparation of UC and (U,Pu)C by the fluidized-bed technique is directed toward exploring the operating conditions which appear most likely to yield stoichiometric monocarbides at high production rates. These conditions are: temperature, 700 to 900°C; pressure, 5 to 10 atm; and fluidizing gas, 2 to 10 v/o methane in hydrogen. Installation of a 2½-in. dia. reactor which can be used with the above ranges of conditions for preparation of UC on a kilogram scale has been completed. This reactor is constructed of type 304 stainless steel and has a jacketed heating section which will be pressurized with argon in order to balance the internal pressure and thus minimize the stress on the heated wall. The off-gas from the reactor will be discarded in initial tests, but, at a later date, equipment to recirculate the gas will be installed. A similar reactor is being designed for operation in a helium-atmosphere glovebox for preparation of (U,Pu)C.

During this period of equipment construction, UC has been prepared in a 1½-in. dia. fluidized-bed reactor which is capable of operation at near atmospheric pressure and at temperatures up to 750°C. The purpose

of these experiments was to demonstrate that a stoichiometric monocarbide of low oxygen content could be obtained by the fluidized-bed technique. In these experiments 100 to 200 g of uranium rods were hydrided at 250°C to form fine UH_3 powder suitable for fluidization. This powder was dehydrided and converted to UC by heating at 600 to 750°C while fluidizing with a propane-hydrogen gas mixture. The temperature was maintained at the final level for 5 to 20 hr to complete the reaction.

In some of the early runs, oxygen impurity levels of 0.5 to 1.0 w/o were obtained. It is believed that the oxygen contamination was caused partly by oxygen leakage into the equipment and partly by oxidation of residual carbide left in the reactor from previous runs. The amount of oxygen contained in the fluidizing gas taken from the cylinders is not a serious source of contamination in these experiments.

Stoichiometric UC with an oxygen content as low as 0.1 w/o was produced in recent experiments. Results from some of these runs are shown in Table IV-3. The carbon contents of the products from the first two runs in the table were very close to the stoichiometric value of 50 a/o (4.8 w/o) carbon. These runs were conducted under carburizing conditions which would be expected to yield the monocarbide (see footnote a in Table IV-3). The third run produced hyperstoichiometric carbide as was to be expected from the high propane concentration.

TABLE IV-3. Preparation of Uranium Monocarbide in a Fluidized Bed
(200-g scale; run duration, 10 hr)

Temperature (°C)	Propane in Fluidizing Gas ^a (v/o)	Product Composition				
		Carbon		Oxygen		Uranium ^b (a/o)
		a/o	w/o	a/o	w/o	
600	3	47.2	4.5	2.5	0.32	50.3
700	1.5	48.6	4.6	0.8	0.10	50.6
700	9	56.5 ^c	6.2 ^c	0.5	0.08	43.0

^aThe balance is hydrogen. The following C_3H_8 concentrations in hydrogen were calculated for C:H ratios equivalent to the equilibrium gas compositions in the systems $\text{CH}_4\text{-H}_2\text{-UC-UC}_2$ and $\text{CH}_4\text{-H}_2\text{-UC}_2\text{-C}$:

Temperature (°C)	C_3H_8 Concentration (v/o)	
	UC-UC ₂	UC ₂ -C
600	5.5	8.6
700	2.0	3.6

^bCalculated by difference.

^cCarbon deposition on the reactor walls indicated the likelihood of a high free carbon content.

It is believed that UC or (U,Pu)C powder of low oxygen content and near-stoichiometric carbon content can be routinely prepared by the fluidized-bed process. Such powder would be suitable for pressing and sintering into fuel pellets without further processing.

d. Preparation and Analysis of (U,Pu)C Pellets

The (U,Pu)C products from four thermobalance experiments were pressed and sintered into pellets²⁵ for metallographic and electron microprobe analyses.

Before pelletizing, the powders were heated to approximately 1000°C in vacuum to remove gases, primarily hydrogen. The powders were then pressed into 1/4-in. pellets at pressures of 25,000 to 30,000 psi. The pellets were sintered for 2 hr at 1900°C in argon and then weighed and measured in order to determine the density. Samples of the pellets were taken for chemical analysis. The results are summarized in Table IV-4. The density and purity of these pellets appear to be satisfactory. There was a small loss of carbon during sintering as a result of reaction with oxygen (present as an impurity in the sample) to form carbon monoxide.

TABLE IV-4. Analytical Data for Pressed and Sintered (U,Pu)C

Samples were pressed in 1/4-in. dia. dies and then
sintered in argon at 1900°C for 2 hr

	Thermobalance Run No. ^a		
	21	23	24
% Theoretical density	92.4	91.6	92
Chemical analysis of pellet (w/o)			
Carbon (powder)	4.62	4.80	4.72
Carbon (pellet)	4.27	4.68	4.59
Hydrogen	0.0004	0.0004	0.0009
Oxygen	-	0.18	0.19
Nitrogen	-	0.025	0.083

^aSee Table IV-1.

As an aid in identifying the products, the microstructures of these materials were examined utilizing metallographic techniques. The photomicrograph of the polished and etched specimen from run 24 (Fig. IV-7) shows a typical monocarbide structure. The photomicrograph of the pellets from run 21 was similar but that for the specimen of run 23 contained small lines typical of the presence of the sesquicarbide.

²⁵The pelletizing and sintering were performed by the Metallurgy Division through the courtesy of Owen Krueger.

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Fig. IV-7. Photomicrograph of Pressed and Sintered (U, Pu)C.
Polished specimen etched with equal volumes
HNO₃, acetic acid, H₂O.

plutonium data conformed to statistical fluctuation. The standard deviation from the mean for the uranium results was $1\frac{1}{2}$ times the statistically derived standard deviation.

On the basis of these results, it appears that the samples were homogeneous with respect to uranium and plutonium content. The carbon also appeared to be evenly distributed but the data were more difficult to interpret because of interference from N-series X-rays from the uranium.

C. Calorimetry

The program of the calorimetric laboratory is directed toward the determination of thermodynamic properties of substances that are of interest to high-temperature chemistry and nuclear technology. The method of fluorine bomb calorimetry has been developed to obtain the enthalpies of formation (ΔH_f°) of substances not amenable to more conventional types of

Two of the pellets (from runs 21 and 24) were studied under an electron probe micro-analyzer.²⁶ The objective of the electron microprobe examination was to ascertain the homogeneity of the sample.

The microprobe procedure consisted of examining several areas of the two pellets and measuring the uranium and plutonium contents simultaneously. In several instances, step scans across the field were made. The standard deviation from the mean for the plutonium scans was usually within the expected value based on counting statistics. The standard deviation from the mean for the uranium scans was approximately twice the standard deviation based on counting statistics.

In addition, a series of readings was taken while the beam was focused on one spot on the sample. The standard deviation from the mean for the

²⁶J. Sanecki of the Metallurgy Division assisted in operating the electron probe microanalyzer.

calorimetry (combustion in oxygen, solution, etc.). This method has now been used to determine enthalpy-of-formation values for 25 elemental fluorides and seven, binary, high-melting compounds.

For some substances, thermochemical measurements are more advantageously made by the use of fluorine flow calorimetry than fluorine bomb calorimetry. A fluorine-flow calorimetric system has been constructed for studying such substances and is now undergoing testing.

A drop calorimeter for measuring the enthalpies of compounds up to 1500°C has been designed and constructed. It has been used to determine enthalpy increments for uranium monophosphide. A calorimeter incorporating heating by electron bombardment has been designed for making similar measurements up to about 2500°C. The main components of the latter system have been assembled and are undergoing testing.

1. Reaction Calorimetry

a. Enthalpies of Formation by Fluorine Bomb Calorimetry

(1) Hydrofluoric Acid and Alkali Metal Fluorides

The enthalpy of formation of hydrofluoric acid, $\Delta H_f^\circ(\text{HF}, \text{aq})$, is an important quantity in the solution calorimetry of fluorine-containing compounds. Although $\Delta H_f^\circ(\text{HF}, \text{ideal gas})$ is known to about 0.1 kcal mol⁻¹, difficulties connected with the nonideality of the real gas have prevented accurate determination of the enthalpy of solution of the ideal gas; recent evidence from this laboratory and elsewhere²⁷ indicates that the currently selected value (from circuitous thermochemical cycles) for $\Delta H_f^\circ(\text{HF}, \text{aq})$ may be too positive by 1 to 2 kcal mol⁻¹. To help resolve this uncertainty, one may make use of the fact that there exist excellent data for the heats of solution of the alkali metal fluorides and hydroxides and for the heats of neutralization of the hydroxides with hydrofluoric acid. If by means of fluorine bomb calorimetry the ΔH_f° values for the alkali metal fluorides could be accurately determined, their combination with the solution calorimetric data in appropriate cycles would appreciably reduce the uncertainty in $\Delta H_f^\circ(\text{HF}, \text{aq})$. The acquisition of direct enthalpy-of-formation data for the alkali metal fluorides is itself an attractive by-product of this proposal. Preliminary experiments have shown that bomb combustions of alkali metals in fluorine are feasible.

(2) Nickel Difluoride

Fluorine combustions of metals that form nonvolatile fluorides present special problems. To overcome these problems, there was developed a combustion technique²⁸ in which a suspended metal sample

²⁷Cox, J. D., and Harrop, D., Trans. Faraday Soc. 61, 1328 (1965).

²⁸ANL-6875, p. 125.

is burned in a bomb lined with the fluoride of the metal. This technique was used for combustions of magnesium²⁹ and yttrium³⁰ in fluorine. For metals that are even more difficult to burn completely, the technique was modified³¹ so that the combustion proceeded in a series of steps. The modified technique was used for the combustion of nickel in fluorine and gave the following result:

(3) Gadolinium Trifluoride

The modified technique was also used for combustions of gadolinium and lanthanum. The results obtained with lanthanum were not precise and the measurements will be repeated. The following result was obtained for GdF_3 :

(4) Thorium Tetrafluoride

The modified technique was also applied to thorium. However, post-combustion examination of the thorium fluoride liner in the bomb disclosed that the liner was contaminated with metal, mostly nickel. Since the amount of unburned thorium in the liner is determined by measuring the volume of hydrogen evolved when the liner is dissolved in an acid solution, the presence of metals other than thorium made the analysis very uncertain. A new series of combustions with improved techniques is planned.

(5) Boron Compounds

(a) Boron Trifluoride

The values of $\Delta\text{Hf}_{298}^\circ$ determined in this laboratory for boron nitride and zirconium diboride were found on close examination to show a consistent bias when compared to values determined by methods other than fluorine bomb calorimetry. This led to the suspicion that the value³² $\Delta\text{Hf}_{298}^\circ(\text{BF}_3, \text{g}) = -269.8 \pm 0.2 \text{ kcal mol}^{-1}$, common to both determinations, was incorrect. Reanalysis of the specimen of boron used in the determination of $\Delta\text{Hf}^\circ(\text{BF}_3, \text{g})$ uncovered additional impurities. When corrected for these additional impurities, $\Delta\text{Hf}_{298}^\circ(\text{BF}_3, \text{g})$ became $-271.6 \pm 0.9 \text{ kcal mol}^{-1}$, and the bias mentioned above disappeared. Because of the large uncertainty

²⁹Rudzitis, E., Feder, H. M., and Hubbard, W. N., J. Phys. Chem. 68, 2978 (1964).

³⁰Rudzitis, E., Feder, H. M., and Hubbard, W. N., J. Phys. Chem. 69, 2305 (1965).

³¹ANL-7020, p. 168.

³²Wise, S. S., Margrave, J. L., Feder, H. M., and Hubbard, W. N., J. Phys. Chem. 65, 2157 (1961).

associated with the impurity content of the original boron, a redetermination was made using a purer specimen of boron and two different combustion techniques. The results of this study³³ yielded the following:

(b) Boron Nitride and Diborides of Zirconium, Hafnium, Niobium, and Tantalum

The revision of the value for $\Delta \text{Hf}_{298}^\circ(\text{BF}_3, \text{g})$ affects our previously reported ΔHf° values for boron nitride³⁴ and for the diborides³⁵ of zirconium, hafnium, niobium, and tantalum. The revised values are given below:

	$\Delta \text{Hf}_{298}^\circ (\text{kcal mol}^{-1})$
$\text{B(c)} + 1/2 \text{N}_2(\text{g}) \rightarrow \text{BN(hex.)}$	$-59.9_7 \pm 0.3_7$
$\text{M(c)} + x\text{B(c)} \rightarrow \text{MB}_x(\text{c})$	
M = Zr, x = 1.996 ± 0.006	-77.8 ± 1.5
M = Hf, x = 2.009 ± 0.007	-78.9 ± 2.5
M = Nb, x = 1.880 ± 0.007	-59.0 ± 1.8
M = Ta, x = 1.925 ± 0.006	-44.5 ± 1.7

The energy of combustion of BN according to the reaction

was measured³⁴ at this laboratory in 1961 to enable derivation of $\Delta \text{Hf}^\circ(\text{BN})$. The latter value was of considerable interest at that time because of the large discrepancy between the results based on oxygen bomb calorimetry and decomposition pressure measurements. We delayed publication of our value of $\Delta \text{Hf}_{298}^\circ(\text{BN})$ because of uncertainty concerning the correct value for the auxiliary datum $\Delta \text{Hf}_{298}^\circ(\text{BF}_3)$ (see Part (a) above). The revised value for $\Delta \text{Hf}^\circ(\text{BN})$, recently published,³⁶ is in excellent agreement with many recent values determined by a variety of experimental methods, and the above-mentioned discrepancy no longer exists.

(c) Boric Oxide

The enthalpy of formation of boric oxide is of basic importance in the thermochemistry of boron compounds but is difficult

³³Johnson, G. K., Feder, H. M., and Hubbard, W. N., J. Phys. Chem. 70, 1 (1966).

³⁴ANL-6477, p. 159.

³⁵ANL-7020, p. 166.

³⁶Wise, S. S., Margrave, J. L., Feder, H. M., and Hubbard, W. N., J. Phys. Chem. 70, 7 (1966).

to determine accurately by direct reaction of boron with oxygen. The difficulties, incomplete combustion and poorly defined products, have led modern investigators to resort to circuitous methods for deriving $\Delta H_f^\circ(\text{B}_2\text{O}_3)$. However, the values thus derived have a spread of about 2 kcal mol⁻¹. The determination of $\Delta H_f^\circ(\text{B}_2\text{O}_3)$ by combustion in fluorine according to the reaction

offers a method dependent only on the value of $\Delta H_f^\circ(\text{BF}_3, \text{g})$ which has already been determined by fluorine bomb calorimetry. Experimental investigation of this reaction, using both the crystalline and amorphous modifications of B_2O_3 , is now in progress. The preliminary results are:

	ΔH_f° (kcal mol ⁻¹)
$2\text{B}(\text{c}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{c})$	-303.0 ± 0.5
$2\text{B}(\text{c}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{amorph.})$	-299.5 ± 0.5

(6) Alpha Silicon Carbide and Carbon Tetrafluoride

Fluorine combustions of two different specimens of α -silicon carbide were reported³⁷ to give discordant enthalpies of combustion. A new specimen of α -silicon carbide with finer particle size was obtained. The new specimen yielded a satisfactory series of combustions from which the following result was derived:

$\Delta H_f^\circ_{298}(\text{SiC}, \alpha)$ is 0.4 kcal mol⁻¹ less negative than $\Delta H_f^\circ_{298}(\text{SiC}, \beta)$.³⁷ This difference in the enthalpies of formation lies between the 0.2 kcal mol⁻¹ calculated by d'Entremont and Chipman³⁸ from the data of Grieveson and Alcock³⁹ and the 1.1 kcal mol⁻¹ found by Humphrey et al.⁴⁰

The enthalpy-of-formation values derived from the SiC combustion data depend on the value selected for $\Delta H_f^\circ_{298}(\text{CF}_4, \text{g})$ for which the recent literature shows a spread of about 8 kcal mol⁻¹. An effort is being made to resolve the uncertainty in $\Delta H_f^\circ(\text{CF}_4)$ by calorimetric combustions of natural and pyrolytic graphites in fluorine.

³⁷ANL-7020, p. 170.

³⁸d'Entremont, J. C., and Chipman, J., J. Phys. Chem. **67**, 499 (1963).

³⁹Grieveson, P., and Alcock, C. B., in "Special Ceramics," Heywood and Co., Ltd., London, 1961, p. 183.

⁴⁰Humphrey, G. L., Todd, S. S., Coughlin, J. P., and King, E. G., U. S. Bureau of Mines RI 4888, 1952.

A newly constructed two-chambered reaction vessel, shown in Fig. IV-8 will be used for the graphite combustions. The principal advantage of this vessel over the two-chambered vessel previously described⁴¹ is that higher final fluorine pressures (25 atm or more) are attainable in the combustion chamber. The higher pressures, required for complete combustion of graphite, are achieved by using higher initial fluorine pressures and a more favorable volume ratio of storage chamber to combustion chamber (3.2 versus 0.8). The fluorine storage chamber, instead of being thin walled and detachable, is of heavy construction and is an integral part of the vessel.

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Fig. IV-8. Two-chambered Reaction Vessel

(7) Phosphorous and Arsenic Pentafluorides

The enthalpy of formation of $\text{PF}_5(\text{g})$ from red IV phosphorus⁴² was previously reported.⁴³ The same combustion technique was subsequently used to measure the energies of combustion of three other allotropes of phosphorus: amorphous red I, red V, and α -white. Results obtained to date are as follows:

⁴¹Nuttall, R. L., Wise, S. S., and Hubbard, W. N., Rev. Sci. Instr. 32, 1402 (1961); ANL-6875, p. 126, Fig. IV-2.

⁴²The nomenclature for the phosphorus allotropes follows that used by J. R. Van Wazer in "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, p. 105.

⁴³ANL-7020, p. 165.

	$\Delta H_{f298}^{\circ} (\text{kcal mol}^{-1})$
$\text{P}(\alpha\text{-white}) + 5/2 \text{F}_2(\text{g}) \rightarrow \text{PF}_5(\text{g})$	$-380.7_1 \pm 0.3_1$
$\text{P}(\text{red I}) + 5/2 \text{F}_2(\text{g}) \rightarrow \text{PF}_5(\text{g})$	$-376.9_0 \pm 0.1_7$
$\text{P}(\text{red V}) + 5/2 \text{F}_2(\text{g}) \rightarrow \text{PF}_5(\text{g})$	-377.8
$\text{P}(\text{red IV}) + 5/2 \text{F}_2(\text{g}) \rightarrow \text{PF}_5(\text{g})$	-378.4

The value for $\Delta H_f^{\circ}(\text{PF}_5)$ from α -white phosphorous is in good agreement with that obtained by Gross et al.,⁴⁴ namely, $-381.4 \pm 0.4 \text{ kcal mol}^{-1}$. No other values for $\Delta H_f^{\circ}(\text{PF}_5)$ have been published. The last two results are only tentative owing to large and uncertain corrections for oxygen impurity content in the specimens used.

Similar techniques were used for combustions of arsenic in fluorine to determine the enthalpy of formation of arsenic pentafluoride. The results of this study were recently published,⁴⁵ and the abstract of the publication follows:

"The energy formation of arsenic pentafluoride was measured by direct combination of the elements in a bomb calorimeter. From these measurements the standard enthalpy of formation, $\Delta H_{f298.15}^{\circ}(\text{AsF}_5, \text{g})$, was calculated to be $-295.5_9 \pm 0.1_9 \text{ kcal.mole}^{-1}$. The average bond strength in AsF_5 ($92.4 \text{ kcal. mole}^{-1}$) is about $20 \text{ kcal. mole}^{-1}$ less than it is in AsF_3 ."

(8) Sulfur, Selenium, and Tellurium Hexafluorides

Preliminary values of the enthalpies of formation of $\text{SF}_6(\text{g})$ and $\text{SeF}_6(\text{g})$ were previously reported.⁴³ The experimental techniques employed have since been applied to the determination of $\Delta H_f^{\circ}(\text{TeF}_6, \text{g})$. The work on the chalcogen hexafluorides is reported in a paper⁴⁶ from which the following abstract is taken:

"The energies of formation of the hexafluorides of sulfur, selenium, and tellurium were measured by direct combination of the elements in a bomb calorimeter. From these measurements the standard enthalpies of formation $\Delta H_{f298.15}^{\circ}(\text{g})$, were calculated (in kcal mole^{-1}): SF_6 , $-291.7_7 \pm 0.2_4$; SeF_6 , $-266.9_5 \pm 0.1_4$; TeF_6 , $-327.2_0 \pm 0.5_6$. These values are substantially more negative than those reported by Yost and Claussen in 1933. The thermodynamic properties of these compounds have been computed and tabulated from 0 to 1500°K ."

⁴⁴Gross, P., Hayman, C., Levi, D. L., and Stuart, M. C., Final Technical Report R.146/4/23, Fulmer Research Institute Limited, Stoke Poges, England, November 1960.

⁴⁵O'Hare, P. A. G., and Hubbard, W. N., J. Phys. Chem. **69**, 4358 (1965).

⁴⁶O'Hare, P. A. G., Settle, J. L., and Hubbard, W. N., Trans. Faraday Soc. **62**, 558 (1966).

The average bond dissociation energies of these hexafluorides are 78.5, 71.5, and 81.2 kcal mol⁻¹, respectively. This interesting nonmonotonic variation appears to result from the operation of two opposing effects as one proceeds from sulfur to tellurium: bond weakening owing to decreasing d-orbital overlap, and bond strengthening owing to increasing amount of double-bond character.

b. Fluorine Flow Calorimetry

The advantages of fluorine flow calorimetry for the combustion of fluorine-sensitive substances (e.g., uranium compounds) were previously discussed.³⁷ After preliminary experiments with a mocked-up, glass apparatus gave favorable results, construction of a fluorine-flow calorimetric system was begun. Assembly of the various parts is now nearing completion.

Operation of the system's analytical train is currently being tested by passing fluorine over sulfur and analyzing the gaseous reaction products by infrared, gravimetric, and gas chromatographic methods. Sulfur was chosen mainly because similar analytical problems are likely to be encountered when the flow calorimeter is used to determine the enthalpy of formation of uranium sulfides.

c. Calorimetry of Plutonium Compounds

Thermochemical data on plutonium compounds are sparse. A recent monograph⁴⁷ on the thermochemistry of plutonium compounds indicates that precise values are available only for PuO₂ and plutonium(III) halides. Because of the great need for additional data in this field, this laboratory is planning to explore various experimental methods for their accumulation. The methods to be investigated include bomb and flow calorimetry using various oxidants (oxygen, fluorine, etc.), solution calorimetry, and other types of reaction calorimetry. When methods and techniques appropriate to plutonium are developed, a program of calorimetric measurements on plutonium compounds will be initiated.

2. Enthalpy Increment Calorimetry

a. 1500°C Drop Calorimeter

The 1500°C enthalpy calorimeter system⁴⁸ has been in operation during the past year. The system was tested by measuring the enthalpy increments of aluminum oxide (synthetic sapphire, National Bureau of Standards--Calorimetry Conference standard) over a range of temperatures.

⁴⁷Rand, M. H., "The Thermochemical Properties of Plutonium Compounds," International Atomic Energy Agency, 1966, in press.

⁴⁸ANL-7020, p. 172, Fig. IV-4.

Preliminary calculations show that the enthalpy differences, $H_T - H_{298}$, obtained from about 1000 to 1400°K agree to $\pm 1\%$ with those reported by the National Bureau of Standards. The enthalpy increments of uranium monophosphide from 800 to 1200°C were also measured. A provisional value for the mean heat capacity of uranium monophosphide at 1300°K is $13.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$.

The measurements to date have been made using a constant-temperature-environment, copper-block calorimeter. A more versatile adiabatic calorimeter is being assembled for incorporation into the system along with other improvements.

b. 2500°C Calorimeter System

The 2500°C enthalpy calorimeter system⁴⁹ differs from the 1500°C system principally in the method of heating (electron bombardment instead of electrical resistance) and in the method of transferring the sample capsule from the furnace to the calorimeter proper (piston accelerated instead of free fall). Assembly of the entire system is nearing completion; before assembly was begun, the individual components (such as the sample transfer mechanism, the target drive, the electron beam furnace) were first tested separately and appropriate modifications made.

Figure IV-9 shows the furnace proper (heated by two opposed electron beam guns) with its beam locator plates, spiral-wound

Fig. IV-9
Furnace for the 2500°C
Calorimeter System

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⁴⁹ANL-7020, p. 174, Fig. IV-5.

tantalum radiation shield, and cavity for the tantalum target. Prior to hitting the target, the beam must pass through a slot determined by the relative positions of the four locator plates. Optimum conditions were established for transmitting beam power to the target without excessive heating of the locator plates and radiation shield. The power capability of the electron beam guns was shown to be adequate by the heating of a solid 75-g tungsten rod to its melting point (3410°C).

D. Liquid Sodium Coolant Chemistry

The chemistry of liquid sodium is being studied to obtain information on the equilibria and kinetics of chemical reactions that can affect its use as a heat transfer fluid in nuclear reactors. The work is mainly directed toward understanding the influence of sodium's common contaminants--carbon, oxygen, hydrogen, and nitrogen--on corrosion of structural and cladding materials. Because of limited manpower, the major emphasis is devoted to the contaminant carbon and, in particular, to its characterization and removal.

1. Nature of Carbon Species in Sodium

Experience in this laboratory has confirmed the heterogeneity of carbon in sodium and has shown that a significant part of the variability of carbon analyses arises from this fact. Efforts are being made to characterize the amount and size distribution of carbon-bearing particulates and to determine the composition of the carbon-bearing species and, if possible, their origins.

a. Mass Spectrometric Observations

Previous work at this and other laboratories has shown that distillation of sodium does not reduce its carbon content below 50 to 75 ppm. One plausible explanation for this observation is the presence of carbon compounds whose volatilities are similar to that of sodium. To explore this possibility, the vapor phases over various samples of sodium heated to ~300°C were examined by means of a Bendix Time-of-Flight mass spectrometer.

Commercial reagent-grade sodium that had been cast in oil- or kerosene-coated molds gave mass peaks (i.e., m/e) of 207 and higher, as well as an appreciable intensity of low-mass (<100) peaks (besides those due to sodium). The low-mass species can be ascribed to hydrocarbon fragments, such as $\text{CH}_3^+(15)$, $\text{CH}_4^+(16)$, $\text{C}_2\text{H}_2^+(26)$, and $\text{C}_2\text{H}_3^+(27)$. The same result was obtained even after distillation of such sodium, but not when the sodium was merely remelted. Reactor-grade sodium, which is dry cast, gave no evidence of the presence of high-mass species (>100) in the vapor phase, nor did sodium that had been in contact with graphite powder for four months at 250°C. The latter samples of sodium did show a small amount (just above instrument background) of low-mass species presumed to be light hydrocarbons.

These results, although not entirely conclusive, suggest that most sodium does not contain significant amounts of volatile carbon compounds except when mold-coating fluids have been employed during casting. Hence, the failure of distillation to free sodium from carbon-bearing impurities may be caused by the entrainment of particulate matter. The mass spectrometric results also show that organic compounds of high molecular weight can exist for extended periods of time in liquid sodium at relatively high temperatures.

Two new graphite electrodes of the type employed in the electrolytic manufacture of sodium were also examined mass spectrometrically. Only low-mass species (<103) were evolved up to 900°C , and these gradually disappeared with time; at about 1025°C , no peaks above background were observed. These results indicate that volatile organic compounds of high molecular weight are not likely to be introduced into sodium during its manufacture.

b. Aqueous Dissolution Experiments

Information concerning the nature of carbon-containing species in sodium is being sought by experiments which involve dissolution of sodium in water and examination of the reaction products. Information thus obtained is indirect in that changes in the original carbon-bearing species may occur during the reaction.

The gases evolved on dissolution of United States Industrial Co. (U.S.I.) reactor-grade sodium (containing 40 ppm total carbon) were pumped through a liquid-nitrogen-cooled silica gel trap. After dissolution, the trap was detached from the system and the absorbed gases were analyzed by gas chromatography. Methane (0.7 to 1.6 ppm equivalent carbon) was the only gas detected as an off-gas from the alkaline solution. The methane may have existed as such or as an organometallic compound in the sodium. When the alkaline solution was acidified, carbon dioxide (~ 6 ppm equivalent carbon) was given off. The carbon dioxide probably originated from Na_2CO_3 in the sodium. Acetylene, ethylene, and ethane were not detected as off-gases from either alkaline or acid solution; carbon monoxide was not determined. A residue of dark particles that remained after the sodium had dissolved was collected on a fine-porosity quartz frit. The residue was analyzed for total carbon and found to contain 14 ppm carbon based on the original sodium. Summarizing, approximately 55% of the carbon in U.S.I. sodium has been accounted for by three products.

Sodium from other sources also yielded insoluble residues. The analytical results for total carbon in these residues (and in the residue from U.S.I. sodium) are given in Table IV-5. The data show that 30 to 70% of the carbon in the sodium samples was recovered as particulates after dissolution.

TABLE IV-5. Particulate Carbon Found after
Dissolution of Sodium in Water

(Samples, ~1.5 g)

Sodium	Initial Carbon (μg)	Carbon Found as Particles ^a	
		(μg)	(%)
MSA ^b	400	110	28
MSA ^b	400	290	73
Distilled Reagent Grade	370	120	32
U.S.I. Reactor Grade	320 ^c	112	35

^aConsidered to be lower limits because of incomplete recovery.

^bMine Safety Appliance Research Corp. Sodium from this source had been zirconium-gettered at 600°C and filtered through a 5 μ -porosity stainless steel frit.

^cAbout 8-g sample.

c. Liquid-Liquid Extraction

Mass spectrometric studies (see Part a) indicated that stable organic compounds could exist in sodium. If such compounds are present, their extraction by a hydrocarbon solvent might be feasible.

This concept was tested by repetitive extraction of reactor-grade sodium (40 ppm carbon) with high-purity n-nonane under a helium atmosphere at 125°C in a Pyrex glass vessel. The n-nonane extracts were filtered and examined spectrophotometrically with ultraviolet light; n-nonane was used in the reference cell. None of the fractions showed any absorption between 2200 and 4000 Å. The sensitivity of the method of detection was estimated by using xylene as a stand-in for aromatic compounds which absorb strongly in the ultraviolet region. It was found that as little as 5 ppm of an extractable organic compound with an absorbancy similar to that of xylene could be detected. Apparently, the sodium that was used contained less than 5 ppm of carbon in the form of extractable organic compounds that absorb in the ultraviolet.

d. Hexasodium Hexacarbonyl

The possibility exists that there are organic compounds in sodium which are not extracted by hydrocarbon solvents and which are stable even after aqueous dissolution of sodium. An example would be the sodium salt of hexahydroxybenzene, otherwise called hexasodium hexacarbonyl, $\text{Na}_6(\text{CO})_6$, which is known to be a product of the reaction between sodium and carbon monoxide. Accordingly, U.S.I. sodium was dissolved in distilled water

and the clear solution was examined spectrophotometrically; dilute sodium hydroxide was used in the reference cell. No significant absorption was found in the ultraviolet and visible regions (2150 to 7000 Å), indicating that the sodium did not contain any significant amount of stable, sodium hydroxide-soluble, aromatic compounds. The sensitivity of detection was such that sodium hydroxide solutions containing hexahydroxybenzene equivalent to ~1 ppm of carbon in sodium would give discernible absorption peaks in the ultraviolet.

e. Centrifugation Experiments

Previous experience has shown that particulate matter containing carbon is present in sodium and that these particles can pass through a 5 μ -porosity filter.⁵⁰ Calculations indicate that for small density differences (about 0.2 g/ml) between the particles and liquid sodium, particles larger than 1 μ in diameter should be separable by centrifugation at reasonable speeds and temperatures. The feasibility of centrifugal separation of particulate carbon from sodium was tested with a small, commercial centrifuge which was modified to enable heating of the sodium.

Stainless steel (SS) capsules were filled with sodium in an inert-atmosphere glovebox, sealed, removed from the glovebox, and centrifuged at 2000 rpm (335 to 625 g) at about 200°C. In one experiment, after centrifuging for 30 min, the SS capsule was rapidly cooled by immersion in liquid nitrogen and the sodium was analyzed for carbon. No significant difference in the carbon content was found between the top (180 ppm), middle (140 ppm), and bottom (220 ppm) portions of the sodium. In another experiment, after centrifuging for one hour, the heating was discontinued and the sodium was allowed to solidify while being centrifuged. Analysis of the top and bottom portions of the sodium indicated no significant carbon displacement. These results indicate that if carbon-containing particles were present in the sodium, they were probably less than 1 μ in diameter.

Further experiments of this type with an ultracentrifuge are planned.

f. Reactions of Carbon Compounds with Liquid Sodium

Identification of the products of reaction between common carbon compounds and liquid sodium may, in addition to elucidating the course of reaction, provide clues as to the chemical forms in which carbon can exist in relatively pure sodium. With this purpose in mind (and to gain experience with gas chromatographic techniques), several preliminary experiments were performed with sodium- Na_2CO_3 , a previously investigated reaction, and with sodium-lampblack and sodium-graphite.

⁵⁰ANL-6925, p. 92.

The experiments consisted of heating two grams of U.S.I. reactor-grade sodium with 0.1 g of the carbon-containing material for 2 to 16 hr at 700°C in stainless steel or nickel capsules in a helium atmosphere. After cooling, the (unfiltered) reaction products were treated with dilute sulfuric acid; the gases evolved were analyzed by gas chromatography. The results may be summarized as follows:

1. Na_2CO_3 is unstable in liquid sodium at 700°C, yielding decomposition products whose relative amounts vary with heating time. A carbide or carbide-like compound is formed as shown by the evolution of acetylene on dissolution of the sodium. The final product of Na_2CO_3 decomposition appears to be carbon, which is observed as insoluble, black particles after the dissolution.

2. Lampblack and graphite do not react with sodium at 700°C to give carbides, as indicated by the absence of any significant amounts of carbon-containing gaseous products on dissolution.

These results are in qualitative agreement with the findings of Hobart (Pratt and Whitney Aircraft, CANEL) who studied the effect of temperature on the sodium- Na_2CO_3 reaction at constant time (2 hr).

Experiments similar to those above were made in which sodium was heated (500 to 700°C) in various metal capsules (Ni, Ta, Mo, SS 304, SS 316) in the presence of nitrogen, nitrogen and Na_2CO_3 , or $(\text{NH}_4)_2\text{C}_2\text{O}_4$. In all cases cyanide was found in the aqueous dissolution products as previously reported.⁵¹

2. Ultrapurification of Sodium

Ultrapurification of sodium from impurities present at the ppm level, such as oxygen, hydrogen, and carbon, is of interest for several reasons. The study of reactions between liquid sodium and impurities would be greatly simplified if ultrapure sodium were available. The reliability and accuracy of analytical methods for impurities could also be tested if sodium requiring a negligible blank correction were available. Furthermore, the development of economical, on-line, ultrapurification methods would be of considerable interest for reactor loops.

With respect to carbon, there is no a priori way of knowing that a particular purification technique will be effective, since the chemical nature of carbon in sodium is not fully understood. It is apparent that a considerable fraction of the carbon in sodium is present as submicron-sized particles.

a. Electromigration

An effective means of ridding sodium of carbon might be one whereby sodium ions are made to migrate through an electrolyte in a

⁵¹Hobart, E. W., and Bjork, R. G., Nucl. Appl. 1, 490 (1965).

selective fashion so that carbon species are left behind. A cell to accomplish this purpose can be represented by $\text{Na}(\text{crude}) \mid \text{Na}^+(\text{molten halides}) \mid \text{Na}(\text{pure})$. About a dozen such cells using various cell configurations and electrolytes have been operated. A schematic diagram of the last design, and most successful to date, is shown in Fig. IV-10. The procedure and results are discussed below.

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Fig. IV-10. Electromigration Cell for Purification of Sodium

sodium had been transported. Samples of sodium for carbon analysis were removed from the mid-region of the anode pool (dregs) and cathode pool (pure). The results of numerous analyses of these fractions and of the original crude sodium are shown below:

Fraction	Ppm Carbon
Crude	35.4 ± 4.3
Cathode	27.4 ± 4.0
Anode	38.6 ± 6.6

The uncertainty given is the standard error. The data indicate that at the 80% confidence level, a significant difference in carbon content exists between the crude and pure sodium (also between the pure and dregs). Thus,

The cell reagents and equipment were handled and assembled in a helium-atmosphere glove-box to avoid contamination of the sodium by environmental carbon. In this manner, any change in carbon concentration could be attributed to the electrolytic process only. The crude sodium had been filtered through a Pyrex glass frit. The electrolyte, a ternary mixture of 15 m/o NaF, 32 m/o NaCl, and 53 m/o NaI, had been dried under vacuum at 400°C, melted (m.p., ~535°C) under helium, and filtered. The cell was enclosed by a stainless steel furnace tube and operated under these conditions: sodium, 52 g; ternary salt, 102 g; current, 1 amp; time, 27 hr; temperature, ~550°C; atmosphere, 1300 torr He.

At the end of the experiment, the cell was disassembled in the glovebox for examination and sampling. Approximately half the crude

it appears that some reduction in carbon content was effected by the electromigration process. The reason for the appearance of carbon in the purified product is not known at present. Further electromigration experiments are planned.

b. Thermoelectrodiffusion

The concept of purification by thermoelectrodiffusion may be explained as follows. An emf is developed between two similar metal electrodes when a temperature difference exists between them. If an electrolyte containing this metal is interposed between them, the metal can, in principle, be transported through the electrolyte and be deposited at one temperature while being dissolved at a different temperature. (A return path of low electrical resistance must be provided.)

The utility of thermoelectrodiffusion is dependent on the rate of transport of the metal and was evaluated by conducting an experiment with lithium. (Lithium, instead of sodium, was used because its lower vapor pressure permitted simplification of the apparatus.) A gradient of 119°C was maintained for about six hours between the lithium at 663°C and a stainless steel collector sponge immersed in a LiF-LiCl electrolyte. No lithium was transported to the collector region. Further thermoelectrodiffusion experiments are not planned at the present time.

c. Electrodiffusion

It was reported⁵² that oxygen migrates through liquid sodium at $\sim 600^{\circ}\text{C}$ under the influence of high-density direct current. A liquid-state electrodiffusion apparatus was constructed to determine if carbon, as well as oxygen, would migrate preferentially toward either electrode under the influence of high-density, direct current. The apparatus consisted of a 9-mm dia. Pyrex U-tube that was filled with sodium and fitted with aluminum electrodes. The U-tube was heated in an oil bath at 100 to 110°C while a direct current density of ~ 140 amps/cm² was maintained. Analyses of the sodium after one week of operation indicated that preferential migration of carbon and oxygen had not occurred.

d. Directional Freezing

An experiment was performed to determine if slow freezing of liquid sodium would lead to segregation of carbon-containing impurities. About 75 g of filtered U.S.I. sodium was sealed in a 1.7-cm dia. by 60-cm. long Pyrex tube. The sodium was melted in a horizontal position (filling about 75% of the tube) in a furnace having about a 20°C temperature gradient from end to end. After 24 hr, the molten sodium was slowly cooled so that

⁵²Nevzorov, B. A., "The Nature of Oxygen in Liquid Sodium," USAEC Report AEC-tr-5412, November 28, 1962.

it froze progressively from one end of the tube to the other over a period of about six hours. Analysis of several fractions of the sodium for total carbon indicated that significant segregation had not occurred.

Multicycle directional freezing (analogous to zone refining) will be tested in a future experiment.

3. Carbon Analyses

A series of experiments related to the determination of graphitic carbon in sodium has been completed. Graphite thread (Union Carbide, Grade WCB, 99.96% graphitic carbon) was added to samples of U.S.I. sodium which were then carried through the analytical procedure.⁵³ The results, shown in Table IV-6, indicate that elemental carbon in sodium can be determined by our usual analytical procedure. However, the variability in recovery found at the higher carbon concentrations is somewhat surprising.

TABLE IV-6. Recovery of Graphitic Carbon Added to Sodium

Wt. of Sodium (g)	Carbon (μ g)		Total	Found	% Recovery
	In Sodium	In Graphite Thread			
0.71	20	44	64	67	105
0.94	27	38	65	52	80
0.97	28	189	217	187	86
0.57	16	224	240	245	102
1.09	31	337	368	324	88
1.01	29	275	304	289	95
0	0	86	86	92	108

Recent analytical results for carbon in reactor-grade sodium have been erratic. Our previous results with U.S.I. sodium had indicated that a linear correlation between carbon content and sample size existed. Recently, however, the results of analyses of the same sodium have varied above and below this correlation line in a nonrandom manner. Apparently, a nonsystematic variable exists in our determination. Possible sources of variability being investigated are: (a) contamination of the sample via the helium atmosphere of the glovebox and by mechanical handling, and (b) non-uniform distribution of carbon species in the sodium.

E. Chemistry of Liquid Metals

These studies are directed toward a better understanding of the basic factors which influence the chemical and physical properties of liquid metals. In a formal sense, the determination of many of the properties of a liquid metal may be reduced to the calculation of a configurational integral. However, only for the simplest liquids whose interatomic potentials are known (e.g., liquid argon) has there been any notable success in the evaluation of the configurational integral. In the case of metallic liquids, lack of

⁵³Combustion in an alumina boat with pure oxygen, followed by dissolution in dilute sulfuric acid and manometric measurement of liberated CO₂.

knowledge of the nature of the interatomic potential has severely limited attempts to evaluate this integral. Therefore, before the theoretical problem can be solved, or indeed, before one can determine whether present approximation methods are applicable, it is necessary to know considerably more about the nature of the interatomic potential in liquid metals. A part of our studies is designed to give information which may be related to the interatomic potential in liquid metals.

It is most likely, however, that progress in the quantitative prediction of chemical properties by purely theoretical means will be slow. Therefore, a part of our studies with metallic systems is designed to relate thermodynamic properties to the factors which cruder theoretical models suggest may be important. One such factor is the "size" of atoms. Two thermodynamic studies are under way to determine the relation of thermodynamic properties and atomic size in well-controlled situations, i.e., those in which extraneous factors have been minimized.

Virtually nothing is known concerning interatomic complexes in liquid metal solutions. Indirect evidence, such as abrupt breaks in curves of viscosity or electrical resistance vs. composition, has often been cited as evidence for complex-formation. A study using high-frequency sound for the detection of complex-formation in liquid metal solutions is under way. The method to be employed has been successfully used to determine or confirm the existence of complexes in aqueous solutions.

The magnetic properties of metallic materials are often very revealing of their electronic constitutions. Although not specifically related to the problems of liquid metals, magnetic measurements on the heavy elements have been fruitful in the past and have been continued. This report presents results on the ferromagnetic compound uranium monosulfide.

1. Thermodynamics of Sodium-Potassium System

The only notable successes in calculating thermodynamic functions for metals by purely theoretical means have been achieved with the alkali metals. At least one attempt⁵⁴ has been made to compute the enthalpy of formation of a liquid binary mixture of alkali metals from first principles by means of reasonable approximations. The results of this computation were within a factor of three of the observed value. One expects that future tests of better approximations will be made by computing thermodynamic functions for various mixtures of the alkali metals. Therefore, it is desirable to have on hand accurate experimental data for such mixtures. The present study of the sodium-potassium system is part of a program to obtain accurate values for the free energy of formation of liquid binary mixtures of the alkali metals. These values, when combined with calorimetric data⁵⁵ for enthalpies of mixing, yield entropies of mixing and thus fairly complete thermodynamic descriptions of the systems.

⁵⁴Christman, J. R., and Huntington, H. B., Phys. Rev. 139A, 83 (1965).

⁵⁵Yokokawa, T., and Kleppa, O. J., J. Chem. Phys. 40, 46 (1964).

The free energies of formation of liquid sodium-potassium alloys were computed from comparisons of the optical absorption by the vapors in equilibrium with the alloys with the optical absorption by the vapors in equilibrium with the two pure metals. Because the measurements were made with radiations emitted by excited sodium and potassium atoms, i.e., the sodium D_2 line (5890 Å) and the corresponding potassium line (7665 Å), the absorptions may be readily related to the partial pressures, p_i , of atomic species in the vapor. To a very good first approximation, the Beer-Lambert equation may be used to compute the alkali metal activities in the alloys:

$$a_i = \frac{p_i}{p_i^0} = \frac{\log(I_0/I_i)}{\log(I_0/I_i^0)} \quad (1)$$

where a_i is the activity of the i -th component in the alloy, I_0 the incident light intensity, I_i the intensity of the light transmitted through the vapor in equilibrium with the alloy, and I_i^0 and p_i^0 indicate the corresponding quantities for the pure metal. The measurements for the alloy and the pure metal were made at the same temperature in cells having equal optical path lengths.

The use of the Beer-Lambert equation implies that the absorption coefficient of an absorbing species is independent of its partial pressure. This assumption is strictly valid only if a single, sharply defined wavelength is involved. When the absorption is due to several very closely spaced lines whose separations are comparable with the Doppler line width, then a correction must be applied. In the present case, both the sodium 5890 Å and potassium 7665 Å "lines" are split into groups of six, closely spaced lines; this splitting is caused by interaction between the angular momentum of the nucleus and the total angular momentum of the extranuclear electrons and is called nuclear hyperfine splitting (NHFS). For sodium, the NHFS of the ground state ($^2S_{1/2}$) amounts to 0.0591 cm^{-1} and the separation of the lines is large enough to lead to significant error if the activities are computed from the uncorrected Beer-Lambert equation. The activity data for the sodium were therefore corrected for NHFS; the correction was largest, 3%, for the most dilute sodium alloy. The influence of NHFS on the activities computed for potassium is negligible.

The activities of both sodium and potassium in Na-K alloys containing from 12.5 to 82.6 a/o sodium were determined and used to compute the partial molar excess free energies, $\bar{G}_i^{\text{xs}}$, with Eq. 2:

$$\bar{G}_i^{\text{xs}} = RT \ln (a_i/x_i) \quad (2)$$

where x_i is the atom fraction of the i -th component in a liquid solution at temperature T in $^\circ\text{K}$. The potassium measurements were made at 345°K and the sodium at 414°K . Both sets of data were corrected to 384°K using the enthalpy data reported by Yokokawa and Kleppa.⁵⁵ Within the experimental

uncertainty, the two sets were found to be consistent with the requirements of the Gibbs-Duhem equation. Two tests of consistency were made: (1) the area test,

$$\int_0^1 \bar{G}_{\text{Na}}^{\text{xs}} dx_{\text{Na}} = \int_0^1 \bar{G}_{\text{K}}^{\text{xs}} dx_{\text{Na}}; \quad (3)$$

and (2) the composition resolution test⁵⁶ whereby the values of $\bar{G}_{\text{Na}}^{\text{xs}}$ and $\bar{G}_{\text{K}}^{\text{xs}}$ obtained from the intercepts of the tangents to the smoothed curve of ΔG^{xs} vs. composition are compared with the experimental values of the partial excess quantities.

The excess free energies of mixing computed from the results of the present study are shown in Fig. IV-11 together with the calorimetric enthalpies of mixing determined by Yokokawa and Kleppa.⁵⁵ The difference between the two quantities, $\Delta H^{\text{M}} - \Delta G^{\text{xs}}$, is equal to the excess entropy of mixing, $T\Delta S^{\text{xs}}$.

100-0501

Fig. IV-11. Excess Free Energy and Enthalpy of Mixing in the Sodium-Potassium System at 384°K

The positive enthalpy of mixing of this alloy indicates a tendency toward demixing of the components, i.e., the energy of a Na-K "bond" is less than the mean of the energies of K-K and Na-Na "bonds." Hence, the lowest enthalpy of mixing is obtained when the smallest possible number of K-K and Na-Na "bonds" are destroyed on forming the mixture. Thus, the asymmetry of the enthalpy-of-mixing curve suggests that relatively fewer Na-K "bonds" are formed in potassium-rich solutions than in sodium-rich solutions. Furthermore, in potassium-rich solutions, the excess entropy of mixing is negative, whereas in sodium-rich solutions it is zero. These facts suggest that when sodium is added to liquid potassium, completely

⁵⁶VanNess, H. C., Chem. Eng. Science 11, 118 (1959).

random substitution of the sodium atoms for potassium atoms in the quasi-crystalline lattice of liquid potassium does not occur, the nonrandomness being such as to reduce Na-K contacts. On the other hand, when potassium is added to liquid sodium, the substitution of potassium atoms for sodium atoms appears to be nearly random. In a simple way, one might rationalize this in terms of the atomic volumes of potassium and sodium, 76.1 and 39.5 cubic angstroms, respectively, which stand in a ratio of close to two-to-one. Because of the size difference, a substantial number of pairs of sodium atoms rather than single atoms may be substituting for a single potassium atom in the potassium-rich solutions. The result of this would be a smaller positive heat of mixing and a less random mixing process than if an exclusively atom-for-atom substitution took place. Thus, qualitatively, the shape of the enthalpy-of-mixing curve and the sign of the excess entropy can be accounted for in terms of the atomic size effect.

2. Thermodynamics of Rare Earth-Cadmium Intermetallic Compounds

The rare earth or lanthanon metals, Ln, have nearly constant electronegativities (~ 1.2) and valences (3) and gradually decrease in atomic size with increasing atomic number. Intermetallic compounds formed by the lanthanons with some common partner offer the opportunity of isolating the effects of atomic size on compound stability from the large effects of electronegativity and valence.

The lanthanons and cadmium form series of intermetallic compounds having such formulas as LnCd_{11} , LnCd_6 , $\text{LnCd}_{4.5}$, LnCd_3 , LnCd_2 , and LnCd . Certain members of the series, however, do not occur; e.g., (a) lanthanons heavier than europium do not form LnCd_{11} , (b) lanthanum forms $\text{La}_2\text{Cd}_{17}$ rather than LaCd_6 , and (c) LnCd_3 compounds with Ln heavier than terbium are not found. Thus, although there are many similarities in the Ln-Cd phases formed, there are also some striking differences. The free energies and enthalpies of formation of Ln-Cd compounds were desired so that quantitative differences between the various systems could be established and related to changes in atomic size.

A vapor pressure method was used to determine the thermodynamic properties of selected Ln-Cd systems. The method consisted of measuring by means of a recording Knudsen effusion balance the pressure of cadmium in equilibrium with each pair of contiguous phases, i.e., the cadmium pressure for the equilibrium

The difference in the free energies of formation of two contiguous phases, ΔG_{ij} , may be computed by the relation

$$\Delta G_{ij} = \Delta G_{fi} - \Delta G_{fj} = (i - j) RT \ln \left(\frac{p_{ij}}{p_0} \right) \quad (5)$$

where p_{ij} is the partial pressure of cadmium according to Eq. 4 at temperature T in $^{\circ}\text{K}$, and p_0 is the corresponding vapor pressure of pure (liquid) cadmium. Measurement of the partial pressure of cadmium for the equilibrium

permits one to calculate the standard free energies of formation of each of the contiguous intermetallic compounds.

During this report period, measurements of cadmium decomposition pressures as functions of temperature corresponding to reaction 6 were completed for $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Tm, and Lu}$. From these data, the free energies and enthalpies (ΔH_f°) of formation of the 1:1 Ln-Cd compounds have been computed and are given in Table IV-7. The free energy data are the more reliable since the enthalpies involve the temperature coefficients of partial pressure and the latter were obtained over relatively small temperature ranges.

TABLE IV-7. Free Energies and Enthalpies of Formation of LnCd Intermetallic Compounds at 500°C

Compound	$-\Delta G_f^{\circ}$ (kcal/mole)	$-\Delta H_f^{\circ}$ (kcal/mole)
LaCd	14.3	14.9
CeCd	13.7	a
PrCd	13.8	a
NdCd	14.5	16.0
SmCd	14.5	18.5
GdCd	14.7	18.8
TbCd	14.2	17.6
HoCd	14.6	20.6
TmCd	14.0	18.5
LuCd	13.6	16.9

^aTemperature range of data not large enough to obtain ΔH_f° .

The magnitude of the free energies and enthalpies of formation suggest that significant electron transfer occurs on compound formation. This is consistent with the difference in electronegativity between cadmium (~ 1.7) and the lanthanon metals (~ 1.2). One also expects increased electron transfer to be accompanied by bond shortening and strengthening. The ΔG_f° values do not reveal a significant dependence on the bond lengths, but the ΔH_f° values, which are expected to be more sensitive to small changes, do indicate the expected trend. Figure IV-12 shows the variation of ΔH_f° with the volume of the unit cell. (The LuCd compounds have simple cubic (CsCl) structures; thus, one atom of each kind occupies the unit cell volume a_0^3 .) The trend of more negative ΔH_f° values with decreasing bond

length is evident, although the exact quantitative relation is apparently masked by uncertainties in the experimental data.

108-9500

Fig. IV-12. Variation of Enthalpy of Formation of LnCd Compounds with Unit Cell Volume

3. Ultrasonic Measurements in Liquid Metal Solutions

Spectroscopy has been a valuable tool in elucidating the nature of species in nonmetallic solutions. The usefulness of this tool for metallic solutions, however, is hampered by their opacity. Of the possible spectroscopic methods, ultrasonic absorption appears to offer the greatest potential for studies of species in liquid metal solutions, as metal solutions are not opaque to sound.

Ultrasonic methods have come into prominence in recent years as a means for detecting complex species in aqueous⁵⁷⁻⁶⁰ solutions and for studying the kinetics of their formation. However, for liquid metals,⁶¹⁻⁶³ ultrasonic investigations have so far provided only suggestive evidence for the existence of association and their potential has not yet been fully explored. For example, the method of continuous variations (method of Job⁶⁴) has been combined successfully with ultrasonic velocity measurements to detect aqueous complexes,⁶⁰ but it has not yet been tried with liquid metal solutions.

We are planning to study the existence of association in liquid metal solutions by using the method of continuous variations in conjunction with ultrasonic velocity measurements. Initially, ternary liquid metal systems formed by mixing two dilute binary solutions having a common solvent, e.g., Mg-Cd + Sn-Cd, will be examined by ultrasonic velocity measurements. The systems which show some degree of ordering of minor components will then be studied more thoroughly by an ultrasonic absorption method.

⁵⁷Saraf, J. R., and Sharma, P. N., J. Sci. Res. Inst. (Tokyo) 49, 236 (1955).

⁵⁸Bose, P. C., and Srivastava, L. N., Z. Physik. Chem. (Leipzig) 205, 96 (1955).

⁵⁹Satyavati, T., Reddy, P. J., and Subrahmanyam, S. V., J. Phys. Soc. Japan 17, 1061 (1962).

⁶⁰Prakash, S., Ichhaporia, F. M., and Panday, J. D., J. Phys. Chem. 68, 3078 (1964).

⁶¹Jarzynski, J., Proc. Roy. Soc. 81, 745 (1963).

⁶²Abowitz, G., and Gordon, R. B., Trans. AIME 227, 51 (1963).

⁶³Jarzynski, J., and Litovitz, T. A., J. Chem. Phys. 41, 1290 (1964).

⁶⁴Job, P., Ann. Chim. (Paris)[10] 9, 113 (1928).

4. Magnetic Susceptibilities of Uranium Monosulfide-Thorium Monosulfide Solid Solutions⁶⁵

Various models have been proposed to describe the electronic configuration of uranium monosulfide.^{66,67} To choose between these models,

108-9067

Fig. IV-13. Variation of Reciprocal Molar Susceptibility of Uranium in US-ThS Solid Solutions with Temperature and Composition

information about the number of magnetic electrons per uranium atom and about the extent of quenching of angular momentum was needed. By using the technique of magnetic dilution,^{68,69} such information can be obtained from magnetic susceptibility studies. Accordingly, the magnetic susceptibilities of a series of solid solutions between strongly ferromagnetic uranium monosulfide (US) and weakly paramagnetic thorium monosulfide (ThS) were measured. The results of these measurements are shown in

Fig. IV-13 where the reciprocal molar susceptibility of uranium⁷⁰ is plotted against absolute temperature.

Pure US was found to have a linear (Curie-Weiss) dependence on temperature and a Curie temperature (intersection at the temperature axis) of 181°K. A comparison of our results with those of other investigators^{67,71-74} is shown in Table IV-8. It can be seen that there is a considerable spread in both the magnetic moment and absolute susceptibility

⁶⁵Collaborative effort with D. Gruen and C. Thalmayer of the Chemistry Division.

⁶⁶Kazmierowicz, C. W., "Galvanomagnetic Properties of Uranium Monosulfide," Master of Science thesis, Illinois Institute of Technology, June 1963.

⁶⁷Allbutt, M., Junkison, A. R., and Dell, R. M., International Symposium on Compounds of Interest in Nuclear Reactor Technology, 1964 Nuclear Metallurgy Symposium AIME, Edward Bros., Inc., Ann Arbor, Michigan, p. 65.

⁶⁸Selwood, P. W., *J. Am. Chem. Soc.* **55**, 3161 (1933).

⁶⁹Trzebiatowski, W., and Selwood, P. W., *J. Am. Chem. Soc.* **72**, 4504 (1950).

⁷⁰These values have been corrected for the paramagnetism of both UOS and ThS and the diamagnetism of both ThOS and the core electrons of uranium. Impurity corrections were made on the assumption that all the solid solutions contained proportionately the same impurities found in the 27% US-ThS solution by electron probe microanalysis and chemical analysis.

⁷¹Didtschenko, R., and Gortsema, F. P., *J. Inorg. Chem.* **2**, 1079 (1963).

⁷²Trzebiatowski, W., and Suski, W., *Roczn. Chem. Pol.* **37**, 117 (1963).

⁷³Picon, M., and Flahaut, I., *Compt. Rend.* **241**, 655 (1955).

⁷⁴Eastman, E. D., Brewer, L., Bromley, L. A., Gilles, P., and Lofgren, H. L., *J. Am. Chem. Soc.* **72**, 4019 (1950).

values. In view of the difficulties associated with the preparation of pure US, much of the discrepancy can probably be associated with sample purity.

TABLE IV-8. Magnetic Moment, Room-temperature Molar Susceptibility and Curie Temperature of Uranium in Uranium Monosulfide

Investigators	Magnetic Moment, μ_B (Bohr Magnetons)	Molar Susceptibility; $\chi_M \times 10^6$ at 298°K (emu)	Curie Temp. (°K)
This study	2.51	6667	181
Didschenko and Gortsema ⁷¹	2.46	6280	180
Trzebiatowski and Suski ⁷²	2.22	5773	185
Allbutt et al. ⁶⁷	2.25	5022	178
Picon and Flahaut ⁷³	2.09a	4603	-
Eastman et al. ⁷⁴	1.99a	4180	-

^aCalculated from the measured room-temperature susceptibility by assuming that the system follows a Curie-Weiss law with $\Delta = 180^\circ\text{K}$.

The Curie temperature of the alloy was progressively lowered by dilution with ThS, reaching $\sim 0^\circ\text{K}$ for the 37% US solution. Dilution was so effective that no ferromagnetic ordering was detected for either the 37% or 27% US solutions down to 4.2°K. Dilution to 27% US yielded a susceptibility curve typical of a paramagnetic system with a negative Weiss constant. Our results contradict those of Allbutt et al.⁶⁷ who reported that dilution with ThS to 10 m/o US did not affect the Curie temperature. Failure to attain complete solid solution in their US-ThS preparations is the most probable explanation for their results.

A tentative interpretation of the present results in terms of electronic structure is as follows. These alloys may be regarded from the tight-binding point of view as composed of S^{2-} ions, Th^{4+} (Rn core) ions, and U^{5+} ($5f^1$ outside Rn core) ions. The remaining electrons populate a s-d conduction band. The curvature of the magnetic susceptibility of the 27% US solution may be interpreted in terms of the influence of a crystal field of cubic symmetry on a single 5f electron.⁷⁵ Preliminary calculations reveal that an overall splitting of the $^2F_{5/2}$ multiplet of approximately 660 cm^{-1} provides a reasonable single-parameter fit to the experimental susceptibility curve.

⁷⁵Gruch, D. M., and Hutchison, C. A., Jr., J. Chem. Phys. 22, 386 (1954).

V. REACTOR SAFETY

The program on reactor safety comprises two major areas of research: (1) the study of metal-water reactions, and (2) studies relating to the safety of fast reactors.

A. Metal-Water Reactions

The study of metal-water reactions is important because a large liberation of heat and hydrogen gas could conceivably result from an accident in a water-cooled reactor. A coolant failure or a severe nuclear excursion could cause melting and rapid dispersion of the reactor core metals into the cooling water. This might lead to a highly exothermic chemical reaction between the metals and the cooling water. It is possible that the energy released by such a reaction could exceed the energy released by the fission process during a nuclear excursion.

Studies of metal-water reactions can be divided into three broad categories: (1) basic studies of the reactions under idealized conditions, (2) studies under simulated reactor accident conditions, and (3) calculational studies. The first category includes the experimental determination of isothermal rate laws and rate constants; these data are needed to develop mathematical expressions of reaction rates as a function of time and temperature for use in accident calculations. Isothermal studies also locate, for a particular reaction, characteristic temperatures at which the nature of the reaction mechanism or products changes sharply. Also included in the category of basic studies under idealized conditions are nonisothermal studies of the reactions of small metal particles with water. These studies were performed by condenser discharge heating of submerged metal wires (see, for example, ANL-6766, p. 99) and by laser-beam heating of small submerged particles (see, for example, ANL-7020, p. 180). The small particle studies have been completed for the metals of interest in reactor safety, namely, zirconium, aluminum, uranium, and stainless steel. The second category, accident simulation studies, includes both experiments designed to simulate the environment experienced by power reactor fuel elements following a loss-of-coolant accident and in-pile simulation of reactor excursion accidents. In the third category are included calculational studies and accident analyses in which the experimental results from different methods are compared and methods of accident analysis devised.

1. Isothermal Reaction Rate Studies

Metals of primary concern in the safe operation of water-cooled reactors are uranium, zirconium, aluminum, and stainless steel. Enough isothermal data have been accumulated on uranium and zirconium reactions with steam to meet current needs in safety analyses. However, additional studies are required of the reactions of aluminum and stainless steel with steam. Previous isothermal studies were performed by induction or

induction-levitation heating of metal samples in flowing steam (ANL-6875, p. 133 and ANL-6766, p. 100). The reaction of stainless steel with steam was studied at temperatures up to 1400°C. Above that temperature, the reaction rate increased sharply, owing to the disintegration of the metal to form an oxide foam. Sample disintegration and foaming resulted in a loss of coupling between the induction coil and the sample, thereby limiting useful studies to 1400°C and below. It became necessary, therefore, to develop a method of study that did not involve direct induction heating.

In addition to the need for high temperature isothermal studies of the stainless steel-steam reaction, there has been a need for isothermal studies of the aluminum-steam reaction at elevated pressures, since results of in-pile studies have indicated that an increase in extent of aluminum-water reaction results from an increase in pressure (ANL-6875, p. 139). Although the isothermal reaction of aluminum with steam at one atmosphere pressure had been studied (ANL-6875, p. 133), laboratory studies had not been performed with steam at higher pressures.

A high pressure, high temperature furnace was constructed for the study of the reactions of stainless steel and aluminum with steam. The preliminary design of the high pressure furnace was described in previous reports (ANL-6875, p. 135 and ANL-7020, p. 175). The furnace, which is contained in a steel pressure vessel, consists of two zones, an inner steam-filled zone and an outer argon-filled zone. The outer zone contains molybdenum heater windings and zirconia insulation. The two zones are separated by an alumina tube; the pressures in the two zones are automatically matched to avoid stresses on the tube. The sample is loaded into the lower part of the inner steam-filled zone, which is maintained at about 800°C. To begin an experiment, the sample is raised into the upper part of the steam-filled zone by an external crank mechanism. Temperatures as high as 1700°C can be attained in the hottest part of the steam zone; maximum operating pressure is 1000 psig. A flow of steam through the furnace is maintained. Effluent steam containing hydrogen produced by metal-steam reaction is condensed outside of the furnace. The hydrogen is collected continuously in order to determine the extent of metal-water reaction.

Preliminary experiments were performed with type 304 stainless steel (16.8 w/o Cr, 8.3 w/o Ni, 1.7 w/o Mn, 73.2 w/o Fe) discs, 3/4-in. in dia. and 1/4-in. long. Molten metal samples were contained in alumina crucibles. Results of experiments performed at 1400°C at 1, 2, and 12 atm pressure are shown in Fig. V-1. The extent of reaction is expressed in terms of hydrogen generation per gram of sample, instead of the more usual terms of hydrogen generation per square centimeter of sample surface area. This was necessary because of the swelling and foaming of the sample which resulted in a rapidly changing surface area. The results given in Fig. V-1 indicate that the reaction rate was independent of steam pressure and that approximately one-third of a sample had reacted in about 10 min. The nature of the reaction (swelling and foaming) implies that the reaction rate will be

a function of sample size and shape and, moreover, that the reaction rate may be greater with thinner sample sections.

108-9415

Fig. V-1. Hydrogen Evolution from the Reaction between Type 304 Stainless Steel and Steam at 1400°C and Various Pressures. (High pressure furnace apparatus.) (Sample size: 3/4 in. dia. by 1/4 in. thick.)

To determine the stoichiometry of the stainless steel-steam reaction, a series of four experiments was performed in which small samples of type 304 stainless steel were completely reacted with steam at 1500°C. The results of the experiments are given in Table V-1. The average yield of hydrogen is 0.51 ± 0.01 liter (STP)/g, which is somewhat greater than values calculated previously. These calculations, which were based on the assumptions that the reaction products are Cr_2O_3 and FeO and that nickel does not react, yield a value for hydrogen generation of 0.40 liter (STP)/g. If it is assumed that the nickel forms NiO , a value of 0.44 liter (STP)/g is obtained. The experimental value of 0.51 liter (STP)/g indicates that higher oxides are formed.

TABLE V-1. Determination of the Total Hydrogen Generated by the Reaction of Type 304 Stainless Steel with Steam at 1500°C and 1-atm Pressure
Steam flow rate, 10 ml water/min

Sample Weight (g)	Approximate Time of Completion of Reaction (min)	Total Exposure Time (min)	Hydrogen Generated [liter (STP)/g of SS]
4.83609	60	100	0.522
3.87858	45	90	0.516
1.14582	12	26	0.510
2.34223	16	25	0.492
			Average 0.510

X-ray diffraction studies¹ were made of the oxidation products of the four experiments and showed that the major phase was of the Fe_3O_4 or spinel type. Other likely spinels, FeCr_2O_4 , NiFe_2O_4 , and NiCr_2O_4 , could not be distinguished from Fe_3O_4 by X-ray analysis. Calculation of the hydrogen yield on the basis of complete conversion to spinel compounds of the type M_3O_4 results in a value of 0.54 liter (STP)/g, which is only slightly greater than the observed value. It was therefore concluded that the oxidation by steam of type 304 stainless steel leads primarily to the formation of spinel type oxides in which the nickel and chromium atoms substitute freely into the Fe_3O_4 lattice.

Preliminary experiments were also performed in the high pressure furnace with aluminum samples (Alcoa, 99.99+ % purity). Samples were cut from 3/4-in. dia. rod into nominal 1/2-in. lengths and were contained as molten metal in alumina crucibles. Results of a series of experiments at 1400°C and 1, 2, 4, 8, and 16 atm pressure are given in Fig. V-2. The results show that the reaction rate is approximately linear and increases with increasing pressure. The reaction rate increases approximately in proportion to the square root of the pressure. Additional data at other temperatures are required before the pressure dependence or the mechanistic explanation for it can be determined.

108-9417 Rev. 2

Fig. V-2. Hydrogen Evolution from the Reaction between Aluminum and Steam at 1400°C and Various Pressures. (High pressure furnace apparatus.) (Sample size: 3/4 in. dia. by 1/2 in. thick.)

¹Performed by R. Schablaske of the CEN Analytical Laboratory.

A series of experiments was performed in the high pressure furnace to evaluate the reaction between $\text{UO}_{2.0}$ and steam to produce a higher oxide of uranium and hydrogen gas. The reaction of the metallic constituents of a reactor core with water or steam is believed to be the major source of hydrogen generation during a reactor accident; however, large quantities of UO_2 are employed as fuel in power reactors so that even a slight oxidation of UO_2 by steam could add significantly to the hydrogen produced during an accident. Thermodynamic calculations have indicated that at 1500°C an oxide having the composition $\text{UO}_{2.17}$ would be in equilibrium with pure steam. The experiments with UO_2 in the high pressure furnace were performed in order to verify the thermodynamic prediction and to evaluate the reaction rate with typical reactor fuel pellets.

The UO_2 samples consisted of pressed and sintered cylinders ($>95\%$ theoretical density) $1/2$ in. in dia. by $1/2$ in. high and were contained in alumina crucibles. The usual experimental procedure employed for studies with the high pressure furnace was altered to avoid any contact between UO_2 and air at elevated temperature. The amount of UO_2 oxidation was determined by four independent methods: sample weight gain during an experiment, gravimetric analysis of residues, X-ray diffraction, and hydrogen evolution. Good agreement between the four methods of measurement was obtained. A plot of the final composition (O/U ratio), taken from weight gain data, as a function of the square root of time is shown in Fig. V-3. The reaction rate follows an apparent parabolic law for the first

Fig. V-3
Oxygen-to-Uranium Ratio after
Exposure of UO_2 to Steam at
 1500°C and 1 atm Pressure

70 min and then tapers off at a final composition of about $\text{UO}_{2.17}$. The oxidized samples were noticeably darkened by oxidation; however, they did not crack or fragment.

The extent of reaction of UO_2 at 1500°C , after long exposure to steam, was in good agreement with the value calculated from thermodynamic data. Similar thermodynamic calculations have indicated that, if the steam phase contains about 10% hydrogen, then the equilibrium composition of the solid is about $\text{UO}_{2.02}$ at 1500°C . It is therefore apparent that the UO_2 -steam reaction will be greatly suppressed if some hydrogen remains in contact with the solid oxide. For this reason UO_2 clad with a reactive metal such as stainless steel or Zircaloy is not expected to react until the metal has been completely oxidized.

2. Simulation of Loss-of-coolant Accidents

In a loss-of-coolant accident in a water-cooled reactor, the cooling water would be lost suddenly through a break in the piping or in the reactor pressure vessel. The reactor core, which would then be in a steam environment, would self-heat from nuclear decay energy. The fuel elements in a typical power reactor would reach temperatures above 1000°C in five to ten minutes after a pipe break occurred. As self-heating continued, the fuel cladding would begin to react with steam. Eventually the reactor core would collapse because of the accumulation of energy from nuclear decay and chemical reaction under conditions which allowed very little energy loss to occur.

The initial phase of a loss-of-coolant accident has been simulated in the high pressure furnace (see ANL-7020, p. 176). In that study, a type 304 stainless steel-clad, UO_2 -core fuel element and a Zircaloy-2-clad, UO_2 -core fuel element were exposed to a relatively slow flow of steam for several hours. Although extensive cladding oxidation occurred, it was apparent that the reaction rate was limited by the low flow rate of steam past the samples.

In more recent experiments in the high pressure furnace, the steam flow rate was increased by a factor of ten, resulting in a linear steam flow rate of 3.2 ft/sec past the sample. Each sample (8 in. long by 0.4-in. OD) consisted of a number of high density UO_2 pellets clad with either type 304 stainless steel or Zircaloy-2 tubing, each having a 27-mil wall thickness. Each sample was raised into the high temperature section of the furnace at the rate of 1 in./min, thus requiring a total of 8 min for complete insertion. The sample was then allowed to remain in the high temperature section for an additional 2 min, after which it was rapidly withdrawn to the original position in the cooler part of the furnace.

The typical appearance of a stainless steel-clad fuel element which had been exposed to steam at 1 atm under the conditions outlined above

may be compared with that of an unexposed element in Fig. V-4. The temperature-time history of the top (hottest) end of this fuel element and a plot of the hydrogen evolution are given in Fig. V-5. The top of the fuel element reached a maximum temperature of about 1600°C and the bottom, a maximum of about 900°C, thereby creating an axial temperature gradient of about 700°C. The top one-third of the stainless steel cladding appeared to be completely reacted, whereas the remainder was only slightly reacted. The demarcation between the two reaction zones can be readily seen in Fig. V-4. The maximum temperature at the demarcation has been estimated to be about 1400°C from the results of other experiments. The total hydrogen evolved corresponded to 37% reaction of the stainless steel present in the fuel element.

108-8757

Fig. V-4. Type 304 Stainless Steel-clad, UO_2 -core Simulated Fuel Pin before and after Exposure to One atm Steam at 1600°C for 10 min

stainless steel oxides. X-ray analysis of the stainless steel oxides showed a structure of the $\gamma\text{-Fe}_3\text{O}_4$ type.

108-8845

Fig. V-5. Hydrogen Evolution and Sample Temperature during Experiment with Type 304 Stainless Steel-clad Fuel Rod in High Pressure Furnace in a Steam Environment

Photomicrographs of a cross section near the top of the fuel element showed areas of interaction between the UO_2 and the

Additional experiments were conducted to determine the effects of both steam flow rate and steam pressure. In the first of these experiments, the pressure was maintained at 1 atm and the steam flow rate was doubled. In the second and third experiments, the pressure was increased to 4 and 11 atm, respectively, with the original steam flow rate. The results of these experiments indicated that there was no significant effect of flow rate or pressure.

108-8758

Fig. V-6. Zircaloy-2-clad, UO_2 -core Simulated Fuel Rod before and after Exposure to One atm Steam at 1600°C for 10 min

The typical appearance of a Zircaloy-2-clad fuel element which was exposed to steam at 1 atm under these same conditions may be compared with that of an unexposed element in Fig. V-6. The temperature-time history of the top (hottest) end of the element and a plot of the hydrogen evolution are given in Fig. V-7. The top and the bottom of the fuel element reached maximum temperatures of 1600°C and about 900°C , respectively, resulting again in an axial temperature gradient of about 700°C . The hot upper end of the sample was embrittled, and only the outer surface was converted to ZrO_2 . There was no apparent interaction between the UO_2 and the cladding. In the case of Zircaloy-2-clad fuel pin, there was no sharp demarcation between reaction zones; however, the attack on the

108-8846

Fig. V-7. Hydrogen Evolution and Sample Temperature during an Experiment with Zircaloy-2-clad Fuel Rod in High Pressure Furnace in a Steam Environment

cladding was more severe at the hotter end than at the cooler end. Measurement of the evolved hydrogen indicated that the overall extent of reaction of Zircaloy-2 in the fuel element was 18%.

Experiments with Zircaloy-2-clad fuel elements were also performed at pressures of 4 and 11 atm. As in the case of the experiments with stainless steel, there was no significant effect of pressure on either the rate or the extent of the Zircaloy-2-steam reaction.

The parabolic oxidation law, reported previously for zirconium (see ANL-6548) was used to calculate the rate and extent of reaction of the fuel element. The parabolic oxidation law can be expressed as follows:

$$\frac{-dr}{dt} = \frac{K}{(r_0 - r)} \exp\left(\frac{-\Delta E}{RT}\right) \quad (1)$$

where r = the radius of unreacted metal in the pin, cm,

r_0 = its original radius, cm,

K = the rate law constant, $0.3937 \text{ cm}^2/\text{sec}$,

ΔE = the activation energy, 45.5 kcal/mole ,

R = the gas constant, $1.987 \text{ cal}/(\text{mole})(^\circ\text{K})$, and

T = temperature, $^\circ\text{K}$.

The equation was programmed on the CDC-3600 digital computer for integration using small time intervals. An arbitrary temperature-time function could be inserted into the calculation. The temperature-time functions that were programmed into the computer are plotted in Fig. V-8 and represent the approximate temperature history experienced by various portions (seven regions) of the Zircaloy-2 cladding. The corresponding calculated reaction rates for these regions, expressed in terms of mils of cladding reacted during the course of the exposure, are also plotted in Fig. V-8.

The amount of cladding reacted at the top (hottest) region of the fuel rod was calculated to be 13.1 mils (see uppermost curve in Fig. V-8). The calculated reaction compares favorably with the measured thickness of the oxide film in photomicrographs taken of the oxidized fuel element. The calculated reaction of each region of surface was summed over the seven regions and the total hydrogen evolution and percent reaction for the entire fuel rod calculated. The calculated extent of reaction was 3.40 liters H_2 (21.3% reaction) compared with measured values of 2.96 liters H_2 (18.5% reaction). Thus the extent of reaction calculated from the parabolic rate law is only about 15% higher than that observed.

108-9419

Fig. V-8. Calculation of Reaction Rate of Zircaloy-2 Cladding on Fuel Element in High Pressure Furnace Experiment

scale experiment is being designed in which 19 fuel elements, each 3 ft long, will be used to simulate a portion of a power reactor. The Zircaloy-2-clad, UO_2 -core elements will be heated using a tungsten rod located in a central hole within the UO_2 pellets. Resistance heating of the tungsten rods will provide simulation of nuclear decay energy generation. Variable heating rates and variable steam flow rates through the bundle of elements will allow simulation of a wide range of accident conditions. The accident will be modeled only up to the point at which the fuel element begins to fail. At this point, electrical heating will probably fail owing to attack of the exposed tungsten heaters by steam.

The results of the experiments with stainless steel-clad and Zircaloy-2-clad fuel elements indicate that above 1400°C the reaction of stainless steel with steam is more rapid than the reaction of Zircaloy-2 with steam. The rapidity of the stainless steel reaction under these conditions is due to the melting and foaming (and the subsequent large increase in surface area) of the mixture of stainless steel oxides. The rapidity of the oxidation of the stainless steel as it reaches about 1400°C results in observable self-heating of the cladding, as indicated in the temperature-time history in Fig. V-5. Neither Zircaloy nor ZrO_2 are melted under the conditions of these experiments. However, the overall heat of reaction of Zircaloy with steam is much greater than the heat of reaction of stainless steel with steam.

Because of the great importance of information on a loss-of-coolant accident in the safety analysis of thermal power reactors, several additional experiments are planned which will simulate various phases of the accident. A large-

A later phase of the accident will be studied in the Transient Reactor Test Facility (TREAT). In these experiments, a bundle of fuel elements (from 3 to 9 elements) will be suspended above a water pool and melted by a transient neutron burst generated by the reactor. The normally rapid neutron burst developed by the TREAT reactor will be slowed as much as possible to allow a slower nuclear heating rate. The fuel bundle will be melted over a 10-sec period and the nature of the failure and the chemical reactions occurring as the melted structure falls into the water pool will be observed.

3. In-pile Simulation of Nuclear Excursion Accidents

The reactions of specimens of typical reactor fuel in a water environment are being studied by subjecting the fuel to a burst of neutrons in TREAT. The Kiwi-TNT destructive transient in Nevada also provided an opportunity for several short-period experiments. These in-pile experiments are intended to provide a more direct simulation of the conditions prevailing during a nuclear excursion in a water-cooled reactor.

In the in-pile experiments, a stainless steel autoclave contains the specimen and the water. Extent of metal-water reaction is determined by measuring the quantity of hydrogen evolved. Subsequently, particle sizes are determined and metallographic studies are made.

The status of the in-pile studies is indicated in Table V-2. Experiments in TREAT were performed initially with single short pins or small plates of each fuel type in 25°C water with a 20 psia helium overpressure. Later, experiments were performed to determine the effects of: (a) heated water (285°C, 1000 psia steam overpressure), (b) preirradiation of the fuel, and (c) clustering of nine 6-in. long fuel elements. The short-period experiments listed in Table V-2 were performed by placing 24 small

TABLE V-2. Status of In-pile Studies

Fuel Type	Room-temp. Water ^a (20 psia He)	Heated Water ^a 285°C (1000 psia)	Preirradiated Fuel ^a	Photographic Experiments ^a	Large-scale Fuel Clusters ^a	Short Period ^b
<u>Metallic</u>						
Uranium metal (including uranium- rich alloys)	Completed	Completed	Completed	-	2 runs	6 runs
Aluminum-rich uranium alloys	Completed	Completed	Completed	10 runs	-	6 runs
Zirconium-rich uranium alloys	Completed	Completed	Samples Preirradiated	-	-	-
<u>Cermet</u>						
Aluminum-U ₃ O ₈	Completed	Completed	-	4 runs	-	-
Stainless steel-UO ₂	Completed	-	-	-	-	-
<u>Oxide (UO₂ or Mixed Oxide Core)</u>						
Aluminum clad	Completed	-	-	-	-	-
Zirconium clad	Completed	2 runs	Samples Preirradiated	-	2 runs	6 runs
Stainless steel clad	Completed	-	Samples Preirradiated	-	2 runs	6 runs

^aIn TREAT.

^bKiwi-TNT Test, Mercury, Nevada, January 12, 1965.

autoclaves from 1 to 12 ft from the periphery of the Kiwi nuclear rocket reactor during the Kiwi-TNT destructive test conducted in Nevada on January 12, 1965 (see ANL-7020, p. 187). The value of the Kiwi experiments resulted from the short period (the time for the reactor power to increase by a factor of 2.718) in the excursion. The period in the Kiwi excursion was 0.6 msec whereas the shortest period available in TREAT is 40 msec. The results from the Kiwi experiments with metallic uranium fuel pins are compared in Fig. V-9 with TREAT results and with results of laboratory studies by the condenser discharge method. In general, the results of the Kiwi experiments agreed with those of experiments conducted in heated water in TREAT and in the laboratory experiments.

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Fig. V-9. Extent of Uranium-Water Reaction: A Comparison of Experimental Data

Scale-up experiments in which nine fuel pins are irradiated simultaneously in TREAT were continued. The apparatus for these experiments was described in a previous report (ANL-7020, p. 186). Current scale-up experiments have been performed with Zircaloy-2-clad, UO_2 -core fuel elements

108-9427

Fig. V-10. Results of Meltdown Experiments in TREAT with UO₂ Core, Zircaloy-2-clad Fuel Pins Submerged in Water

alloy. The extent of aluminum-water reaction is plotted as a function of fission energy input in Fig. V-11. The plot effectively demonstrates the energy threshold required for initiation of extensive reaction. The HFIR fuel samples retained their plate-like shape at fission energy inputs as high as 440 cal/g, even though 230 cal/g of energy is sufficient to melt the aluminum cladding and the aluminum in the matrix of the fuel. This is shown in Fig. V-12 where the progressive damage to fuel plates at increasing fission energy inputs is apparent. The extents of reaction of the HFIR fuel plates were quite similar to those of aluminum-uranium alloy fuel plates studied previously (see ANL-6875, p. 142). The principal difference between the two types of fuel was the ability of the Al-U₃O₈ cermet fuel to retain its plate-like shape at energies greater than that required to melt the aluminum. This high temperature strength has been postulated to be due to development of a rigid U₃O₈ ceramic matrix.

and with stainless steel-clad, UO₂-core fuel elements. In both cases, the results of the scale-up experiments did not differ markedly from those of the previous single-pin tests. In Fig. V-10 the results of two scale-up experiments with Zircaloy-2-clad fuel are compared with previous results of single-pin experiments. The results of the experiments with the 9-pin clusters add considerable confidence in the application of the TREAT results to the analyses of hypothetical nuclear excursion accidents in water-cooled power reactors.

A series of experiments was performed in TREAT with single plates of fuel of the kind that is to be employed in the High Flux Isotope Reactor (HFIR). The plates used were aluminum-U₃O₈ cermet fuel, clad with 10 mils of 6061 aluminum

108-9245 Rev. 1

Fig. V-11. Results of Meltdown Experiments in TREAT with HFIR Fuel. (41.45 w/o U₃O₈, 93.17% enriched, 58.55 w/o aluminum cermet plates clad with 10-mil 6061 aluminum on two sides; 1.0 in. x 0.5 in. x 0.05 in.)

108-8767 Rev. 1

Fig. V-12. Photographs of Samples of HFIR Fuel Plate Subjected to Transient Fission Heating in TREAT in 30°C Water with 20 psia Helium Overpressure. (Energy inputs less than 500 cal/g.)

4. Calculational Studies

The major calculational effort during the past year was undertaken in the area of accident analysis. The effort was a continuation of the analysis of a loss-of-coolant accident in a water-cooled power reactor described in the preceding report (ANL-7020, p. 190). The reactor conceived for the LOFT (Loss of Fluid Test) facility² was used as a model for these calculations. In the proposed accident, the core temperature rises because of decay heating, after a 10-sec blowdown which completely uncovers the reactor core. The core eventually collapses owing to melting of the cladding. In this study the temperature and the extent of cladding-steam reaction for the core were calculated as a function of time. To facilitate these calculations, the core was divided into ten sections represented by various rates of decay heating. The calculations were performed for each section by numerically solving two equations on an IBM-704 computer. One equation described the rate of reaction of the cladding metal with steam while the other was an energy balance, in which the energy accumulation in the fuel and cladding was equated to the chemical energy and decay energy developed in them. Heat losses were ignored. Several other simplifying assumptions were made, namely, that the decay energy was distributed in the same manner as the reactor power, that the temperature of the cladding was equal to that of the fuel at any point along individual fuel rods, and that the heating and reaction of support structures could be ignored.

The previous calculations were performed for UO_2 fuel clad with 25 mils of zirconium. In the present study, the calculations were extended to the case of an identical reactor in which the UO_2 fuel was clad with 15 mils of stainless steel instead of zirconium. The calculations for the zirconium cladding had used the parabolic oxidation law for zirconium (see ANL-6548) when the reaction was not limited by the quantity of steam. When the reaction was limited by the steam flow through the core, the reaction rate was assumed to be equal to a constant calculated by dividing the mass steam flow rate by the total cladding area. For the stainless steel cladding, the nature of the reaction (swelling and foaming) has prevented development of a simple reaction rate law. For the present calculations, the following assumptions are believed to be adequate: (1) below 1400°C , no reaction occurs between stainless steel and steam; (2) above 1400°C , a very rapid reaction occurs which is limited only by the availability of steam.

Calculations were performed for four cases according to the availability of steam to the reactor core: (1) unlimited steam flow, (2) a steady flow rate of 1000 pounds of steam per hour through the core, (3) a steady flow rate of 100 pounds of steam per hour through the core, and (4) no steam flow, i.e., no metal-steam reaction. The rate of chemical

²Wilson, T. R., et al., "An Engineering Test Program to Investigate a Loss-of-Coolant Accident," Report IDO-17049, Phillips Petroleum Co., October 1964.

reaction of the entire reactor core was calculated for each case of steam availability and for both the zirconium-clad and the stainless steel-clad

fuels. The results of these calculations (Fig. V-13) show that the reaction of the stainless steel cladding is only slightly lower than that of the zirconium cladding.

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Fig. V-13. Calculated Percent Reaction-time Curves for Entire Reactor Core with Various Quantities of Steam in Loss-of-coolant Analysis Accident

The reaction regime represented in Fig. V-13 comes to an end when the energy accumulation in the reactor core (nuclear decay and chemical energy) is sufficient to result in core collapse. A very simple core collapse model was used, i.e., the core was assumed to collapse when the average energy in the core was sufficient to melt the fuel rods (either the cladding metal, 1370°C for stainless steel and 1852°C for zirconium, or the urania fuel, 2800°C). The core collapse times and the extents of cladding reaction at these times are tabulated in Table V-3.

The results in the table show clearly that the large amount of energy from the zirconium-steam reaction greatly reduces the core collapse time whereas the small amount of energy from the stainless steel-steam reaction is almost negligible in comparison with the nuclear decay energy. (The course of the accident subsequent to core collapse depends on various factors, such as the amount of residual water present and the time required to melt through the support structure.)

TABLE V-3. Time Required for Collapse of Core after Blowdown and Extent of Reaction Based on the Average Nuclear Decay and Chemical Energy Content

Steam Flow	Case of Average Core Energy Sufficient to Fully Melt Metal Cladding (Zr, 1852°C; SS, 1370°C)				Case of Average Core Energy Sufficient to Begin to Melt Fuel (2800°C)			
	Collapse Time (sec)		Percent Metal Reacted		Collapse Time (sec)		Percent Metal Reacted	
	Zr-clad	SS-clad	Zr-clad	SS-clad	Zr-clad	SS-clad	Zr-clad	SS-clad
Unlimited	465	830	40	44	765	2560	62	80
1000 lb/hr	740	910	21	18	1080	2580	41	65
100 lb/hr	1200	918	6.0	2.0	2090	2700	13	20
No flow (No metal-water reaction)	1400	920	none	none	2600	2750	none	none

The results of the calculational studies are being used by reactor designers in evaluating the quantity of chemical energy and hydrogen gas that must be safely dissipated within reactor buildings.

B. Fast Reactor Safety Studies

The research program to investigate certain potential problems in fast reactor safety is continuing. The five problem areas being studied are: (1) interaction of fuel and cladding materials with liquid sodium, (2) transient heat transfer, (3) fuel migration and segregation in mixed uranium-plutonium compounds, (4) high temperature physical properties of fast reactor materials, and (5) reaction of sodium with air. Progress in these studies is reported below.

1. Interaction of Fuel and Cladding Materials with Liquid Sodium

A knowledge of interactions that may occur when abnormally hot reactor materials contact liquid sodium is necessary for assessment of the problems associated with fast reactor meltdown accidents. Initial experiments have been performed to observe chemical or physical effects of the interaction of sodium with selected fuels and cladding materials. The purpose of the survey study was to discover any unusual interactions such as exothermic chemical reactions, extensive surface attack, frothing, disintegration, or alloy formation.

The experiments were performed in an argon-filled glovebox (see ANL-7020, p. 196) in which the oxygen and water vapor concentrations were maintained at about 15 ppm each. In order to simulate the contact of coolant with reactor materials in a meltdown accident, small samples of the materials of interest were heated to a predetermined temperature and dropped into a pool of liquid sodium. The quenched samples were subsequently removed from the sodium, and examined for evidence of interaction.

Thus far, the reactor materials studied have been several potential cladding metals, plus uranium metal and UO_2 pellets. The metal samples (generally in the form of short cylinders which on melting formed nominal 1/4-in. spheres) were heated to temperatures as high as 2400°C in an induction-levitation coil. (The UO_2 pellets could not be levitated and were, therefore, heated by radiation from an inductively heated tantalum susceptor.) The heated samples were dropped into a vessel containing liquid sodium maintained at 250°C . Sample temperatures were measured by a recording two-color optical pyrometer. Heat transfer calculations indicated that sample temperatures decreased only about 100°C during the nominal 24-in. drop into the sodium.

The first potential cladding metals studied were vanadium-20 w/o titanium, niobium, niobium-1 w/o zirconium, vanadium, tantalum, and molybdenum. In initial tests, the specimens were heated to 1800°C , 2250°C ,

2175°C, 1950°C, and 2200°C respectively. At these temperatures the samples were not melted. The heated solid specimens were dropped into the molten sodium and immediately disappeared below the surface; thereafter the sodium bubbled for a brief period. Fastax motion pictures showed only moderate surface turbulence as the solid metal samples entered the sodium. The quenched samples showed no visual evidence of chemical attack by the sodium. Samples were sectioned and mounted for metallographic examination. The photomicrographs gave no evidence of interaction.

Some of the same metals were then tested at drop temperatures at which the metal samples were molten. Figure V-14 shows the appearance of typical sample residues after drops at the following temperatures: vanadium at 2200°C, titanium at 2050°C, and vanadium-20 w/o titanium at 2100°C. These materials fragmented upon contact with the liquid sodium. The contact brought about the expulsion of some of the sodium. The fragmented material, after being freed of sodium by immersion in alcohol, had a shiny metallic appearance suggesting that no chemical reaction had occurred. Figure V-15 shows the results of a series of drop tests with zirconium at various initial temperatures from 1700 to 2350°C. Violent fragmentation occurred only at 2350°C, the highest drop temperature studied in this series. At 2100°C, the particle was hollow and some material had been ejected from the center. At 2000°C, the residue was a nearly perfect sphere. At lower temperatures melting had been incomplete. In all cases the residue showed no evidence of chemical interaction.

V, 2200°C Drop

Ti, 2050°C Drop

V-20 w/o Ti, 2100°C Drop

108-9010 Rev. 1

Fig. V-14. Residues of Several Molten Metals Dropped into 250°C Sodium

108-8654

Fig. V-15. Zirconium Residues from Sodium Interaction Experiments at Various Drop Temperatures

The most violent interactions that were observed occurred with stainless steel. The residue from some drops with stainless steel and mild steel are shown in Fig. V-16. Stainless steel fragmented when dropped into molten sodium at drop temperatures as low as 1600°C, except in the case in which a ragged plate-like residue was formed at a drop temperature of 2100°C. At 2300°C, the stainless steel formed particles having an average diameter of about 10 mils. The result of the stainless steel experiments at this temperature have been quite reproducible. Many small particles of sodium, 2 to 3 mm in dia., were expelled from the sodium container. Moreover, up to 15% of the stainless steel was also ejected during the violent fragmentation of the specimens. In experiments with stainless steel in which the drop distances from the levitation coil were 6 and 2 in., the fragmentation was as violent and extensive as that observed in the standard 2-ft drop experiments. It was therefore concluded that the impact velocity is not a critical parameter for drop fragmentation.

108-8655

Fig. V-16. Stainless Steel and Mild Steel Residues from Sodium Interaction Experiments at Various Drop Temperatures

Experiments in which molten mild steel and molten nickel were dropped 2 ft into 250°C sodium showed similar behavior; however, the fragmentation appeared to be slightly less violent. Chemical analyses were performed on the residues from drop experiments with zirconium, stainless steel, mild steel, and nickel and indicated that no sodium was retained by the metal. This fact and the shiny metallic appearance of the particles indicated that there had been no chemical interaction.

The only fuel materials studied to date have been uranium metal and UO_2 pellets. Uranium metal (m.p., 1133°C) fragmented over a wide range of drop temperatures (1700 to 2450°C). The fragmentation was somewhat less violent than with stainless steel. The stainless steel samples broke up into approximately spherical particles, whereas the uranium samples formed a fragile filamentary network. The samples of UO_2 that were dropped as solid pellets (UO_2 m.p., ~2700°C) did not fragment; however, extensive cracking occurred in an experiment in which a UO_2 pellet was heated to 2100°C. Sodium was absorbed into the cracks and was not removed by a brief alcohol rinse. Sodium oxide appeared to exude from the cracks for several days after the experiment.

The principal finding in the experiments described above has been the violent fragmentation that occurs when molten metals, heated well above their melting points, are dropped into liquid sodium. This spontaneous breakup was surprising because it appeared to be contradictory to our previous experience of dropping very hot molten metals into water. Molten pellets of zirconium, uranium, stainless steel, and aluminum do not fragment when dropped into water. It was believed, at first, that the oxide film formed in drops into water may have helped to prevent fragmentation in that medium. To test this hypothesis spheres of noble metals were dropped both into water and into sodium. Although silver and gold do not form oxide films in water, they did not fragment when dropped into that medium; however, silver at 1900°C dropped into sodium did fragment. Thus it was concluded that the difference in behavior between water and the liquid sodium is not caused by the formation of oxide films, but by differences in the physical properties of water and sodium.

A likely explanation for the fragmentation process is that the driving force for breakup might be the violent growth and collapse of sodium vapor bubbles which are characteristic of subcooled boiling in the transition and nucleate regimes. In general, it would be expected that the transition and nucleate boiling regimes would extend from near the boiling point to around the critical point. For sodium, this is a range of temperatures from 900 to about 2300°C . All of the fragmentations occurred when molten metals cooled through some part of this temperature range. According to this hypothesis, fragmentation would also be expected to occur with molten metals in water, but only in the temperature region of violent boiling. For water at one atm, the boiling point is 100°C and the critical point is 373°C . Figure V-17 shows the residues from some experiments in which small samples of some low-melting metals were dropped into water. All of the samples were initially heated to 825°C , a temperature considerably above the melting points of the test metals. Bismuth, tin, and lead (with melting points below the critical temperature for water) did fragment, while zinc and aluminum (with melting points above the critical temperature for water) did not fragment.

According to our present view, the fragmentation process occurs as a molten material cools through the region of boiling of the liquid medium where there is violent growth and collapse of vapor bubbles. Metals useful for construction, such as aluminum, stainless steel, zirconium, and some of the more refractory metals, will fragment on cooling in molten sodium. However, they will not fragment on quenching in water because cooling and solidification occur in a nonviolent film boiling regime and these metals are fully solidified before they reach the temperature of violent boiling in water.

High speed motion picture studies of molten stainless steel entering liquid sodium have shown that, beginning with the contact of the metal with the sodium, have shown that, beginning with the contact of the metal with the sodium, a parabolic depression appears in the sodium and deepens over

Bismuth (M.P. 271°C)

Tin (M.P. 232°C)

Lead (M.P. 327°C)

Zinc (M.P. 420°C)

Aluminum (M.P. 659°C)

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Fig. V-17. Residues of Low Melting Metals Dropped into 0°C Water.
(All samples dropped at 825°C)

a period of about 5 msec. Then a cloud, which is presumably sodium vapor, appears. It is at this time when it is presumed that fragmentation occurs. The small particles of hot steel then transfer heat rapidly to a localized region of the sodium, thereby resulting in a burst of vapor which causes ejection of some of the sodium and some of the hot steel pellets. The first sign of particle ejection in one motion picture sequence occurred about 5 msec after contact.

These preliminary studies of the interaction of abnormally hot reactor materials with liquid sodium have identified a fragmentation mechanism which results in extensive subdivision of molten cladding metals. However, it appears that, for the reactor materials studied, chemical attack and alloy formation do not occur to a significant degree during the brief time available in a rapid quench. This knowledge should be useful in the interpretation of the results of in-pile meltdown tests of fast reactor fuel elements.

2. Transient Heat Transfer Studies

An experimental study of the transient heat transfer from small hot particles moving through a liquid coolant has been initiated. Studies in liquid sodium are of primary interest; however, studies in water are also being pursued. Knowledge of the rate and quantity of energy transfer that occurs between fuel particles and the coolant is necessary in order to analyze the consequences of a reactor incident in which hot fuel materials may be dispersed into a liquid coolant. The study was initiated because neither theoretical nor experimental information is available to allow calculation of the heat transfer which occurs when small particles at high temperatures are rapidly dispersed in either water or liquid sodium.

Preliminary experiments have been performed with a swinging-arm apparatus, in which a small heated metal sphere is either pulled or pushed through a tank of water. These studies were performed with a 1/4-in. nickel sphere which is connected by means of thermocouple wires to a swinging arm which causes the sphere to pass through a tank of water at about 12 ft/sec. The sphere, which is initially heated to temperatures from 150 to 1000°C, contacts the water for 0.1 to 0.2 sec, emerges from the water, and then cools slowly in air. The temperature drop of the sphere, measured by a platinum thermocouple, is converted into an overall boiling heat transfer rate. Data are reduced with the aid of a digital computer code which takes into account the temperature distribution within a sphere subjected to rapid cooling at the surface.

Typical results for the overall heat transfer rate from a nickel sphere to water at 30, 60, and 94°C at 1 atm pressure are shown in Fig. V-18. The measured heat transfer rates in subcooled water (30 and 60°C water) are considerably greater than the values predicted on the basis of existing knowledge. Further studies will determine the effects of sphere velocity, sphere diameter, and sphere material. Bubble behavior will be studied, also, by means of high speed motion pictures.

108-9423

Fig. V-18. Computed Heat Fluxes from Swinging-arm Experiments with 1/4-in. dia. Nickel Spheres (Velocity of sphere through water = 12 ft/sec.)

Similar studies of boiling heat transfer in liquid sodium are in the apparatus development stage. A remotely operated, motor-driven, swinging-arm apparatus is under development. A tantalum sphere with an imbedded tungsten-rhenium thermocouple has been constructed for use as the first specimen to be studied. The sodium studies will be carried out in an argon-filled glovebox.

3. Fuel Migration and Segregation in Mixed Uranium-Plutonium Compounds

Studies of fuel migration and segregation in mixed uranium-plutonium compounds are continuing. Segregation of the uranium and plutonium compounds within the fuel may seriously decrease the effectiveness of Doppler broadening as a shutdown mechanism in a nuclear reactor, since more time will be required before heat generated within the plutonium can be transferred to the uranium. Experiments are planned in which the degree of segregation will be measured in typical uranium-plutonium mixed fuels.

The initial experiments will be performed with samples of mixed uranium-plutonium oxide fuel. Small pellets of fuel will be heated for extended periods of time in a furnace which imposes a sharp temperature

gradient across one dimension of the sample. Samples will then be cut into wafers and concentration gradients induced by the temperature gradient will be determined by chemical analysis of individual wafers. A furnace which achieves a satisfactory temperature gradient has been constructed and is presently being relocated in a plutonium glovebox facility for studies with the plutonium-bearing oxide fuel.

4. Determination of High Temperature Physical Properties of Fast Reactor Materials

A program is under way to determine the physical properties of fast reactor materials at high temperatures. Data on properties such as specific heat, thermal conductivity, and density are needed for application to fast reactor accident models. Work has been initiated on the measurement of the specific heat of molten UO_2 which was determined to be a property of great importance in the analysis of fast reactor accidents.

Initial experiments have proven that UO_2 can be melted and heated to 3350°C in sealed tungsten containers. Induction heating of the tungsten container was used. It is presently planned to use the method of drop calorimetry for the specific heat measurements.

Measurements of the specific heat of other materials important in fast reactor technology or measurements of other properties will be undertaken as specific requirements in fast reactor safety analyses arise.

5. Studies of the Sodium-Air Reaction

Studies of the sodium-air reaction are needed to increase confidence in safety analyses for fast reactor installations. Fast reactor installations may contain large quantities of liquid sodium which will at times be pressurized. A leak in sodium-containing vessels or pipes could result in the spraying of liquid sodium into an air-filled enclosure. Rational analysis of such an accident requires a knowledge of the rate of reaction of sprayed droplets of sodium with air in order to predict the pressure-time history of such an accident. It is also necessary to know the chemical nature and state of subdivision of the oxidation products that would be formed under various conditions.

Preliminary studies of the reaction have concentrated on the thermodynamic calculation of the maximum adiabatic temperatures and pressures that can be obtained with mixtures of sodium and air. The results indicated that the maximum temperature is 1950°C for a mixture consisting of 5 gram atoms of sodium per mole of oxygen, whereas the maximum pressure is 102 psig for a mixture of 7 gram atoms of sodium per mole of oxygen.

The maximum theoretical pressures are, in general, higher than the usual design pressure ratings of reactor containment buildings. Thus, experimentation with sodium sprays in model enclosures is required to determine what practical maximum pressures must be anticipated in hypothetical accidents. An injector for spraying liquid sodium has been designed and is now being fabricated.

VI. ENERGY CONVERSION

Work on regenerative galvanic systems has continued throughout the year on basic physical-chemical and electrochemical studies with a parallel engineering research effort.

A regenerative electrochemical system is a system into which energy is fed (usually heat) and from which electrochemical energy departs; it is an energy conversion system that is closed with respect to mass. In the systems studied in this laboratory, an emf cell would function in the low temperature isothermal leg of a Carnot cycle to form a cell product and produce electrical energy. In the high temperature isothermal leg the cell product would be decomposed into the cell reactants, which would be separated and returned to their respective anode and cathode compartments of the cell. The two isothermal legs would be connected by an adiabatic countercurrent heat exchanger. In actual practice, imperfections in these cyclic operations would not allow the maximum Carnot efficiency to be achieved. The Carnot cycle efficiency limitation represents the price paid for converting random kinetic energy (thermal energy) into directed energy (electrical) and regardless of the method of regeneration, e.g., thermal or electrical, the Carnot cycle efficiency is the maximum theoretical efficiency of the cycle.

Energy conversion systems which have received the most research and development attention in the past ten years are the metal vapor turbines, thermionic diodes, magnetohydrodynamic generators, and thermoelectric devices. In comparison to any one of these four systems, much less effort has been directed toward the development of regenerative electrochemical systems. Nevertheless, conservative estimates of the practical cyclic efficiencies for several bimetallic systems and the lithium hydride system (see ANL-6925, p. 243) indicate that these efficiencies compare favorably with values estimated for the other systems. One outstanding difference exists, however, between the regenerative electrochemical converter and all the other systems, namely, the ability to operate at high power densities in the temperature region below 1500°C. This is potentially an important advantage, because a larger number of heat sources are available at the lower temperatures and also because problems with materials of construction are markedly reduced.

The regenerative electrochemical converter can be virtually free of mechanical parts and, in comparison to the other systems, the flowing liquids or gases are very low velocity streams. However, liquid metal-fused salt corrosion data under static and dynamic conditions are needed; little reliable information is available in the literature on systems of interest. A literature survey made in 1965 on corrosion data of container materials by the liquid metals, bismuth, lead, and tin, and by fused alkali

and alkaline earth fluorides, chlorides, and hydroxides indicated that two major problems are associated with this type of data. The first problem is that a great deal of the work was done with impure metals, wet salts, or under poorly controlled experimental conditions, so that the results do not represent the actual situation for clean systems and pure liquid salts or liquid metals. The second problem is that the scope of the data is too limited in many of the systems. This is especially true for the temperature variable; very few results above a temperature of about 800°C have been obtained. Also, relatively few dynamic corrosion data obtained under temperature gradients such as would exist in a cyclic electrochemical converter have been published. Probably the most severe and limiting materials problem in the electrochemical converter systems will be due to mass transport of material between the two temperature regions.

However, for the systems under study at Argonne, promising materials have been found which are not subject to corrosion in a dynamic system. The recent development of refractory metal vapor deposition techniques opens the door to relatively cheap fabrication of complex components, e.g., heat exchangers and boilers, which can be made from metals such as tantalum, niobium, and tungsten.

An American Chemical Society monograph¹ has been prepared for 1966 publication which will give a comprehensive review of all the known work on regenerative galvanic systems. Five chapters in this monograph are contributions based on the Chemical Engineering Division's program.

A. Regenerative Emf Cells--Physical-Chemical Laboratory Studies

1. Intermetallic Systems

a. Thermodynamic Studies of Binary Metal Systems

The open circuit potentials of regenerative bimetallic cells have been measured and used to elucidate the thermodynamic properties of the binary alloys, the standard free energy of formation of the intermetallic compound formed in the cell, and (by extrapolation) the partial pressure of the alkali metal at 1273°K.

Emf data were obtained for the Li-Bi, Li-Sn, and Li-Te systems. In each case, a reference electrode of Bi(l) saturated with Li₃Bi was used in place of a pure lithium electrode and the potentials converted to those for a galvanic cell with a pure lithium anode. A comparison of these data is shown in Table VI-1.

¹Crouthamel, C., and Recht, H., Eds., Regenerative Electrochemical Systems, American Chemical Society, Washington, D. C., in press.

TABLE VI-1. Comparison of Bimetallic Systems for the Cell:
 $\text{Li}(\ell)/\text{LiCl}-\text{LiF}(\ell)/\text{Li-Alloy}$

Alloy System	Cathode Composition Range (atom fraction Li, X_{Li})	Open Circuit Cell Potential Range (volts) at 800°K	Partial Pressure of Li (mm Hg) at 1273°K over Alloy with $X_{\text{Li}} = 0.6$	Solid Compound Formed in Cell	Standard Free Energy of Formation at 800°K (kcal/mole)
Li-Bi	0.1-0.6	0.7-0.9	0.15	Li_3Bi	-50.5
Li-Sn	0.1-0.6	0.4-0.7	30	Li_5Sn_2	-61.4
Li-Te ^a	0.01-0.39	1.67-1.81	unknown	Li_2Te	-77.9

^aStudied only at 798°K. No basis exists for extrapolation to higher temperatures.

Although open circuit voltages are good (0.7-0.9 volt) in the Li-Bi system, the low vapor pressure of lithium (and the fact that the vapor will be contaminated with bismuth) makes regeneration by distillation unlikely. Open circuit voltages for the Li-Sn cells are only fair (0.4-0.7 volt), but regeneration by distillation of relatively pure lithium vapor appears thermodynamically feasible. While the open circuit potential of the Li-Te cell is very attractive (1.67-1.81 volts), few possibilities exist for its use as a regenerative cell, owing to the corrosive character of tellurium and the expected difficulties with regeneration (Li_2Te is extremely stable). However, the temperature coefficient of cell potential remains an unknown factor--if it is sufficiently high, electrothermal or even thermal regeneration may be thermodynamically possible.

b. Studies of the Sodium-Bismuth System

In preliminary studies of cells of Type 1:

it was observed that the nonelectrochemical (or irreversible) transfer of sodium metal through the electrolyte to the cathode was sufficiently large to cause a steadily decreasing cell potential as the concentration of sodium in the cathode alloy increased. Therefore, a cell of Type 1 could be operated only at a single temperature, thereby necessitating the use of an extrapolated initial cell potential in the calculation of thermodynamic properties.

In order to obtain data at more than one temperature in each experiment, cells of Type 2:

were utilized. Electrolytes for these cells were in the form of cups fabricated from single crystals of NaCl. The cup dimensions were approximately 2.4-cm OD and 4.5 cm high, with 0.32-cm thick wall and bottom.

These cups contained the pure sodium anodes and were immersed about 1 cm into the cathode alloys. Experimentally observed internal resistances of cells with these electrolyte cups ranged from approximately 10^2 ohms at $\sim 973^\circ\text{K}$ to 2×10^7 ohms at $\sim 523^\circ\text{K}$. It was necessary, therefore, to use voltage measuring instruments with high input impedances. A potentiometric recorder with an off-balance input impedance of $>4 \times 10^6$ ohms, an electrometer amplifier with $\sim 10^{14}$ ohms input impedance, and a five-dial potentiometric electrometer with 10^{13} ohms input impedance were used.

The results of emf measurements of various cells with solid electrolytes are shown in Fig. VI-1. The cell potentials were stable

108-9292

Fig. VI-1. Potential-temperature-composition Characteristics of the Cell:
 $\text{Na}(l)/\text{NaCl}(s)/\text{Na}$ in $\text{Bi}(l)$.
 $(X_{\text{Na}} = \text{atom fraction Na.})$

over several hours, thereby indicating negligible irreversible transfer. The scatter of data is indicated in Fig. VI-1 by the standard deviation (σ) of the points from the least-squares curves. The curve indicated by triangles is for the cell:

In all cells with solid electrolytes, the cell potential was reproducible on temperature cycling and on passing small currents through the cell in either direction. The thermocell voltage was found to be <0.004 volt in a separate experiment carried out in the temperature range of about 520 to 975°K.

Two cells with liquid electrolytes (Type 1) which had an initial cathode composition of 0.30 atom fraction sodium ($X_{\text{Na}} = 0.30$) were operated at temperatures of 817 and 883°K, respectively. Both cells had electrolyte depths of about 4.4 cm and both were placed inside a massive copper holder so that any temperature gradients in the cells would be minimized. This was done in an attempt to restrict irreversible transfer to concentration diffusion alone by repressing thermal convective mixing in the electrolyte. A plot of cell potential as a function of time is given in Fig. VI-2 for the first cell. From these data, the initial open circuit

108-9282

Fig. VI-2. Emf of the Cell:

$\text{Na}(\ell)/\text{NaI-NaCl-NaF}/\text{Na in Bi}$
 $(X_{\text{Na}} = 0.30 \text{ initially})$ versus time.
 Temperature = 817°K.

potential of the first cell was estimated to be 0.6084 volt at a cell temperature of 817°K. The rate of irreversible transfer was indicated by the falling cell potential (4.02×10^{-4} volt/hr). From a knowledge of the electrolyte area and the assumption that the cell potential dependence on X_{Na} was the same as in cells of Type 2, the rate of irreversible transfer in this cell was estimated to be 0.002 g/(hr)(cm²) or 0.6 ma/cm² under open circuit conditions. This value indicates the rate of irreversible transfer which may be attained for the cell in the absence of thermal convection. When current is drawn from the cell, this rate would be reduced accordingly (see ANL-7020, p. 214). In the second cell, the initial open circuit voltage was estimated to be 0.5923 volt at a temperature of 883°K. The rate of irreversible transfer in this cell was estimated, in the same manner as previously described, to be 0.0034 g/(hr)(cm²) or an equivalent of 1.0 ma/cm². The rate of irreversible transfer at 883°K is seen to be 1.7 times that at 817°K.

It is to be noted that the open circuit potentials of cells with liquid electrolytes (Type 1) appear to have higher open circuit potentials than those with solid electrolytes (Type 2). At 817°K, the potential of a cell with liquid electrolyte ($X_{\text{Na}} = 0.30$) was 0.6084 volt, whereas for the same cathode compositions the potential of the cell with a solid electrolyte was 0.5861 volt (see Fig. VI-1). Similarly, at 883°K, the cell potentials were 0.5923 and 0.5730 volt for cells of Type 1 and Type 2, respectively. These differences may be due to the degree to which different mechanisms of conduction operate in the two cells. Electrical conductivity in solid alkali metal halides arises both from lattice defect mobility at high temperatures and from metal solubility. In the liquid electrolytes of the kind used in Type I cells, electrical conductivity is due to ionic and electronic mobilities, the latter resulting from the electrons supplied by dissolved metal. The liquid electrolyte is expected to be saturated with sodium metal (0.30 a/o sodium at 817°K and 0.52 a/o sodium at 883°K, see ANL-7020, p. 203). Bredig² has interpreted the increased conductivities of liquid alkali metal halides with changing metal concentrations by postulating that even at infinite dilution of the metal, electrons are available for contribution to current conduction.

Wagner³ has shown that for cells with mixed electronic and ionic conduction, the observed open circuit potential, E , will be lower than the thermodynamic open circuit potential, E_0 , and may be expressed as:

$$E = E_0(1 - \bar{t}) \quad (1)$$

where $\bar{t}$ is an average value of the transport number of the electron in the electrolyte.

²Bredig, M., Molten Salt Chemistry, Blander, M., ed., Interscience, New York, N. Y., 1964, p. 384.

³Wagner, C., Proceedings of the Seventh Meeting of the International Committee on Electrochemical Thermodynamics and Kinetics, 1957, p. 361.

If the uncertainties in the measurements of the open circuit potentials of cells with liquid electrolytes are comparable to those indicated by the standard deviations listed in Fig. VI-1 for experiments using cells with solid electrolytes, then the real potential difference between the two cells may be much less than that discussed above. A small difference may indicate either (1) that the electronic conductivity in the solid electrolyte is too small to cause a large difference between E and E_0 for cells with solid electrolytes (assuming that E_0 is obtained with cells using liquid electrolytes) or (2) that the electronic conductivity in both types of electrolytes is sufficient to preclude direct measurements of E_0 with either type of cell.

Further studies are under way to determine the extent of the electronic conductivity in solid and liquid cell electrolytes. It is possible that a cell having both ionic and electronic conductivity may have a lower internal resistance than a cell having only ionic conductivity. The lower cell resistance would result in a lower voltage loss (owing to IR polarization) at a given current.

c. Intermetallic Compounds in Fused Salt Solutions

Previous studies of the solubilities of intermetallic compounds in molten salts have shown that the solubility of Li_2Te in LiCl-LiF is greater than that of Li_3Bi (see ANL-7020, p. 201). Qualitatively, solution color indicated that the solubilities of Li_7Sn_2 or $\text{Li}_{10}\text{Pb}_3$ were probably less than that of Li_3Bi . This suggests that as one approaches the transition metal series, the trend is to lesser solubilities of intermetallic compounds in fused salts. Indeed, one might predict this on the basis that the bond formed between an alkali metal and a more noble metal is less ionic in character as the more noble metal approaches the transition metal series (e.g., Te-Bi-Pb (or Sn) - Tl-Hg). This is indicated by a smaller difference between the melting point of the most stable intermetallic compound and the melting point of the highest-melting element of the binary pair. Thus the solubilities of intermetallic compounds should decrease in the order $\text{Li}_2\text{Te} > \text{Li}_3\text{Sb} \approx \text{Li}_3\text{Bi} > \text{Li}_7\text{Sn}_2 \approx \text{Li}_{10}\text{Pb}_3 > \text{LiIn} \approx \text{LiTl} > \text{LiCd} \approx \text{LiHg}$.

To test this hypothesis, the solubility of LiHg (m.p. 868°K) in molten LiCl-LiF at 791°K was determined. The intermetallic compound LiHg was prepared from the elements and activated by neutron bombardment for use in this study. By γ -counting the radioactive ^{203}Hg in a sample of LiCl-LiF which had been equilibrated at temperature with the activated LiHg , the solubility of LiHg in LiCl-LiF eutectic at 791°K was found to be 8.6×10^{-5} m/o. As predicted, this is much less than the solubility of Li_2Te , which is estimated to be ~ 3 m/o at the same temperature.

The absorption spectra of Li_2Te in molten LiCl (at 923°K) and LiCl-LiF (at 798°K) and of Cs_2Te in molten CsCl (at 948°K) have been

measured.⁴ All three solutions were clear red. These spectra were obtained in the region 4000-40000 cm^{-1} using a Cary Model 14 H recording spectrophotometer. The Li_2Te and Cs_2Te spectra are characterized by absorption bands with maxima at 21250 and 18200 cm^{-1} . These results indicate forbidden transitions; the oscillator strengths are 0.86×10^{-3} and 2.00×10^{-2} , respectively. The absorption bands are interpreted as arising from $5p \rightarrow 6p$ atom-like transitions centered on tellurium. The formal charge on tellurium was calculated to be -1.1 and -1.2 for solutions of Li_2Te and Cs_2Te , respectively. These values correspond roughly to the species LiTe^- and CsTe^- .

The behavior of tellurium metal in fused salts was compared with that of the tellurides. Tellurium metal in molten CsCl (at 948°K) forms a blue solution. Its absorption spectrum is characterized by two bands with maxima at 15500 cm^{-1} and 20800 cm^{-1} and a total oscillator strength of 3.87×10^{-2} . The following values were determined for the solubility of tellurium in molten salts: in CsCl at 944°K, 1.69×10^{-2} m/o; in KCl at 1075°K, 2.05×10^{-2} m/o; and in LiCl at 900°K, $< 1.66 \times 10^{-4}$ m/o.

Further studies of conductivity, electrokinetic phenomena, and spectra are necessary to understand the nature of fused salt solutions and the character of species in solution. These studies will also elucidate the usefulness of molten salt solutions in other chemical applications, as well as in regenerative cells.

2. Lithium Hydride Cell Studies

The primary emphasis of research on the lithium hydride emf cell has been to provide fundamental data necessary to the development of a successful regenerative electrochemical system. Areas of investigation have included the following: (1) examination of the rates of permeation of hydrogen through various metal diaphragms and testing of the diaphragms in cells for possible application as the cathode in place of the more conventional porous metal electrode; (2) studies of the electrolyte solvent properties which would produce optimum cell operating conditions; (3) establishment of values for thermodynamic functions such as the free energy, enthalpy, and entropy of the cell product, lithium hydride; and (4) investigation of those conditions under which successful regeneration could be accomplished.

In the development of a workable lithium hydride cell, a very significant problem has concerned the gas electrode, or cathode. The immediate region of contact between the reactant, electrolyte, and electrode

⁴Gruen, D. M., McBeth, R. L., Foster, M. S., and Crouthamel, C. E., Absorption Spectra of Alkali Metal Tellurides and of Elemental Tellurium in Molten Alkali Halides, J. Phys. Chem. (in press).

is important because it is here that electron transfer takes place. The hydrogen gas must transfer electrons from the electrode at the time the hydrogen enters the electrolyte as an ion. In conventional operation, the gas electrode requires a three-phase site which must be as large as possible in order to achieve a practical rate for the electrode process. Because gases are nonconductors and have no strength, they must be supplied through a medium which conducts electricity and yet provides the greatest possible area wherein the gas, conductor, and electrolyte are in mutual contact. In the past, electrically conducting porous media, such as sintered metals, have been employed as gas electrodes.

A problem exists with such electrodes, however, in that porous media inherently tend to absorb liquids by capillary action, causing the gas-electrode-electrolyte interface to retreat within the electrode. When this condition (known as flooding) occurs, the electrode is prone to severe polarization and, as a result, the cell output is decreased considerably.

Since certain metals are readily permeable to hydrogen at the cell temperature (400-600°C), it was recognized that an unusual opportunity existed for circumventing the problems of flooding and the need for catalysts for the gas electrode. It seemed reasonable that the gas electrode could be formed of a solid thin sheet of metal through which the hydrogen could be transmitted by means of interatomic diffusion. Hydrogen would thus be supplied in the atomic state at the metal-fused salt interface.

Hydrogen permeation studies were therefore initiated on selected metals compatible with the lithium hydride, lithium metal, and fused salt environment. Materials such as palladium and silver-palladium alloys which have high hydrogen permeability were not considered because of their incompatibility with lithium metal; hence, the permeation studies were restricted to iron, iron-molybdenum alloys, and vanadium.

Data for these systems have been reported in recent literature.^{5,6} Figure VI-3 displays some of the pertinent data obtained from these permeation studies. Even though the permeation rate of hydrogen through iron is low,⁵ and for this reason would be capable of supporting only about 1/10 of the desired current density, iron is still somewhat attractive because it is self-cleaning at cell operating temperatures in a hydrogen atmosphere, i.e., hydrogen readily reduces the iron oxides. The possibility of special cathode design to effect a significant increase in current density may still be practical in a cell using an iron diaphragm. Alloys of molybdenum and iron gave

⁵Heinrich, R. R., Johnson, C. E., and Crouthamel, C. E., J. Electrochem. Soc. 112, 1067 (1965).

⁶Heinrich, R. R., Johnson, C. E., and Crouthamel, C. E., J. Electrochem. Soc. 112, 1071 (1965).

108-8517

Fig. VI-3. Permeation Isobars of
Vanadium and Armco Iron

hydrogen, the metal lattice will be expanded, and the expansion will further increase the permeation rate at the low temperatures.

An electrolyte, to be suitable for use in a lithium hydride cell, should have the following properties: (1) reasonable solubility for lithium hydride, (2) thermodynamic stability with respect to the very electro-positive lithium metal, (3) stability at regeneration temperatures, preferably with a low vapor pressure at this temperature, and (4) low solubility for the anode metal. Halide salts of lithium metal are the only known substances which meet these requirements. Data describing the solid-liquid equilibrium for the lithium hydride-lithium halide systems were obtained by thermal analyses (see ANL-6766, p. 117). A summary of some of the pertinent data is as follows:

Components	Minimum Melting Point (°C)	Eutectic Composition LiH (m/o)
LiH-LiCl	495.6	34.0
LiH-LiBr	453.3	29.7
LiH-LiI	390.8	23.5
LiH-LiF	684	solid solution

The first three systems^{7,8} are simple eutectics with the stated melting points and compositions. Data for the LiH-LiF systems were

⁷Johnson, C. E., Wood, S. E., and Crouthamel, C. E., *Inorg. Chem.* **3**, 1487 (1964).

⁸Johnson, C. E., Wood, S. E., and Crouthamel, C. E., *J. Chem. Phys.* **44**, 884 (1966).

results⁵ that were essentially the same as those for pure iron. Vanadium, on the other hand, appears to be an excellent diaphragm material.⁶ It has a high hydrogen permeability at moderate temperature and is compatible with the cell environment. However, because vanadium is not self-cleaning at normal cell temperatures, some preparation of the metal is needed before its maximum permeation rate is achieved. This preparation consists of baking the metal in vacuum at a temperature of 850°C to remove as much of the surface oxide contamination as possible. Further, vanadium is one of a group of metals (V, Nb, Ta) which have a negative absorption coefficient with temperature, that is, the metal absorbs greater quantities of hydrogen at lower temperatures than at higher temperatures. If vanadium metal is cooled in

obtained from the work of Messer⁹ and are included here for the sake of completeness.

In order to increase the Carnot cycle efficiency and cell voltage, the lithium hydride cell should be operated at low temperatures; thus, low melting electrolytes are desirable. It is probable that the most practical electrolyte for use in the lithium hydride cell will be a ternary system composed of two lithium halides and lithium hydride. Two such ternary systems have been investigated. The first, LiH-LiCl-LiF (minimum melting point, 459°C), is promising because it contains fluoride ion, which is believed to be active in reducing the possibility of metal dispersions in the fused salt. The second, LiH-LiCl-LiI, is also attractive because of its low eutectic melting point, about 330°C.

The only available thermodynamic data for lithium hydride are enthalpy data derived from calorimetric measurements.^{10,11} In view of this paucity of systematic thermodynamic data for lithium hydride, studies were undertaken to establish, by means of emf measurements, values for the standard thermodynamic functions for the formation of lithium hydride.

The lithium hydride formation cell may be represented as

where LiX represents a lithium halide. The half cell reactions, $\text{Li}(\ell) \rightarrow \text{Li}^+ + \text{e}^-$ and, $1/2 \text{ H}_2 + \text{e}^- \rightarrow \text{H}^-$, at the anode and cathode, respectively, when summed give the cell reaction $\text{Li}(\ell) + 1/2 \text{ H}_2(\text{g}) \rightarrow \text{LiH(s)}$. For a cell with all three substances in their standard states, namely, pure liquid lithium metal, pure solid lithium hydride, and pure hydrogen gas at one atmosphere pressure, the Nernst equation,

$$E = E^\circ - RT/nF \ln \left(\frac{a_{\text{LiH}}}{a_{\text{Li}} a_{\text{H}_2}^{1/2}} \right), \quad (2)$$

reduces to $E = E^\circ$.

Emf data were obtained for cells of different lithium halide-lithium hydride compositions. For the temperature range considered, a linear function seemed to fit all the data best. The resultant equation,

$$E^\circ = 0.9081 - 7.699 \times 10^{-4} T$$

⁹Messer, C. E., and Mellor, J., J. Phys. Chem. 64, 503 (1960).

¹⁰Gunn, S. R., and Green, L. G., J. Am. Chem. Soc. 80, 4782 (1958).

¹¹Messer, C. E., Fasolino, L. G., and Thalmayer, C. E., J. Am. Chem. Soc. 77, 4524 (1955).

is for the temperature range from 673 to 853°K, with a standard deviation of ± 2 mv. Calculations were made of ΔG_f° , ΔH_f° , and ΔS_f° for lithium hydride at 800°K, and also at 298°K by integrating the best available heat capacity data over the temperature range 800-298°K. These data and comparison values from the literature^{10,11,12} are given in Table VI-2.

TABLE VI-2. Calculated Values^a and Literature Values for the Enthalpy, Free Energy, and Entropy of Lithium Hydride

	This Work 800°K	This Work 298°K	Literature 298°K
ΔH_f° , cal mole ⁻¹	-20,940	-21,790 $\pm$ 290	-21,340 ¹¹ -21,670 ¹⁰
ΔG_f° , cal mole ⁻¹	-6,740	-16,160 $\pm$ 50	-16,450 ^{11,12} -16,800 ^{10,12}
ΔS_f° , cal deg ⁻¹ mole ⁻¹	-17.7	-18.9 $\pm$ 0.4	-16.3 ¹²

$$^a \Delta H_f^\circ = nF \left[T \left(\frac{\partial E^\circ}{\partial T} \right)_p - E^\circ \right], \Delta G_f^\circ = -nFE^\circ, \Delta S_f^\circ = nF \left(\frac{\partial E^\circ}{\partial T} \right)_p \text{ where}$$

$$E_{800^\circ K}^\circ = 0.2922 \text{ volt}, \left(\frac{\partial E^\circ}{\partial T} \right)_p = -7.699 \times 10^{-4} T \text{ volt deg}^{-1}.$$

Studies have also been made of the reactions taking place at the cathode. The equilibrium potential obtained for any experiment was always the same whether pure iron or vanadium was used. The rate of achieving this equilibrium potential for vanadium, however, was very low.

The following mechanisms and relative rates agree with the experimental results and describe the important steps by which the equilibrium potential is established at the hydrogen-hydride electrode:

Rate 1 is the activated adsorption of hydrogen on the metal surface. Rate 2 combines the formation of the gas-metal solid solution and the diffusion of atoms into the metal as a composite rate. The diffusion of hydrogen through the metal lattice is the rate-controlling step. The low rate at which hydrogen saturates the metal also controls the rate at which the cell equilibrium potential is established.

¹² Kelley, K. K., and King, E. G., "Entropies of the Elements and Inorganic Compounds," Bulletin 592, Bureau of Mines (1961).

The reaction rate, R_3 , was assumed to be very high with respect to rates R_1 and R_2 . Atomic hydrogen on the electrode surface is rapidly stripped off as the hydride ion by an electron exchange.

The diffusion of atomic hydrogen from the metal surface into the bulk metal lattice was considered to be the lowest rate. This was consistent with the fact that, in the operation of a metal diaphragm under a hydrogen gas pressure differential of one atmosphere, the permeation rate is inversely proportional to the diaphragm thickness. Vanadium, compared to iron, has extremely high hydrogen solubility. Thus it is not surprising that an equilibrium population of atomic hydrogen could not be maintained on the fresh vanadium electrode surface until the bulk metal was saturated. Evidence of this condition was the low initial cell potential obtained using a vanadium electrode compared to the immediate equilibrium potential obtained for the iron electrode. With vanadium, equilibrium was attained in hours or days, depending on the cell temperature. Once equilibrium had been attained, on the other hand, the potential of a lithium hydride cell with a vanadium cathode dropped slowly even when the hydrogen gas atmosphere was removed from the cell, in contrast with the very rapid potential drop when iron cathodes were used.

As presently visualized, the lithium hydride cell should function at the lowest temperature possible in order to take advantage of the higher voltages obtained. This can be accomplished through the use of the LiH-LiCl-LiI electrolyte system. Operation at a low temperature may necessitate some modification in the construction of the cathode. Data indicate that by reducing the diaphragm thickness to 0.002 in., a theoretical current density of about 300 ma/cm² can be expected at 375°C and one atmosphere pressure of hydrogen. Experiments are presently under way to demonstrate the feasibility of this approach.

3. Liquid-Vapor Equilibrium Studies

In order to gather data on liquid-vapor equilibria relevant to the regeneration cycle of a sodium-bismuth regenerative cell, two types of measurements have been made: (1) total vapor pressure measurements by the quasi-static technique (Rodebush-Dixon)¹³ or by a boiling point method, and (2) vapor density and composition measurements by the transpiration method.

The data for the total vapor pressure measurements are presented in Fig. VI-4 and the data for the transpiration experiments, in Table VI-3. The breaks in the curves (Fig. VI-4) for the 75 and 80 a/o sodium systems are interpreted as corresponding to the pressures at which the liquid-vapor loop in the phase diagram intersects the liquid-solid

¹³Rodebush, W. H., and Dixon, A. L., Phys. Rev. 26, 851(1925).

region. The opposite directions of the breaks indicate that these two regions of the phase diagram become tangent as the pressure is lowered at a composition point between 75 and 80 a/o sodium. The curves also indicate that a pressure of at least 240 mm is needed to separate the two areas and, thus, avoid the solid Na_3Bi deposition problem that arises at lower pressures.

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Fig. VI-4. Total Vapor Pressure over Various Sodium-Bismuth Alloys

The temperatures at which the breaks occur serve to trace out the liquid-solid equilibrium curve of the phase diagram. Our results show that the phase diagram in Hansen and Anderko¹⁴ is in error. The melting point of Na_3Bi is 840°C, rather than 775°C. Confirmation of this conclusion has been obtained by thermal analysis.

¹⁴Hansen, M., and Anderko, K., Constitution of Binary Alloys, McGraw-Hill, New York, 1958, p. 321.

TABLE VI-3. Results from Transpiration Experiments for
Two Sodium-Bismuth Melts at 900°C

	20 a/o Na-80 a/o Bi	40 a/o Na-60 a/o Bi
P_{Na} , mm Hg	0.82	4.7
P_{Na_2} , mm Hg	2.3×10^{-4}	8.0×10^{-3}
P_{Bi} , mm Hg	0.24	0.14
P_{Bi_2} , mm Hg	0.17	5.6×10^{-2}
$P(=\Sigma p_i)$, mm Hg	1.2	4.9
γ_{Na}	5.7×10^{-3}	1.7×10^{-2}
γ_{Bi}	0.67	0.52

In Table VI-3, partial pressures for monatomic and diatomic species of sodium and bismuth are given. The activity coefficients, γ_{Na} and γ_{Bi} , are indicative of the strong negative deviations from ideality in this system.

A pressure-composition diagram, Fig. VI-5, for 900°C was constructed from the transpiration experiment data and from the total pressure data. The shape of this diagram, when inverted, will indicate the approximate shape of a temperature-composition diagram. For the crucial pressure of 240 mm, it can be shown from such an approximate temperature-composition diagram, that for a regenerative cell with a probable cathodic composition of about 70 a/o bismuth, a regeneration temperature of about 1200-1300°C would be needed. At the present time, techniques and materials are not available to construct a regenerator which would resist the corrosive action of bismuth at such a high temperature. For this reason, it is believed that full development of a sodium-bismuth regenerative cell must await development of the necessary high temperature technology. In the meantime, examination of other systems has been started.

108-9321

Fig. VI-5. Pressure-Composition Diagram
for the Sodium-Bismuth System
at 900°C

which the low boiling component, at a pressure between 1 and 10 mm, had a boiling point above the melting point of the highest melting point compound.

To select potentially good systems for a regenerative cell, all bimetallic pairs with components melting below 600°C were examined, and the pairs which formed compounds melting below 600°C were selected. From these, pairs were chosen for

Amalgam systems were rejected because of inefficiency inherent in operating cells based on such systems. The Bi-Te, Li-Zn, Se-Tl and Te-Tl systems were rejected because of their corrosive nature. The most promising systems, in the preferred order of study, are Na-Pb, Na-Tl, and K-Tl.

B. Regenerative Emf Cells--Engineering Studies

Engineering studies were continued to investigate the feasibility of developing a practical thermally regenerative emf cell, which would ultimately be suitable for coupling to a reactor, isotopic, or other heat source. Both the bimetallic and hydride cells were studied. However, most of the engineering test work involved sodium-lead and sodium-bismuth systems.

1. Sodium-Bismuth "Open" Cell Studies of Non-Faradaic Sodium Transfer

Experimental sodium-bismuth "open" cells (cells in open top crucibles) have been operated with a molten salt electrolyte (31.6 m/o NaCl-53.2 m/o NaI-15.2 m/o NaF) to study irreversible or non-faradaic transfer (i.e., without a corresponding production of cell current) of sodium from anode to cathode. This type of transfer is the result of the solubility of sodium in the electrolyte and the resultant electronic conductivity of the electrolyte. Preliminary experiments were reported in ANL-7020, p. 213.

In the more recent experiments, a stainless steel crucible containing the electrolyte was placed in a stainless steel well attached to a helium inert-atmosphere box and was heated by a resistance furnace surrounding the well. In each experiment, the cathode consisted of a stainless steel cup containing bismuth supported by two tubes which served both as thermocouple wells and as electrical connectors. The cup was immersed in the electrolyte. The anode consisted of a stainless steel cup containing sodium, also supported by two tubes. The anode cup had a hole in the bottom; a layer of porous stainless steel sponge covered the hole. In this way the sodium was retained in the cup and yet was allowed to contact the electrolyte when the bottom of the anode cup was dipped slightly into the electrolyte.

Previously (see ANL-7020, p. 213), the non-faradaic transfer was defined as

$$q_1 = \frac{Q - AIt}{t} \quad (3)$$

where

q_1 = non-faradaic transfer, g/hr

Q = total amount of sodium transferred from anode to cathode during a run, g

$A = (3600)(23)/96,500 = 0.857 \text{ g/}(amp)(hr)$

I = average cell current, amp

t = time of run, hr.

Experimental data for a sodium-bismuth cell showed that the non-faradaic transfer increased as the cell temperature was increased and decreased as the cell current was increased. Figure VI-6 shows the non-faradaic or irreversible transfer for a cell with anode and cathode diameters of 2.3 and 2.2 cm, respectively, as a function of cell current. Figure VI-7 shows the non-faradaic transfer of an open cell as a function of temperature. Values of the cell electrical conductance are also shown on the latter figure for comparison.

108-9479

Fig. VI-6. Irreversible Sodium Transfer-current Output Characteristics of Sodium-Bismuth Cell at 590°C. Cell dimensions: anode diameter, 2.3 cm; cathode diameter, 2.2 cm. Electrolyte: NaCl-NaI-NaF eutectic.

Fig. VI-7.

Open Circuit Irreversible Sodium Transfer Rate versus Temperature Characteristics of Sodium-Bismuth Cell. Electrolyte-- 31.6 m/o NaCl- 53.2 m/o NaI- 15.2 m/o NaF.

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2. Sodium-Bismuth "Closed" Cell Studies

The closed sodium-bismuth cell apparatus (see ANL-7020, p. 215) with 3-in. dia. electrode sections, but without a thermally operated regenerator, is still in operation as a battery. This cell has a frozen electrolyte-silicone rubber combination electrical insulator and pressure seal, and contains 313 g of salt electrolyte (31.6 m/o NaCl, 53.2 m/o NaI, and 15.2 m/o NaF), 400 g of bismuth, and 15.5 g of sodium. The cell has been recharged periodically by reversing the current. On March 9, 1966, it had been in operation for 15 months at 535 to 650°C with no evidence of deterioration of the cell components.

3. Sodium-Lead Regenerative Emf Cell System

As a part of an overall investigation of a sodium-lead regenerative emf cell system, an experimental apparatus for the study of regeneration of the electrode metals was constructed. The regenerator, which was fabricated of stainless steel, is being used to study some of the engineering aspects associated with the separation of sodium from lead by distillation. Among the parameters being investigated are distillation and circulation rates of the cathode metals; temperatures of the still, column, condenser, and reservoir; mole fraction of sodium in the lead; and distillation pressure.

The apparatus, shown in Fig. VI-8, consists of a vertical cylindrical reservoir for containing the cathode metal (a 30 a/o sodium-70 a/o lead alloy) and a vertical cylindrical still and column with a sodium

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Fig. VI-8. Sodium-Lead Thermal Regenerator

condenser at its upper end. The reservoir is connected to the still by two tubes through which the bimetallic alloy is thermally circulated back and forth between the reservoir and the still. The sodium vapor distilled from the sodium-lead alloy is condensed at the upper end of the still and returned to the reservoir, where it mixes with the sodium-lead alloy for continuous circulatory operation. During a test run, a cup can be positioned under the sodium return tube to catch the distilled sodium for a predetermined period of time (usually 15 to 20 min). This allows measurement of the distillation rate and provides a sample of the distilled sodium (up to 5 g) for analysis. A test run must be terminated to remove the sample; prior to the subsequent run, an amount of sodium equal

to the sample removed is added to the reservoir to maintain the alloy composition.

To date, 33 test runs have been made under various operating conditions for a total operating time of 112 hr for the regenerator. Still temperatures of about 750 to 830°C and distillation pressures of from 3 to 8 mm Hg have been used. Total maximum distillation rates of about 14 g of sodium/hr or specific distillation rates of about 4.8 g of sodium/(hr)(cm² of still evaporating surface) have been attained. Distilled sodium containing less than 0.5 a/o lead has been obtained; this is suitable for use in the anode of a sodium-lead cell.

Following the satisfactory operation of the sodium-lead regenerator, a complete sodium-lead bimetallic cell apparatus with attached thermal regenerator was assembled and is now being operated. The cell proper is constructed with a frozen electrolyte-silicone rubber insulator-seal similar to that of the sodium-bismuth cell now in operation as a battery (see above). The regenerator is similar to the regenerator just described which has been used to demonstrate the feasibility of regenerating sodium from lead. This sodium-lead bimetallic cell apparatus is shown in Fig. VI-9. The cell has 3-in. dia. anode and cathode sections, and the regenerator has a 1-in. dia. evaporation surface. This cell system

was charged with 240.1 g of electrolyte (31.6 m/o NaCl-53.2 m/o NaI-15.2 m/o NaF) and 532.7 g of a 70 a/o lead-30 a/o sodium alloy before being placed in operation. The cathode metal (sodium-lead) was circulated to and from the regenerator thermally.

108-9488

Fig. VI-9. Sodium-Lead Thermally Regenerative Emf Cell System

Eleven runs have been made in which the regenerator was used to distill sodium for operating the cell. The runs varied in length from 2 to 7 hr for a total operating time of 45 hr. The cell was operated at temperatures ranging from 543 to 600°C; the regenerator was operated at temperatures ranging from 775 to 875°C and at pressures from 5.7 to 9 mm Hg.

At 875°C and 8 mm Hg pressure, the regenerator furnished sufficient sodium to operate the cell continuously at 7.5 amperes; at 850°C and 7 mm Hg pressure, 5 amperes; and at 825°C and 6 mm Hg pressure, 2.5 amperes.

Cell open circuit voltages as high as 0.41 volt at 575°C were noted during the runs, thereby indicating that the regenerator had reduced the amount of sodium in the cell cathode from the original value of 30 a/o to about 18 a/o.

Typical cell-voltage versus cell-current performance at a cell temperature of 575°C (regenerator at 875°C and 8 mm Hg pressure) was as follows:

Cell Voltage (volt)	Cell Current (amperes)
0.39	0
0.355	1
0.28	2.5
0.165	5
0.055	7.5

The limiting factor in this system at present seems to be the sodium-evaporating capacity of the regenerator, which is dependent upon the evaporating surface area and the temperature. The regenerator evaporator surface area is only 0.78 sq in., while the cell electrode cross-sectional area is 7.0 sq in. The effective anode area of the cell is, to a large extent, determined by the quantity of sodium in the anode. The cell resistance is, in turn, determined by the electrolyte temperature and thickness and by the anode and cathode effective areas. The cell voltage-current characteristics shown above can be improved by reducing the electrolyte thickness and by furnishing more sodium to the cell by a regenerator with larger capacity. Future studies will be concerned with determining the ratio of evaporator surface area to cell electrode cross-sectional area that will result in the optimum performance of the entire cell system.

4. Determination of Densities, Surface Tensions, and Viscosities of Molten Electrolyte and Bimetallic Alloys

Knowledge of the densities, viscosities, and surface tensions of electrolytes and bimetallic mixtures is needed in order to compute or estimate volumes, liquid levels, flow rates, and surface effects for the engineering design of bimetallic cell and regenerator apparatus. Although information on many physical properties is available in the literature for pure salts and metals, very little information is available for mixtures of various salts and for alloys or mixtures of metals at temperatures at which regenerative cells are expected to operate.

The density, viscosity, and surface tension of an electrolyte consisting of the eutectic 17.7 w/o NaCl-6.1 w/o NaF-76.2 w/o NaI (31.6 m/o NaCl-15.2 m/o NaF-53.2 m/o NaI) were measured at various temperatures above the melting point (~535°C) of the electrolyte. The values of these physical properties were found to vary as follows with temperature:

$$\begin{aligned}\text{density, g/cc} &= 3.05 - 0.0009 T \text{ (540 to 800°C)} \\ \text{viscosity, centipoises} &= 3.40 - 0.003 T \text{ (560 to 800°C)} \\ \text{surface tension, dynes/cm} &= 136 - 0.06 T \text{ (550 to 750°C)}\end{aligned}$$

where T is the temperature in °C.

The densities of sodium-bismuth alloys containing 0, 10.4, 20, 30, 40, and 50 a/o sodium were measured at temperatures from near the alloy freezing points to 800°C. The densities were found to vary from about 10.7 to 5.6 g/cc, as shown in Fig. VI-10.

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Fig. VI-10. Densities of Sodium-Bismuth Alloys

little variation (242 to 260 dynes/cm). The results are compared in Fig. VI-12 with values given in the literature for the pure components.

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Fig. VI-11. Densities of Sodium-Lead Alloys

The densities of sodium-lead alloys containing 0, 10, 20, 30, 41, and 50 a/o sodium were measured at temperatures from near the alloy freezing point to 700 or 800°C. The densities were found to vary from about 10.7 to 5.6 g/cc, as shown in Fig. VI-11.

The surface tension values of sodium-bismuth alloys containing 30, 40, 45, and 50 a/o sodium were measured at temperatures from about 400 to 700°C. Over this range of composition and temperature, the surface tension showed

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Fig. VI-12. Surface Tension of Sodium-Bismuth Alloys

The measured densities of the sodium-bismuth and sodium-lead alloys (Figs. VI-10 and VI-11) are considerably greater than densities computed by additive volumes of the pure metals. On the other hand, the measured densities of the NaCl-NaF-NaI eutectic are very nearly the values computed by additive volumes.

5. Engineering Material Corrosion Studies

Possible materials of construction for thermally regenerative bimetallic emf cell systems are being tested. In such cells, which are regenerated by distillation, the cell section of the system would be at about 550°C; the temperature of the regenerator would range from about 800°C or higher for the sodium-lead or sodium-tin systems to above 1000°C for the sodium-bismuth or lithium-tin systems. Normally, the fused salt electrolyte (at about 550°C) would remain in the cell. The cathode metal alloy, however, would be circulated between the regenerator at the high temperature and the cell at the lower temperature. This could lead to dynamic corrosion; owing to flow between these regions at different temperatures, material might be dissolved in the high temperature regions and precipitated in the low temperature regions. For these reasons, the corrosion of proposed materials of construction by liquid cathode metals at temperatures near 1000°C has been studied. Both static and dynamic tests are being conducted. Preliminary work was previously reported (ANL-7020, p. 216).

For static tests, the materials under study (such as low carbon steel, pure iron, and stainless steels) were usually cut from sheet stock in the form of coupons, 1/2 by 1 by 1/8 in. The liquid metal and coupons were contained in a crucible fabricated of molybdenum-30 w/o tungsten, an alloy which is considered to be nearly inert to attack by bismuth, tin, or lead. The loaded crucible was placed in a stainless steel bomb located in a resistance-heated furnace and was held at the test temperature (600 to 1000°C) for a predetermined period of time.

The test results to date have indicated that although steel or stainless steel may be suitable for the cell portion of sodium-lead and sodium-bismuth systems, the only promising container materials for sodium-bismuth regenerators or sodium-tin cells and regenerators are some refractory metals and their alloys. (However, niobium and its alloys, which became brittle after exposure to either bismuth or tin at 1000°C, do not appear to be promising.)

Dynamic corrosion tests are being conducted by means of loops fabricated of the test material; molten metals are circulated in the vertical loops by thermal convection. The loops are constructed in the form of parallelograms about 10 in. high and 6 in. wide of 1/4-in. pipe (0.54-in. OD and 0.364-in. ID). Electric heaters are used to maintain the four legs or

sections of the loop at different predetermined temperatures. At the end of each experiment, the loop is dissected radially and the internal cross-sectional areas which were exposed to the liquid metal are determined by means of enlarged photographs and a planimeter. Minimum thicknesses of the pipe walls are also measured.

The results of all dynamic corrosion tests conducted to date using steel and stainless steel loops are summarized in Table VI-4. Results of these tests clearly confirm that neither stainless steel nor low-carbon steel is suitable for use in a sodium-bismuth cell system at temperatures above 800°C; however, the results for Loop 9 support the view that low-carbon steel can be of use in the low-temperature operating section of such a cell. Experiments with sodium-lead mixtures in stainless steel loops are currently in progress, as indicated in Table VI-4.

TABLE VI-4. Dynamic Corrosion of Steel and Stainless Steel by Bismuth, Lead, Sodium-Bismuth Alloys, and Sodium-Lead Alloys

Loop Number	Test Material	Liquid Metal	Max Hot Leg Temp. (°C)	Min Cold Leg Temp. (°C)	Time (hr)	Results
2	1020 Steel	Bi	550	450	1000	Dissolution, <250 μ depth.
3	1020 Steel	Bi	800	700	24	Slight dissolution. Plugs formed, stopping circulation.
4	1020 Steel	Bi	850	450	430	Leak developed. ^a Extensive mass transfer. Dissolution of <60% loop metal at the hot leg.
5	1020 Steel	Bi	850	450	279	Leak developed. ^a Extensive mass transfer. Dissolution of <50% loop metal at the hot leg. Slight intergranular penetration.
6	1020 Steel	Bi-20 a/o Na	850	450	125	Leak developed. ^a Extensive mass transfer. Dissolution of <50% loop metal at the hot leg.
9	1020 Steel	Bi-30 a/o Na	650	550	1506 ^b	Slight mass transfer.
12	1020 Steel	Pb	850	650	690	Plugs formed, stopping circulation.
7	316 Stainless Steel	Bi	850	450	300	Leak developed. ^a Extensive mass transfer. Intergranular penetration. Cr segregated while Ni remained with Fe.
8	316 Stainless Steel	Bi-25 a/o Na	650	550	4426 ^b	Moderate mass transfer.
11	316 Stainless Steel	Pb	850	650	706	Plugs formed, stopping circulation.
13	316 Stainless Steel	Pb-30 a/o Na	850	650	>800	In operation.
10	Mo-30 w/o W	Bi	1050	700	>800	In operation.

^aThe leak developed at the entrance section of the hot leg.

^bNo leaks were found at the termination of experiment.

Loop 10, which was fabricated of molybdenum-30 w/o tungsten, has recently been charged with liquid bismuth and put in operation. Because of the known manufacturing difficulties with this material, very careful measures were taken during its fabrication. This loop has been operated with a hot-leg temperature of 1050°C and a cold-leg temperature of 700 to 900°C for over 800 hr as of January 1, 1966, with no indication of failure.

6. Theoretical Studies of Non-Faradaic Sodium Transfer

The non-faradaic or irreversible sodium transfer (see Equation 3) in a sodium-bismuth bimetallic cell exhibits the phenomenon that irreversible transfer decreases as cell current is increased (ANL-7020, pp. 213-214). A theoretical study was undertaken to explain this effect. In this study electronic conductivity of the electrolyte due to dissolved sodium was considered.

A theoretical differential equation was developed for irreversible transfer in bimetallic cells with parallel electrodes of equal areas, where there are no convection currents in the electrolyte. The equation is, for $Z = 1$,

$$q = - \left\{ \left[\frac{FD\rho}{M} X + \frac{k_e}{F_1} \frac{k_i}{k_i + k_e} R_g T \right] \frac{d \ln (\gamma X)}{d\ell} - \frac{k_e}{k_i + k_e} I \right\} \quad (4)$$

Symbols for the above and the following equations are defined as follows:

- D = coefficient of diffusivity of sodium atoms in electrolyte--very dilute solution ($X \rightarrow 0$), cm^2/sec
- E = cell terminal potential, volts
- E_0 = cell thermodynamic potential, volts
- E_{oc} = cell open circuit potential, volts
- F = Faraday's constant, 96,500 coulombs/mole
- F_1 = Faraday's constant, 23,060 cal/(mole)(volt)
- I = cell current, amperes/ cm^2
- I_0 = value of I when $q = 0$
- k_e = electronic conductivity of electrolyte, $1/(\text{ohm})(\text{cm})$
- k_i = metal anode ion conductivity of electrolyte, $1/(\text{ohm})(\text{cm})$
- $K_e = k_e/X$, $1/(\text{ohm})(\text{cm})$
- ℓ = distance from anode, cm
- L = distance of cathode from anode, cm
- M = molecular weight of electrolyte, g/mole

ρ = density of electrolyte, g/cc

q = anode metal irreversible transfer, amperes/cm²

q_0 = value of q at $I = 0$ (cell open circuit)

R_g = gas constant, 1.987 cal/(°K)(mole)

T = temperature, °K

X = mole fraction anode metal atoms dissolved in electrolyte, dimensionless

X_A = value of X at anode, ($\ell=0$), dimensionless

X_C = value of X at cathode, ($\ell=L$), dimensionless

Z = electrochemical value of anode metal ($Z = 1$ for alkali metals)

γ = activity coefficient of anode metal dissolved in electrolyte

If it is assumed that γ , M , ρ , k_i , and D are independent of X and that K_e is constant, the differential equation can be solved. The solution of the differential equation for the boundary conditions, $X = X_A$ at $\ell = 0$ and $X = X_C$ at $\ell = L$, although not explicit in q or I , is

$$q + I = \left[\frac{k_i R_g T}{F_1 L} + \frac{FD\rho}{LM} \frac{k_i}{K_e} \frac{I}{q + I} \right] \ln \frac{q k_i + (q + I) K_e X_A}{q k_i + (q + I) K_e X_C} + \frac{FD\rho}{LM} (X_A - X_C) \quad (5)$$

These theoretical studies have indicated that the cell voltage loss (thermodynamic potential minus terminal potential) due to cell current flow and irreversible transfer is

$$E_o - E = -\Delta E = \frac{1}{k_i} \left[qL + IL - FD \frac{\rho}{M} (X_A - X_C) \right] \text{volts} \quad (6)$$

and at open circuit ($I = 0$, $q = q_0$) the cell voltage loss is

$$E_o - E_{oc} = -\Delta E_{oc} = \frac{1}{k_i} \left[q_0 L - FD \frac{\rho}{M} (X_A - X_C) \right] = \frac{R_g T}{F_1} \ln \frac{k_i + K_e X_A}{k_i + K_e X_C} \text{volts} \quad (7)$$

The cell thermodynamic voltage is

$$E_o = \frac{R_g T}{F_1} \ln \frac{\gamma X_A}{\gamma X_C} \quad (8)$$

and the open circuit voltage is then

$$E_{oc} = E_o + \Delta E_{oc} = \frac{R_g T}{F_1} \left[\ln \frac{X_A}{X_C} - \ln \frac{k_i + K_e X_A}{k_i + K_e X_C} \right] \quad (9)$$

Equation (5) was solved using the values listed below for the variables:

$$\begin{aligned} D &= 1 \times 10^{-4} \text{ cm}^2/\text{sec} & X_A &= 0.004 \\ k_i &= 1 \text{ ohm}^{-1}\text{cm}^{-1} & X_A/X_C &= 10^4, 10^3, 10^2, \text{ and } 10 \\ K_e &= 100, 200, \text{ and } 400 \text{ ohm}^{-1}\text{cm}^{-1} & T &= 585^\circ\text{C} (858^\circ\text{K}) \\ M &= 105 \text{ g/mole} & \rho &= 2.5 \text{ g/cc} \end{aligned}$$

It was found that the two terms in the equations involving $FD\rho/M$ are small and contribute very little. The fact that the expression $FD\rho(X_A - X_C)/LM$ is relatively small indicates that the irreversible transfer is largely caused by electronic conduction in the electrolyte rather than by direct diffusion of sodium atoms as earlier postulated (ANL-7020, p. 214).

The solution of Equation 5 can be expressed as a correlation of Lq/k_i as a function of LI/k_i for the various values of X_A/X_C and K_e . The results for the case of $K_e X_A/k_i = 0.8$ are shown in Fig. VI-13. From the figure it

Fig. VI-13

Solution of Equation 5

$$\frac{K_e X_A}{k_i} = 0.8$$

$$D = 1 \times 10^{-4} \text{ cm}^2/\text{sec}$$

$$M = 105$$

$$T = 858^\circ\text{K} (585^\circ\text{C})$$

$$\rho = 2.5 \text{ g/cc}$$

$$k_i = 1$$

$$K_e = 200$$

$$X_A = 0.004$$

$$X_A/X_C = 10^4, 10^3, 10^2, 10$$

is seen that the theory predicts a decrease in irreversible transfer with an increase in cell current, which phenomenon has been observed in experiments.

The experimental values of irreversible transfer are being correlated with those predicted by the theoretical equations using estimated values of the ionic and electronic conductivities of the electrolyte.

7. Engineering Thermodynamic Studies

Engineering thermodynamic studies of bimetallic and hydride cell systems have been made. Computed efficiencies for sodium-bismuth, sodium-tin, and lithium-tin bimetallic cells and for lithium hydride cell systems were previously reported (ANL-7020, pp. 222, 224). The computed efficiencies for the sodium-lead bimetallic system have subsequently been determined for 10, 20, 30, and 40 a/o anode metal in the cathode metal; these are listed in Table VI-5.

TABLE VI-5. Computed Efficiencies for Sodium-Lead Bimetallic Regenerative Cell System

	Atom Fraction of Anode Metal in Cathode Metal			
	0.1	0.2	0.3	0.4
Cell open circuit potential at 698°K (425°C), ^a volts	0.483	0.401	0.327	0.260
<u>Efficiency, %</u>				
Regeneration, Ideal Cycle	31	27	23	19
Regeneration, 75% of Ideal Cycle	23	20	17	14
System, 60% Cell Electrical Efficiency	14	12	10	8
Regeneration Pressure, mm Hg at 1100°K (827°C)	2.62	6.38	13.8	28.0
Sodium Condensing Temperature (°K) for Regeneration Temperature of 1100°K	750	795	840	880

^aEmf values calculated from free energies given by R. D. Hultgren et al., Thermodynamic Properties of Metals and Alloys, J. Wiley and Sons, 1965, p. 869.

VII. DETERMINATION OF NUCLEAR CONSTANTS

In order to judge the effect of reactor materials upon the breeding gain of the reactor, detailed data are needed on the neutron reaction rates in these materials as a function of neutron energy. Of particular importance are (1) capture cross sections of structural materials; (2) capture and fission cross sections of the fissionable and fertile species; and (3) neutron inelastic scattering cross sections.

In the present program, each of these types of reactions is being studied. Work on the measurement of radiative capture cross sections as a function of neutron energy in the range occurring in fast reactors (see ANL-7020, p. 228) has been continued. Samples of uranium and plutonium are undergoing irradiation in EBR-II (see ANL-7020, p. 230) for use in the experiments designed to measure the ratio of the capture and fission cross sections of these isotopes. The neutron inelastic scattering experiments (see ANL-7020, p. 226) are awaiting refinements in the development of a lithium drifted germanium diode detector by the Electronics Division. This gamma-ray detector will provide a large increase in energy resolution over that of the presently used sodium iodide crystals; it will allow gamma rays to be studied to a much higher degree of accuracy by substantially reducing interference from other gamma rays.

A. Radiative Capture

The radiative capture reaction absorbs neutrons unproductively in a reactor, and is therefore an unfavorable event in a structural material, and a favorable event in a control material. The cross section for capture as a function of neutron energy is needed in order to estimate what effect a particular material would have on reactor operation. Further, the data are needed to test and improve nuclear reaction theory, so that the theory can be used to predict unknown neutron cross sections.

The experimental technique is the activation method, in which the targets are bombarded with a monoenergetic neutron beam, and the radioactive species produced are counted with a beta counter or a gamma-ray analyzer. The counting rates are converted to cross sections by calibrations which give the absolute neutron flux and the disintegration rate of the capture product. The neutron beam is produced by bombarding lithium or tritium targets with protons from the Van de Graaff accelerator. The neutron flux is measured with a fission chamber, which counts fissions in a thin uranium deposit.

Measurements have been made on the capture cross sections of ^{98}Mo , ^{89}Y , ^{139}La , ^{141}Pr , ^{176}Yb , and ^{175}Lu for neutron energies between a

few keV and about 3 MeV. In Figs. VII-1 to VII-6 the results of these studies are given together with data of earlier workers¹⁻⁶ where available.

Fig. VII-1
Radiative Capture
Cross Section of
Praseodymium-141

108-9275

Fig. VII-2
Radiative Capture
Cross Section of
Lutetium-175

108-9290

¹Gibbons, J. H., Macklin, R. L., Miller, P. D., and Neiler, J. H., Phys. Rev. **122**, 182 (1961).

²Johnsrud, A. E., Silbert, M. G., and Barshall, H. H., Phys. Rev. **116**, 927 (1959).

³Konks, V. A., Popov, Yu. P., and Shapiro, F. L., Zhur. Eksp. Teor. Fiz. **46**, 80 (1964).

⁴Macklin, R. L., Gibbons, J. H., and Inada, T., Phys. Rev. **129**, 2695 (1963).

⁵Macklin, R. L., Lazar, N. H., and Lyon, W. S., Phys. Rev. **107**, 504 (1957).

⁶Kapchigashev, S. P., and Popov, Yu. P., Atomnaya Energiya **8**, 120 (1962).

108-9300 Rev. 1

Fig. VII-3. Radiative Capture Cross Section of Lanthanum-139

108-9422

Fig. VII-4. Radiative Capture Cross Section of Yttrium-89

108-9304

Fig. VII-5. Radiative Capture Cross Section of Ytterbium-176

108-9416

Fig. VII-6. Radiative Capture Cross Section of Molybdenum-98

Also shown in Fig. VII-3 for lanthanum-139 is a theoretical curve representing the results of calculations based upon a statistical compound theory of nuclear reactions. The calculations took into account the variation of radiation width and level spacing with excitation energy and spin of the compound nucleus, and used optical model transmission coefficients to obtain the neutron widths. Also included in the calculations were the variation of neutron widths from level to level and the competition of compound elastic and inelastic scattering.

B. Capture to Fission Ratios in EBR-II

Among the most important quantities needed in calculating the breeding gain of a reactor are the ratios of the capture and fission cross sections of the primary fuels and of the products which build up over a long period through successive captures. It would be greatly preferable to have available all the relevant capture and fission cross sections as a function of neutron energy, and from these basic data, to calculate the needed quantities. However, because of limitations in techniques, and scarcity of samples, it is often not practical to obtain this elaborate set of data. An alternative experimental program would be to measure the cross section ratio in a typical existing fast reactor spectrum. This is the approach being used here to determine the ratio of the capture and fission cross sections of ^{233}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu , and ^{242}Pu at various positions in the core and blankets of EBR-II.

All of the samples have now been irradiated in the reactor for several months, and their scheduled irradiations will be completed in about six more months. Following this, the samples will be returned to ANL for analysis.

VIII. ANALYTICAL RESEARCH AND DEVELOPMENT

The Analytical Chemistry Group provides a broad spectrum of analytical support to the research and development groups of the Chemical Engineering Division. The group includes a large section for elemental analysis, a section for the development of new analytical methods, and sections which specialize in X-ray diffraction and spectroscopy, gas chromatography, and electron probe microscopy.

Research in analytical chemistry is, to a large extent, the outgrowth of the service work. As the Division's program changes, existing analytical methods must be modified or new methods developed to meet the conditions that are imposed by the nature of the samples submitted for analysis. In the vast majority of samples submitted, the element of interest is a minor constituent and emphasis is, therefore, directed toward those instrumental methods and techniques which can provide high sensitivity and, if possible, specificity.

To enhance the capabilities of the Analytical Group, three new instruments were placed in operation during the past year: an atomic absorption spectrometer, a 75-kV X-ray spectrometer, and a lithium drifted germanium diode detector for gamma spectrometry. The use of the lithium drifted germanium diode for analysis of complex gamma-ray spectra increases the resolution of gamma rays by a factor of 25 over that obtainable with sodium iodide detectors. Applications of the atomic absorption spectrometer and the X-ray spectrometer are described later in the report.

A. Elemental Chemical Analysis

During the past year the elemental analysis section used 115 methods to perform more than 13,000 analyses for 45 different elements. The choice of a method of analysis depended on a number of factors, such as the concentration of the element of interest, the matrix material, and the accuracy required.

Recently, requests were made for the analysis of 10 ppm zirconium, ruthenium, and cerium in samples of zinc-magnesium-uranium and cadmium-magnesium-uranium. Analysis at this level required the adoption of methods more sensitive than those previously in use. A spectrophotometric method for zirconium¹ using pyridylazo-naphthol (PAN) as the chromogenic reagent provided the necessary sensitivity, but the high levels of uranium present in the samples interfered. This interference was eliminated by extraction of zirconium with dibutyl phosphate in toluene and removal of the uranium that had also been extracted (~10% of the amount originally present) by repeated aqueous scrubs of the organic phase.

¹Rolf, R., Anal. Chem. 31, 125 (1961).

Modifications in the color development step have resulted in improved color stability and better precision. A previously developed spectrophotometric method for ruthenium using 1-nitroso-2-naphthol² (see also ANL-6875, p. 175) is being used routinely for these samples. The determination of cerium has been accomplished by adapting the spectrophotometric method of Onishi and Toita³ to our use.

B. Atomic Absorption Spectrometry

In principle, atomic absorption spectrometry is analogous to solution spectrophotometry. In practice, monochromatic light from a hollow cathode lamp containing the element being analyzed is passed through a high temperature flame. The sample is aspirated into the flame and the increase in absorbance of the flame measured. Atomic absorption differs from flame emission by measuring absorption of atoms in the flame that are in the ground state rather than emission of those in an excited state. In the 5 years or so since this analytical technique was introduced, it has been used for the trace analysis of over fifty elements. It is characterized by high sensitivity, good precision ($\pm 1\%$), relative freedom from interferences, and simplicity of operation.

Initial applications of atomic absorption spectrometry to the Division's analytical problems have been the determination of zinc and magnesium. These elements, which are of particular importance in the pyrochemical separations program, are especially difficult to determine by other methods at concentrations of 0.1% or less. Without fully optimizing operating parameters, a sensitivity of 0.02 ppm has been attained for both elements. In the optimum working range, 0.2 to 5 ppm, a precision of 1 to 2% has been demonstrated. Plans are now being made to apply atomic absorption to the determination of cadmium, aluminum, tellurium, and bismuth.

C. X-Ray Spectroscopy

The Analytical Group has used X-ray spectroscopy extensively in past years for the determination of many elements. The recently acquired 75-kV instrument increases the sensitivity by a factor of 5 to 10 for many elements and, with its provision for a helium path, provides a means for identifying and determining a number of elements which were hitherto undetectable.

In the fluid-bed fluoride volatility processing of UO_2 - PuO_2 -fission product oxides, analyses for both plutonium and uranium are required on the final alumina bed and also on numerous samples removed from the bed during the course of fluorination. X-ray spectrochemical procedures have

²Kesser, G., Meyer, R. J., Larsen, R. P., Anal. Chem. 38, 221 (1966).

³Onishi, H., and Toita, Y., Anal. Chem. 36, 1867 (1964).

been developed which provide rapid and reliable analyses for both of these elements. A pellet is prepared by mixing a portion of the finely ground aluminum oxide with an equal weight of fine resin and cold pressing.

Analysis consists of a comparison of the plutonium, or uranium, $L\alpha_1$ X-ray emission line intensity of the unknown with those of a set of similar, chemically analyzed or specially prepared standards. The sensitivity of the method is 0.002 w/o; the accuracy in the optimum concentration range, 0.05 to 1.0 w/o, is $\pm 5\%$. Strontium is the only constituent of the alumina beds which has an X-ray emission line which interferes with the plutonium $L\alpha_1$ line. However, this interference can be overcome by correcting the intensity of the observed plutonium $L\alpha_1$ line ($0.868 \text{ \AA}$) for the small contribution from the strontium $K\alpha_1$ line ($0.875 \text{ \AA}$).

Hundreds of analyses have been performed by this X-ray technique with a considerable saving in analysis time. The alternate wet chemical procedure requires a 16-hr fusion at 1000°C to decompose the alumina, a nitric acid dissolution of the melt, solvent extraction of the plutonium and a final alpha assay.

In addition to plutonium and uranium many of the fission product elements (nonradioactive) present in the bed are being monitored by similar X-ray spectrochemical procedures. Strontium, yttrium, zirconium, molybdenum, ruthenium and cesium are elements for which such procedures have been developed.

D. X-Ray Diffraction

The chemistry of liquid metal systems and metallic alloys is being investigated in order to provide basic data for the pyrochemical processing of nuclear fuels. The lanthanon-cadmium systems are among those under investigation.

As a part of this investigation, the lattice constants of a number of the LnCd_2 intermetallic compounds have been determined. These data are presented in Table VIII-1. All of these compounds have the hexagonal $\text{CdI}_2/\text{AlB}_2$ (C6/C32) type structure. Previously published^{4,5} lattice constants for other LnCd_2 compounds are also included in Table VIII-1.

The trend of decreasing lattice constants with increasing atomic number of the lanthanon is observed in Table VIII-1 and provides another example of the well-known lanthanide contraction. Missing from the table are lattice constants for EuCd_2 and YbCd_2 , the two exceptional lanthanons. EuCd_2 either does not exist or does not exist as this structure type; the existence of YbCd_2 is currently under investigation.

⁴Iandelli, A., and Ferro, R., Gazz. Chim. ital. 84, 463 (1954).

⁵Iandelli, A., The Physical Chemistry of Metallic Solutions and Intermetallic Compounds, N.P.L. Symposium, 1958; H.M. Stationery Office, London (1959).

TABLE VIII-1. LnCd_2 Lattice Constants

Compound	Lattice Constants		Reference
	a (Å)	c (Å)	
LaCd_2	5.075	3.458	Iandelli and Ferro ⁴
CeCd_2	5.073	3.450	Iandelli and Ferro ⁴
PrCd_2	5.035	3.466	Iandelli and Ferro ⁴
NdCd_2	5.009	3.469	Iandelli ⁵
SmCd_2	4.940	3.499	Iandelli ⁵
EuCd_2	-	-	-
GdCd_2	4.938	3.470	This study
TbCd_2	4.922	3.448	This study
DyCd_2	4.907	3.445	This study
HoCd_2	4.894	3.435	This study
ErCd_2	4.885	3.420	This study
TmCd_2	4.878	3.401	This study
YbCd_2	-	-	-
LuCd_2	4.866	3.381	This study

E. Electron Probe Microscopy

The electron probe microanalyzer has been used extensively in the elucidation of corrosion problems. Corrosion products were identified and the depths of penetration by the corroding substances were measured. Some of the corrosion problems which have been studied are: the attack of TeF_6 on Monel; the attack of tin and bismuth at 1000°C on niobium, rhenium-50 w/o molybdenum, and various steels; the attack of various liquid metal solutions from the pyrochemical processing schemes on molybdenum-30 w/o tungsten agitator blades; the attack of a bismuth-tin eutectic on type 304 stainless steel and the attack of $\text{UN-Na}_2\text{O-Na}$, UC-Na , and sodium at 760°C on stainless steel.

Electron probe analysis of various uranium-zinc alloys contributed significantly to the delineation of the uranium-zinc phase diagram. The following phases were isolated and identified: $\text{UZn}_{8.5}$, $\text{UZn}_{9.5}$, UZn_{11} , $\text{UZn}_{11.25}$, $\text{UZn}_{11.5}$, and UZn_{12} . A statistical study of the data indicates that a composition range may exist between $\text{UZn}_{11.25}$ and $\text{UZn}_{11.5}$; the others appear to be line compounds. The phase UZn_{11} was found to decompose peritectically between 720 and 729°C . The phase $\text{UZn}_{8.5}$ which was thought to be unstable below 500°C was found to exist in alloys corresponding to an annealing temperature of 435°C .

The electron probe has also been used in a variety of other applications: to characterize the variation of uranium concentration in uranium carbide particles; to identify inclusions in various fuel materials; to

identify mineral inclusions in meteorites;⁶ and to determine calcium-phosphorus ratio variations in bone samples of individuals exposed to radium poisoning.⁷

F. Gas Analysis

1. Determination of Nitrogen and Oxygen in Helium at the Sub-ppm Level

In the monitoring of the impurity content of glovebox atmospheres, the need arose for a determination of nitrogen and oxygen in helium at the 0.1-ppm level. The thermal conductivity detection system which is used in our chromatographs appears to have detection limits for oxygen and nitrogen in the neighborhood of one ppm. However, at this level, highly erratic results have been obtained.

To provide increased sensitivity, the following concentration step was introduced. A sample 10 to 100 times larger than that used in the direct determination is passed through a 3-in. section of chromatographic column kept at liquid nitrogen temperature. The trapped impurities are then subjected to the regular chromatographic analysis. This technique lowered the detection limit to hundredths of a ppm and increased the precision of the low-ppm analyses to about $\pm 10\%$.

2. Analysis of Mixtures of Fluoride Gases

Some success has been realized in the problem of separating such volatile fluorides as BrF , BrF_3 , and BrF_5 from each other. Preliminary results indicate that when columns are cooled to subambient temperatures (-15 to -150°C), either fixed or programmed, the components of selected mixtures may be successfully separated. Multiple peaks have been obtained from several mixtures, but uncertainty remains concerning the identity of some of the peaks. It is suspected that reaction products may be involved in some of these peaks. Infrared and mass spectrometric methods will be used to identify chromatographically separated components.

3. Determination of the Metal Content of Metal-Salt, Metal-Oxide, and Metal-Nitride Mixtures

Gas chromatography was used to determine the metal content of various mixtures. Lithium metal in lithium chloride and magnesium metal in magnesium chloride were determined by hydrolysis of the sample and measurement of the evolved hydrogen. Uranium metal was determined in a uranium-uranium oxide mixture, in a uranium-tungsten-uranium oxide mixture, and in a uranium-uranium nitride mixture by hydriding the sample and measuring the hydrogen evolved when the hydride was decomposed.

⁶Work performed for the Chemistry Division.

⁷Work performed for the Radiological Physics Division.

G. Determination of Burnup in Fast Reactors

A program for the development of analytical methods for the determination of burnup of fast reactor fuels and for the measurement of fast fission yields is being carried out. The initial objective of this program was the development of burnup methods for EBR-II. However, during the past year the objectives have been broadened to include fast reactors in general.

1. Irradiations in EBR-II

Monitoring burnup in reactor fuels can be accomplished in two ways: (1) by measuring the pre- and post-irradiation fissile isotope concentrations and subtracting the two values, and (2) by measuring the concentration of a fission product nuclide in the irradiated fuel and dividing by the fission yield of the nuclide. The first method does not provide burnup values of the requisite accuracy, $\pm 1\%$, when it is applied to fast reactor fuels, since the burnups are low relative to the fissile isotope concentrations, e.g., 2% burnup vs 50 w/o uranium-235 in EBR-II. The second method can provide burnup measurements of the requisite accuracy, if the fission yields are accurately known.

Since the available data on fast fission yields is sparse and of questionable accuracy, a program is being carried out to measure accurately the fast fission yields of the important fission product burnup monitors. This will be done by irradiating 100 mg quantities of fissile isotopes in EBR-II to burnups of about 25%, determining the number of fissions from pre- and post-irradiation heavy element analysis, and determining the number of atoms of the particular fission product and dividing the latter by the former.

Plans call for the irradiation of not only fissile isotopes but other actinide nuclides of importance to fast reactor operations. To determine the effect, if any, of neutron energy on the fission yields, irradiations will be carried out in both the core and the blanket of EBR-II.

The primary encapsulation (in pure nickel) has now been completed. Secondary and tertiary encapsulation will begin shortly and the irradiation, which will last several years, should begin within 6 months.

2. Total Rare Earths for Monitoring Burnup

A total rare earth analysis for determining burnup is being investigated. This method has several advantages over methods based on a single nuclide: (1) more material is available for a determination since the combined fission yield of the rare earths is approximately 50%; (2) existing information of fission yields indicates that the combined fission yield of the rare earth nuclides is independent of the fissioning nuclide and

the fission neutron energy. Approximately 3 mg of rare earths will be formed in every gram of fissionable material at 1% burnup. Because of shielding problems it would be desirable to perform the analysis on as small a quantity of rare earths as possible. None of the methods of total rare earth analysis in the literature meet the $\pm 1\%$ accuracy requirement at the sub-milligram level.

A total rare earth titration with ethylenediaminetetracetic acid (EDTA) reported by Fritz et al.,⁸ has been modified to meet the accuracy-sensitivity requirement by incorporating a photometric end-point detection. The titration is performed at a pH of 5.5 to 6.5 using arsenazo I as the indicator; the absorbance measurements are made at 560μ . Because the total volume of titrant is unusually small, about 1 ml of 0.005N EDTA at the 500- μ g level, the titrant is added with a weight burette. The results obtained at this level show a relative standard deviation of $\pm 0.5\%$ with no bias.

Several of the constituents present in an irradiated fuel, e.g., uranium, zirconium, and iron, will interfere in the rare earth-EDTA titration. A separation procedure which will remove all the interferences has been devised. A preliminary separation of major contaminants is effected by solvent extraction with tributyl phosphate. This is followed by an ion exchange separation⁹ in which the rare earths are adsorbed onto the strongly basic anion exchanger Dowex 1-X8 (nitrate form) from a solution consisting of 90 v/o methanol and 10 v/o 5N nitric acid. The interfering elements, including yttrium, pass through the column. The rare earths are then eluted from the column with 1N nitric acid.

Thus far, solutions containing 500 μ g of lanthanum have been put through both the anion-exchange separation and the rare earth-EDTA titration. The results obtained at the 500- μ g level have a standard deviation of $\pm 0.6\%$ with no significant bias.

3. Determination of the Fast Fission Yield of Praseodymium-141 by Neutron Activation

Praseodymium-141 (stable) is a potentially useful burnup monitor for fast reactor fuels. However, its fast fission yield has not been measured. Of the various analytical techniques which have been used to determine fission yields of individual nuclides, none is applicable to the determination of praseodymium-141.

Neutron activation affords a means for determining praseodymium with high sensitivity and some degree of specificity. However, the precision of the method would have to be improved from the customarily

⁸Fritz, J. S., Oliver, R. T., and Pietrzyk, D. J., Anal. Chem. 30, 1111 (1958).

⁹Korkisch, J., and Tera, F., Anal. Chem. 33, 1264 (1961).

accepted $\pm 10\%$ to $\pm 1\%$ to achieve the desired accuracy ($\pm 1\%$) for a fission yield determination.

The lack of precision in neutron activation analysis is attributable to poor flux monitoring. Because the flux variation with position within most irradiation facilities is often as much as 25% per centimeter, samples and flux monitors (the same element or some other element) do not see the same flux. Successive irradiations of samples and standards in identical containers cannot be carried out successfully since the containers cannot be reproducibly positioned.

The flux monitor technique has been modified in such a way that the problem of integrated flux dependency has been eliminated. A known amount of an element, A (the flux monitor), is dissolved in a solution of the element being determined, B. The solution is then irradiated, and after irradiation the gamma activity of element A is separated from the activity of element B. Both element A and B are gamma counted, and the activity ratio obtained for the "unknown" mixture is compared to the same ratio obtained with an irradiated solution containing known amounts of both A and B.

The technique is now being investigated in the neutron activation analysis of praseodymium-141 using sodium as an internal standard. The neutron reactions are:

After the irradiation the sodium is separated from praseodymium by precipitating praseodymium hydroxide using lanthanum hydroxide as the carrier and sodium hydroxide as the precipitant. Using this technique the relative standard deviation was $\pm 1\%$.

If praseodymium is to be useful as a burnup monitor the following chemical separations are necessary: (1) a separation of the rare earths as a group from the sample and (2) a separation of praseodymium from those rare earths which would interfere in the analysis. The latter separation is the most difficult and is therefore the key to the eventual success of the method.

An ion exchange method using the cation resin Dowex-50 and α -hydroxy-isobutyric acid as the elutriant is being investigated as a means of separating praseodymium from the other rare earths. Results obtained thus far indicate that a complete separation from all the other rare earths except neodymium and cerium can be achieved by this procedure. The separation factor for neodymium and cerium is about 100. Neither neodymium nor cerium will interfere with the determination of praseodymium, but the high level of radioactivity in the cerium fraction (from ${}^{144}\text{Ce}$, 285 days) makes

separation of cerium necessary. This is being done by anion exchange. Cerium (IV) and praseodymium (III) are passed through a Dowex-1 ion exchange column in 7M nitric acid; cerium (IV) is absorbed and praseodymium (III) is not.

This neutron activation technique should also be useful in determining the fission yields of lanthanum-139, barium-138, iodine-127, and iodine-129. The technique is currently being investigated as a means of analyzing alkali metal mixtures. The precision of the results obtained to date for both sodium-potassium and sodium-cesium mixtures is very encouraging.

ADDENDUM

Publications

by

Chemical Engineering Division
Personnel

(From January 1, 1965 to April 30, 1966)

A. Open-Literature Publications

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

Fluorination of UO_2 - PuO_2 Fission-Product Oxide Pellets in a Fluidized-Bed Reactor

Trans. Am. Nucl. Soc. 1965 Winter Meeting, Nov. 15-18, 1965, Washington, D. C., p. 357. Abstract.

Anastasia, L. J. and W. J. Mecham

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

Baker, L., Jr.

Metal-Water Reactions

Section of Chap. 5 (Energy Sources) of U.S. Reactor Containment
Technology, ORNL-NSIC-5, Vol. 1, pp. 5.3-5.56, August 1965.

Baker, Louis and R. O. Ivins

A Calculation Demonstrating the Effect of the Zirconium-Water
Reaction on the Analysis of a Loss-of-Coolant AccidentProc. Intern. Symp. on Fission Product Release and Transport under
Accident Conditions, Oak Ridge, April 5-7, 1965. CONF-650407,
Vol. 2, pp. 938-969.

Baker, Louis, Jr. and Richard O. Ivins

Analyzing the Effects of a Zirconium-Water Reaction
Nucleonics 23(7), 70-74 (1965).

Baker, L., Jr.

Metal-Water Reactions

Nucl. Safety 7(1), 25-34 (1965).

Bennett, G. A., P. A. Nelson, and L. Burris, Jr.

Corrosion of Stainless Steel by Zinc Vapor

Trans. Met. Soc. AIME 233, 1032-1036 (May 1965).

Burris, L., Jr., R. K. Steunenberg, R. D. Pierce, and M. Levenson

Compact Pyrochemical Processes for Advanced Reactor Fuels

Am. Chem. Soc. Meeting, Atlantic City, Sept. 12-17, 1965.

Abstracts of Papers, p. 3R.

Chasanov, M. G.

Fission-Product Effects in Molten-Chloride Fast-Reactor Fuels.

Nucl. Sci. Eng. 23, 189-190 (October 1965). Note.

- Chasanov, M. G., P. A. Nelson, and A. D. Tevebaugh
Wetting of UN and Other Uranium Ceramics by Molten Sodium
J. Nucl. Mater. 16, 227-228 (June 1965). Letter.
- Chemical Engineering Division
Development of Processes for Nuclear Fuel Recovery. Part II. Fluoride Volatility Processes*
Argonne National Laboratory Reviews 2(1), 6-10 (January 1965).
- Chilenskas, A. A., K. S. Turner, J. T. Holmes, J. Kincinas, and G. Potts
Fluid-Bed Fluoride Volatility Processing of Irradiated Fuels in a Hot Cell
Proc. 13th Conf. on Remote Systems Technology, Washington, D. C., 1965, American Nuclear Society, Hinsdale, Illinois, pp. 25-26.
- Crouthamel, C. E., D. C. Stupigia, C. M. Stevens, and P. Kafalas
Capture to Fission Ratios of U^{233} , U^{235} , U^{238} , and Pu^{239} in EBR-I, Mark III*
Nucl. Sci. Eng. 21(2), 179-185 (February 1965).
- Feder, H. M.
Chemistry in Liquid Metal Solvents (Part II)
39th Annual Priestley Lectures, The Pennsylvania State University, April 26-29, 1965, printed report (1965).
- Fischer, A. K.
Phase Diagram Considerations for the Regenerative Bimetallic Cell
149th Mtg. Am. Chem. Soc., Detroit, April 4-9, 1965.
Abstracts of Papers, p. 13-L.
A chapter on this topic accepted for publication in Regenerative Galvanic Cells, monograph, American Chemical Society.
- Gabor, J. D.
Lateral Transport in a Fluidized-Packed Bed: Part I. Solids Mixing*
AIChE (Am. Inst. Chem. Engrs.) J 11(1), 127-129 (January 1965).
- Gabor, J. D., B. E. Stangeland, and W. J. Mechem
Lateral Transport in a Fluidized-Packed Bed: Part II. Heat Transfer*
AIChE (Am. Inst. Chem. Engrs.) J 11(1), 130-132 (January 1965).
- Greenberg, E., C. A. Natke, and W. N. Hubbard
Fluorine Bomb Calorimetry. X. The Enthalpies of Formation of Niobium and Tantalum Pentafluorides
J. Phys. Chem. 69, 2089-2093 (June 1965).
- Heinrich, Robert R., Carl E. Johnson, and Carl E. Crouthamel
Hydrogen Permeation Studies. I. Armco Iron and Iron-Molybdenum Alloys
J. Electrochem. Soc. 112(11), 1067-1070 (November 1965).

*Also listed in ANL-7020.

- Heinrich, Robert R., Carl E. Johnson, and Carl E. Crouthamel
 Hydrogen Permeation Studies, II. Vanadium as a Hydrogen Electrode
 in a Lithium Hydride Cell
 J. Electrochem. Soc. 112(11), 1071-1073 (November 1965).
- Hesson, J. C.
 Thermodynamics and Thermal Efficiencies of Thermally Regenerative
 Emf Cell Systems
 149th Mtg. Am. Chem. Soc., Detroit, April 4-9, 1965.
 Abstracts of Papers, p. 14-L.
 A chapter on this topic, with Hiroshi Shimotake as coauthor, accepted
 for publication in Regenerative Galvanic Cells, monograph, American
 Chemical Society.
- Hesson, J. C., H. E. Hootman, and L. Burris, Jr.
 Diffusivity of Uranium in Various Liquid Metal Solutions
 Electrochem. Tech. 3, 240-243 (Sept.-Oct. 1965).
- Holmes, J. T.
 Simplified Technique for Using the Diaphragm-Type Liquid Diffusion
 Cell
 Rev. Sci. Instr. 36, 831-832. (June 1965).
- Holmes, J. T. and M. G. Baerns
 Predicting Physical Properties of Gases and Gas Mixtures
 Chem. Eng. 72(11), 103-108 (May 24, 1965).
- Holmes, John T., Howard Stethers, and John J. Barghusen
 Engineering Development of a Fluid-Bed Fluoride Volatility Process.
 II. Pilot-scale Studies
 Nucl. Appl. 1, 301-309 (August 1965).
- Hubbard, W. N.
 Calorimetry*
 Science 147, 312-314 (Jan. 15, 1965).
- Johnson, C. E., C. E. Crouthamel, and S. E. Wood
 Properties of Alkali Halides in Solution with Lithium Hydride.
 Abstract
 Extended Abstracts of Electrothermics and Metallurgy Division,
 Vol. 3, No. 1, p. 77 (Electrochemical Society, New York).
- Johnson, C. E. and R. R. Heinrich
 Thermodynamic Data for the LiH Cell
 149th Mtg. Am. Chem. Soc., Detroit, April 4-9, 1965.
 Abstracts of Papers, p. 17-L.
 A chapter on this topic accepted for publication in Regenerative
 Galvanic Cells, monograph, American Chemical Society.
- Johnson, Carl E., Scott E. Wood, and Carl E. Crouthamel
 Studies of Lithium Hydride Systems. II. Solid-Liquid Equilibrium in
 the Sodium Chloride-Lithium Hydride System
 J. Chem. Phys. 44, 880 (1966).

*Also listed in ANL-7020.

- Johnson, Carl E., Scott E. Wood, and Carl E. Crouthamel
Studies of Lithium Hydride Systems. III. Solid-Liquid Equilibrium in
the Lithium Bromide-Lithium Hydride and Lithium Iodide-Lithium
Hydride Systems
J. Chem. Phys. 44, 884 (1966).
- Johnson, C. E., R. R. Heinrich, and C. E. Crouthamel
Thermodynamic Properties of Lithium Hydride by an Emf Method
J. Phys. Chem. 70, 242-246 (January 1966).
- Johnson, G. K., H. M. Feder, and W. N. Hubbard
Fluorine Bomb Calorimetry. XV. The Enthalpy of Formation of
Boron Trifluoride
J. Phys. Chem. 70, 1-6 (1966).
- Johnson, Irving, Martin G. Chasanov, and Robert M. Yonco
Pu-Cd System: Thermodynamics and Partial Phase Diagram
Trans. Met. Soc. AIME 233, 1408-1414 (1965).
- Jonke, A. A.
Reprocessing of Nuclear Reactor Fuels by Processes Based on
Volatilization, Fractional Distillation, and Selective Adsorption
At. Energy Rev. 3(1), 3-60 (1965).
- Jonke, A. A., M. J. Steindler, N. M. Levitz, J. T. Holmes, and
D. Ramaswami
Reprocessing Spent Plutonium and Enriched Uranium Bearing Fuels
by Fluidized-Bed Volatility Methods
Am. Chem. Soc. Meeting, Atlantic City, Sept. 12-17, 1965.
Abstracts of Papers, p. 1R.
- Kesser, Gwendolyn, R. J. Meyer, and R. P. Larsen
Spectrophotometric Determination of Ruthenium with 1-Nitroso-
2-naphthol
Anal. Chem. 38, 221 (1966).
- Kilpatrick, Martin and S. K. Lott
Reaction of Flowing Steam with Refractory Metals. I. Molybdenum
(1100-1700°C)
J. Phys. Chem. 69, 1638-1640 (1965).
- Kilpatrick, Martin and Stanley K. Lott
Reaction of Flowing Steam with the Refractory Metals Niobium and
Tantalum
J. Less-Common Metals 8, 299-305 (1965).
- Kilpatrick, M. and S. K. Lott
Reaction of Flowing Steam with Refractory Metals: II. Rhenium
(850-1700°C)
J. Electrochem. Soc. 113, 15 (1966).
- Kilpatrick, M. and S. K. Lott
Reaction of Flowing Steam with Refractory Metals: III. Tungsten
(1000-1700°C)
J. Electrochem. Soc. 113, 17 (1966).

Knighton, J. B. and R. K. Steunenbergh

Distribution of Transuranium Elements between Magnesium Chloride and Zinc-Magnesium Alloy

J. Inorg. Nucl. Chem. 27, 1457-1462 (1965).

Knudsen, Irving E., Norman Levitz, and Albert A. Jonke

Preparation of Dense Uranium Dioxide Particles from Uranium Hexafluoride in a Fluidized Bed in Preparation and Processing of Particulate Nuclear Fuels -- Proceedings of a Symposium held at New York, Sept. 9, 1963. USAEC Report CONF-117, p. 45.

Kyle, Martin L., Paul A. Nelson, and Leslie Burris, Jr.

Corrosion of Steels and Tantalum by Molten Cadmium-Magnesium-Zinc Systems

Electrochem. Tech. 3, 258-262 (Sept.-Oct. 1965).

Larsen, R. F.

Determination of Burnup on EBR-II Fuel

Trans. Am. Nucl. Soc. 8(1), 8 (June 1965). Abstract.

Lawroski, S. et al.

Reactor Fuel Process. 7(4), (Fall 1964)*

Reactor Fuel Process. 8(1), (Winter 1964-1965)

Reactor Fuel Process. 8(2), (Spring 1965)

Reactor Fuel Process. 8(3), (Summer 1965)

Reactor Fuel Process. 8(4), (Fall 1965).

Levenson, M. and R. M. Adams

Administration of Nuclear Safety at Argonne National Laboratory

Nucl. Safety 7(1), 1-6 (Fall 1965).

Liimatainen, R. C., R. O. Ivins, and F. J. Testa

Metal-Water Reactions Initiated by a Short-Period Nuclear Reactor Excursion (Kiwi-TNT)

Trans. Am. Nucl. Soc. 8(1), 131-132 (1965). Abstract.

Liimatainen, R. C., R. O. Ivins, and F. J. Testa

Reaction of Uranium with Water in TREAT Meltdown Excursion

Trans. Am. Nucl. Soc. 8(1), 306 (1965). Abstract.

Ludlow, J. O., L. F. Coleman, R. F. Malecha, J. H. Schraidt, and

M. A. Slawewski

Inert Atmosphere Enclosure for Environmental Testing

Proc. 13th Conf. on Remote Systems Technology, Washington, D. C., 1965, American Nuclear Society, Hinsdale, Illinois, pp. 129-137.

Martin, A. E. and R. K. Edwards

The Uranium-Uranium Dioxide Phase Diagram at High Temperatures

J. Phys. Chem. 69, 1788 (1965). Note.

*Also listed in ANL-7020.

- Nelson, P. A., D. K. Butler, M. G. Chasanov, and D. Meneghetti
 Fuel Properties and Nuclear Performance of Fast Reactors Fueled
 with Molten Chlorides
 Trans. Am. Nucl. Soc. 8(1), 153-154 (1965). Abstract.
- Nelson, P. A., M. L. Kyle, G. A. Bennett, and L. Burris, Jr.
 Corrosion of Refractory Metals by Zinc-Magnesium-Uranium and
 Halide Salt Systems
 Electrochem. Tech. 3, 263-269 (Sept.-Oct. 1965).
- O'Hare, P. A. G. and W. N. Hubbard
 Fluorine Bomb Calorimetry. XIII. The Enthalpy of Formation of
 Arsenic Pentafluoride
 J. Phys. Chem. 69, 4358-4360 (1965).
- O'Hare, P. A. G., J. L. Settle, and Ward N. Hubbard
 The Enthalpies of Formation of the Hexafluorides of Sulfur, Selenium,
 and Tellurium
 Abstracts of Papers, 20th Annual Calorimetry Conference, held at
 Ames, Iowa, Aug. 11-13, 1965, paper 32.
- Porte, H. A., E. Greenberg, and W. N. Hubbard
 Fluorine Bomb Calorimetry. XII. The Enthalpy of Formation of
 Ruthenium Pentafluoride
 J. Phys. Chem. 69, 2308-2310 (July 1965).
- Ramaswami, D., N. M. Levitz, and A. A. Jonke
 Engineering Development of a Fluid-Bed Fluoride Volatility Process.
 I. Bench-Scale Studies
 Nucl. Appl. 1, 293-300 (August 1965).
- Rudzitis, E., H. M. Feder, and W. N. Hubbard
 Fluorine Bomb Calorimetry. XI. The Enthalpy of Formation of
 Yttrium Trifluoride
 J. Phys. Chem. 69, 2305-2307 (July 1965).
- Rudzitis, E., E. Van Deventer, H. M. Feder, and W. N. Hubbard
 The Enthalpies of Formation of Nickel Difluoride and Aluminum
 Trifluoride
 150th Am. Chem. Soc. Meeting, Atlantic City, Sept. 12-17, 1965.
 Abstracts of Papers, p. 59-V.
- Schnizlein, J. G., J. Brewer, and D. F. Fischer
 Temperature Transducer for Thermogravimetric Studies
 Rev. Sci. Instr. 36, 591-593 (1965).
- Shimotake, H. and J. C. Hesson
 Static and Dynamic Corrosion by Tin, Bismuth and Bismuth-Sodium
 Alloy up to 1000°C
 Trans. Am. Nucl. Soc. 8(2), 413 (1965), 1965 Winter Meeting,
 Nov. 15-18, 1965, Washington, D. C. Abstract.

- Smith, G. W. and D. M. Mongan
The Determination of Thorium in Cerium Matrices by Neutron Irradiation: Use of the Argonne Pneumatic Facility
Intern. J. Appl. Radiation Isotopes 16, 81-89 (1965).
- Smith, G. W., Dino J. Santelli, and Harold Fiess
The Neutron Activation Determination of Lithium in the Presence of Alkali Metals and Magnesium
Anal. Chim. Acta 33, 1 (1965).
- Stupegia, D. C., Marcia Schmidt, and A. A. Madson
Fast Neutron Capture in Rhenium
J. Nucl. Energy A/B (Reactor Sci. Technol.) 19, 767-773 (1965).
- Sympson, R. F., R. P. Larsen, R. J. Meyer, and R. D. Oldham
Amperometric Titration of Uranium(IV) with Iron(III)*
Anal. Chem. 37, 58-60 (January 1965).
- Traylor, E. D., Leslie Burris, and C. J. Geankoplis
Mass Transport from Uranium Sphere to Liquid Cadmium in Highly Turbulent Flow
Ind. Eng. Chem. Fundamentals 4(2), 119-125 (May 1965).
- VonAmmon, Reinhard, J. B. Knighton, and R. K. Steunenberg
Solubility of Uranium and Plutonium in Cadmium-Zinc-Magnesium Melts
Kerntechnik 7(8/9), 400-403 (August-September 1965).
- Wenz, D. A., J. B. Knighton, and R. K. Steunenberg
Liquid Metal-Molten Salt Processing of Fast Breeder Reactor Fuels
Am. Chem. Soc. Meeting, Atlantic City, Sept. 12-17, 1965.
Abstracts of Papers, p. 22-R.
- Wilson, R. E. and C. E. Barnes, Jr.
Metal-Steam Reactions at High Temperatures
Trans. Am. Nucl. Soc. 8(1), 306-307 (1965). Abstract.
- Wise, S. S., J. L. Margrave, H. M. Feder, and W. N. Hubbard
Fluorine Bomb Calorimetry. XVI. The Enthalpy of Formation of Boron Nitride
J. Phys. Chem. 70, 7-10 (1966).
- Wu, Y. C., M. B. Smith, and T. F. Young
Heats of Mixing of Electrolytes Having Common Ions**
J. Phys. Chem. 69, 1868-1872 (June 1965).
- Wu, Y. C., M. B. Smith, and T. F. Young
Heats of Mixing of Electrolytes of the 1-1 Charge Type**
J. Phys. Chem. 69, 1873-1876 (June 1965).

* Also listed in ANL-7020.

**Part of this work was performed at Argonne National Laboratory.

Ziegler, E. N. and J. T. Holmes

Mass Transfer from Fixed Surfaces to Gas Fluidized Beds

Chem. Eng. Sci. 21, 117-122 (1966).

B. Papers Accepted for Publication in the Open Literature

Baker, L., Jr.

Nonisothermal Reaction of Uranium with Water by the Condenser
Discharge Method

Accepted for publication in Nucl. Sci. Eng.

Baker, L., Jr. and R. C. Liimatainen

Chemical Reactions

Accepted for publication as Chapter 17, Vol. 2 of The Technology of
Nuclear Reactor Safety, MIT Press.

Crouthamel, Carl and H. Recht (editors)

Regenerative Galvanic Cells

Accepted for publication as an American Chemical Society monograph.

Dillon, I. G., P. A. Nelson, and B. S. Swanson

High Temperature-High Pressure Cell for Measuring Densities of
Metals by a Radiation Counting Technique

Accepted for publication in Rev. Sci. Instr.

Dillon, I. G., P. A. Nelson, and B. S. Swanson

Critical Temperatures and Densities of the Alkali Metals

Accepted for publication in Chem. Physics.

Foster, Melvin S.

Laboratory Studies of Intermetallic Cells

Accepted for publication as chapter in Regenerative Galvanic Cells,
monograph, American Chemical Society.

Foster, M. S. and C. C. Liu

Free Energy of Formation of Ji_2Te at 798°K by an Emf Method

Accepted for publication in J. Phys. Chem.

Gabor, J. D.

Fluidized-Packed Bed

Accepted for publication in the Chem. Eng. Progr. Symp. Ser.,
Volume on fluidization.

Gruen, D. M., R. L. McBeth, M. S. Foster, and C. E. Crouthamel

Absorption Spectra of Alkali Metal Tellurides and of Elemental
Tellurium in Molten Alkali Halides

Accepted for publication in J. Phys. Chem.

Hubbard, W. N.

Thermochemistry

Accepted for publication in Encyclopedia Britannica.

- Ivins, R. O., R. C. Liimatainen, and F. J. Testa
Reaction of Uranium with Water as Initiated by a Power Excursion in
a Nuclear Reactor (TREAT)
Accepted for publication in Nucl. Sci. Eng.
- Koppel, L. B., J. T. Holmes, and R. D. Patel
Statistical Models for Surface Renewal in Heat and Mass Transfer.
Part I. Dependence of Average Transport Coefficients on Age
Distribution
Accepted for publication in AIChE Journal.
- Koppel, L. B., J. T. Holmes, and R. D. Patel
Statistical Models for Surface Renewal in Heat and Mass Transfer.
Part II. Measurement of Age Distribution at Transport Surfaces
Accepted for publication in AIChE Journal.
- O'Hare, P. A. G., J. L. Settle, and W. N. Hubbard
Fluorine Bomb Calorimetry. Part 14. The Enthalpies of Formation
of the Hexafluorides of Sulfur, Selenium, and Tellurium and Their
Thermodynamic Properties to 1500°K
Accepted for publication in Trans. Faraday Soc.
- Schnizlein, J. G. and D. F. Fischer
The Kinetics of Oxidation of Plutonium Metal and a Plutonium-3.4 a/o
Aluminum Alloy at Temperatures from 140 to 550°C
Accepted for publication in J. Electrochem. Soc.
- Shimotake, Hiroshi and James C. Hesson
Corrosion by Fused Salts and Heavy Liquid Metals
Accepted for publication as chapter in Regenerative Galvanic Cells,
monograph, American Chemical Society.
- Steindler, M. J. and T. J. Gerding
The Absorption Spectrum of NpF_6
Accepted for publication in Spectrochim. Acta.
- Wilson, R. E., C. Barnes, Jr., R. Koonz, and L. Baker, Jr.
Isothermal Reaction of Uranium with Steam between 400 and 1600°C
Accepted for publication in Nucl. Sci. Eng.
- Wolkoff, J., D. A. Woodward, and A. J. Strecok
A Thermocouple for the Measurement of the Surface Temperature of
a Liquid Metal
Accepted for publication in Chem. Eng. Sci.

C. ANL Reports

- Ackermann, R. J., E. G. Rauh, and M. S. Chandrasekharaiah
A Thermodynamic Study of the Urania-Uranium System
ANL-7048.

- Anastasia, L. J., J. D. Gabor, and W. J. Mecham
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 3. Fluid-Bed Fluorination of Uranium Dioxide Fuel Pellets
ANL-6898.
- Baerns, Manfred G.
The Effect of Interparticle Forces on the Fluidization of Fine Particles
ANL-7086.
- Chilenskas, A. A. and G. E. Gunderson
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 7. The Corrosion of Nickel in Process Environments
ANL-6979.
- Dillon, I. G., Leslie Burris, and Milton Levenson
Fuel Management and Inventory in the EBR-II Fuel Cycle
ANL-6735.
- Dillon, I. G., P. A. Nelson, and B. S. Swanson
Critical Temperatures and Densities of the Alkali Metals
ANL-7025.
- Elder, J. P.
Electrode Kinetics
ANL-7072.
- Gabor, John D. and William J. Mecham
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 4. Fluidized-Packed Beds--Studies of Heat Transfer, Solids-Gas
Mixing, and Elutriation
ANL-6859.
- Hariharan, A. V., J. B. Knighton, and R. K. Steunenberg
Preparation of Metals by Magnesium-Zinc Reduction. Part II.
Reduction of Thorium Dioxide
ANL-7058.
- Holmes, John T., Howard Stethers, and John J. Barghusen
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 8. Pilot-Plant Development of a Process for Uranium Alloy Fuels
ANL-6973.
- Knighton, J. B. and R. K. Steunenberg
Preparation of Metals by Magnesium-Zinc Reduction. Part I. Reduc-
tion of Uranium Oxides
ANL-7057.
- Knighton, J. B. and R. K. Steunenberg
Preparation of Metals by Magnesium-Zinc Reduction. Part III. Reduc-
tion of Plutonium Dioxide
ANL-7059.

- Knighton, J. B., R. A. Mancini, and R. K. Steunenberg
Consolidation of Lanthanum Fission Products in Alloys
ANL-7064.
- Ramaswami, D., N. M. Levitz, and A. A. Jonke
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 2. Bench-scale Investigation of a Process for Aluminum-Uranium
Alloy and Stainless Steel-Cermet Fuels
ANL-6830.
- Trevorrow, L. E., R. W. Kessie, and M. J. Steindler
Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility
Processes. Part VIII. Analysis of an Accidental Multigram Release
of Plutonium Hexafluoride in a Glovebox
ANL-7068.
- Vogel, G. J., E. L. Carls, and W. J. Mechem
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 5. Description of a Pilot-Scale Facility for Uranium Dioxide-
Plutonium Dioxide Processing Studies
ANL-6901.
- Vogel, R. C., M. Levenson, and F. R. Masten
Chemical Engineering Division Semiannual Report, July-December,
1964
ANL-6925.
- Vogel, R. C., M. Levenson, and F. R. Masten
Chemical Engineering Division Research Highlights, May 1964-
April 1965
ANL-7020.
- Vogel, R. C., M. Levenson, and F. R. Masten
Chemical Engineering Division Semiannual Report, January-June 1965
ANL-7055.
- Wagner, R. P., W. A. Shinn, Jack Fischer, and M. J. Steindler
Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility
Processes. Part VII. The Decomposition of Gaseous Plutonium
Hexafluoride by Alpha Radiation
ANL-7013.
- Winsch, I. O., K. R. Tobias, R. D. Pierce, and L. Burris, Jr.
Sampling of Liquid Metals
ANL-7088.

D. Papers Presented at Scientific Meetings

- Baker, L., Jr.
Use of Zirconium Cladding on Nuclear Fuel
Presented at the AEC Symposium, Washington, D. C., April 1965.

Burris, L.

Pyrochemical Processes for Nuclear Reactor Fuels

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

Cafasso, Fred A.

Thermodynamic Properties of Sodium-Potassium Solutions--A Study in Atomic Absorption Spectrophotometry

Presented at Temple University, Philadelphia, Pa., May 6, 1965.

Dillon, I. G., P. A. Nelson, and B. S. Swanson

Determination of the Critical Temperatures of Alkali Metals by a Radioactive Counting Technique

Presented at the Symposium on Thermodynamics of Liquid Metal Systems, Am. Inst. Chem. Engr. 56th Annual Meeting, San Francisco, Calif., May 16-19, 1965.

Edwards, R. K. and A. E. Martin

Phase Relations in the Uranium-Uranium Dioxide System at High Temperatures

Presented at Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids, July 22-27, 1965, IAEA, Vienna, Austria, Paper SM-66/81.

Foster, M. S.

Solutions of Intermetallic Compounds in Molten Salts

Presented at Gordon Research Conference on Fused Salts, Meriden, N. H., August 30-September 3, 1965.

Gabor, J. D.

Axial Solids Mixing in Fluidized-Packed Beds

Presented at the Fifty-Eighth National Meeting of the American Institute of Chemical Engineers, Feb. 6-9, 1966, Dallas, Texas, Preprint 16 D.

Greenberg, Elliott

Fluorine Bomb Calorimetry

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

Holmes, J. T.

Applications of Fluid-Bed Fluoride Volatility Processing to Highly Enriched Uranium Alloy Fuels

Presented at Chemical Technology Division, ORNL, March 16, 1965.

Hubbard, W. N.

Fluorine Bomb Calorimetry

Presented at the Symposium on Thermodynamics and Thermochemistry during the Western Regional Meeting of the American Chemical Society, Los Angeles, California, November 18-20, 1965.

Abstract published in SCALACS (bulletin of Southern California Los Angeles Chemical Society), November 1965, p. 22.

Hubbard, W. N.

Summary of Recent Thermochemical Studies

Presented at the Fourth Meeting of the Working Group on Thermochemistry, Chemical Propulsion Information Agency, March 16-18, 1966, Kennedy Space Center, Florida.

Jonke, A. A., M. J. Steindler, and N. M. Levitz

Development of Fluoride Volatility Reprocessing Methods for Plutonium-Containing Fuels

Presented at the AIChE meeting, San Francisco, Calif., May 1965.

Kelman, L. R., H. V. Rhude, J. G. Schnizlein, and H. Savage

Metallic Plutonium Alloys for Fast Critical Experiments

Presented at the Third International Conference on Plutonium, London, November 22-26, 1965.

Knighton, J. B.

The Reduction of Uranium, Thorium, and Plutonium Oxides

Presented at Dow Chemical Co., Rocky Flats, February 4, 1965.

Levenson, M.

General Fuel Cycle Considerations for Advanced Systems

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

Levenson, M.

Long Range Objectives of Fuel Cycles

Engineering Aspects of Nuclear Fuel Reprocessing--Aqueous, Fluoride Volatility, and Pyrochemical Methods

Waste Disposal and Its Relation to Reprocessing

Presented at the Atom Forum, Utrecht, Netherlands, March 11-15, 1966.

Liimatainen, R. C.

Studies in Nuclear Reactor Safety

Presented at Oak Ridge National Laboratory, Oak Ridge, Tenn., May 18, 1965.

Liimatainen, R. C.

Some Aspects of Education and Atomic Energy in Finland*

Presented at Suomi College, Hancock, Mich., March 17, 1965.

Petkus, Edward J., Arthur D. Tevebaugh, Charles C. Payne, and Joseph P. Bartos

The Synthesis of Stoichiometric Uranium Monocarbide in a Fluidized-Bed by the Uranium Metal-Hydrocarbon Gas Reaction

Presented at the Symposium on Fundamental and Applied Fluidization, Part II, held by the American Institute of Chemical Engineers at Dallas, Texas, February 6-9, 1966.

Pierce, R. D.

Engineering Demonstration of Pyrometallurgical Processes

Presented at Dow Chemical Co., Rocky Flats, February 4, 1965.

*Also listed in ANL-7020.

Pierce, R. D.

Recent Developments in Liquid Metal-Fused Salt Processes at ANL
Presented at Institute for Atomic Research, Ames, Iowa, May 13,
1965.

Plambeck, J. A.

Voltammetry of the LiH Cell
Presented at the University of Maryland, Baltimore, Maryland,
March 1965.

Schraidt, J.

Design Philosophy of Pyrometallurgical Equipment
Presented at Oak Ridge National Laboratory, Oak Ridge, Tenn.,
January 1965.

Steunenberg, R. K.

Pyrometallurgical Processing of Uranium-Plutonium Fuel Alloy*
Presented at Chemical Technology Division, ORNL, Feb. 16, 1965.

Swift, David L. and Louis Baker, Jr.

Experimental Studies of the High Temperature Interaction of Fuel
and Cladding Materials with Liquid Sodium
Presented at the Conf. on Safety, Fuels, and Core Design in Large
Fast Power Reactors, Argonne National Laboratory, Oct. 11-14, 1965.

Tevebaugh, A. D., L. Baker, and D. Swift

Explosive Heat Transfer at Liquid-Liquid Interfaces
Presented at Symposium on Molecular Processes in Chem. Eng.,
University of Rochester, Rochester, New York, January 19, 1966.

Tevebaugh, A. D., C. E. Crouthamel, and J. Hesson

Thermally Regenerative Emf Cells
Presented at Washington University, St. Louis, Missouri, October 28,
1965.

Wood, S. E.

Alkali Metal Halide-Hydride Phase Diagrams
Presented at Gordon Research Conference on Fused Salts, Meriden,
N.H., August 30-September 3, 1965.

Young, T. F.

Thermodynamics and Structures of Electrolytic Solutions
Presented at the First Conference on Biology of Hard Tissue
Sponsored by Interdisciplinary Communications Program of the
New York Academy of Sciences, Princeton, New Jersey, June 20-23,
1965.

*Also listed in ANL-7020.