ANL-7902

Chemical Separations Processes
for Plutonium and Uranium

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CHEMICAL ENGINEERING DIVISION
FUEL CYCLE TECHNOLOGY QUARTERLY REPORT
October, November, December 1971

by

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February 1972

Previous reports in this series

ANL-7767, October, November, December 1970
ANL-7799, January, February, March 1971
ANL-7841, April, May, June 1971
ANL-7871, July, August, September 1971

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ABSTRACT

During the period October through December 1971, work was done in the following areas: (1) experiments to determine proper operating conditions and equipment design for a simplified zinc-decladding process to prepare long-cooled $\text{UO}_2\text{-PuO}_2$ for aqueous processing and additional experiments to study the decladding-reduction procedure with unirradiated UO_2 pellets and an intact irradiated fuel element, (2) three runs with uranyl nitrate solution and two initial runs with mixed U/Pu solutions in the pilot-scale reactor for production of $\text{UO}_2\text{-PuO}_2$ by denitration of uranyl nitrate and plutonium nitrate in nitric acid, (3) further study of the effects of bulk density and particle size on X-ray fluorescence signals in determining Pu/U ratios for oxide fuels in the form of green pellets and sintered pellets, (4) continued investigation of the effects of operating conditions on the separating capacity of a centrifugal contactor (for plutonium isolation steps in solvent extraction) when operated with a mixing chamber and in the annular mixing mode, and (5) design and construction of an electrolytic cell for the reduction of plutonium (IV) in nitric acid.

SUMMARY

Liquid Metal Decladding of Reactor Fuels

Head-end zinc-decladding of LMFBR fuel is being investigated as a method for preparing uranium and plutonium for subsequent processing in an aqueous-solvent extraction plant. Stainless steel components of the fuel assembly (the cladding, shroud, and end fittings) are dissolved in zinc at 850°C , and the resulting zinc-stainless steel solution is removed from the fuel pellets. The pellets are reduced with a Zn-Mg-Ca alloy in the presence of liquid CaCl_2 salt at 850°C . The uranium and plutonium dissolve in the liquid metal; another product of the reduction reaction is CaO , which dissolves in the molten salt. The final step of the head-end process after separation of the salt from the liquid metal is recovery of the plutonium and uranium from the liquid metal solution, possibly by retorting. The uranium-plutonium product may then be dissolved in nitric acid for subsequent aqueous solvent extraction processing. This head-end process releases iodine and noble-gas fission products from the fuel. Iodine, which is released upon reduction of the fuel pellets, is trapped in the waste CaCl_2 salt. Xenon and krypton are contained in the small volume of the processing furnace atmosphere.

Engineering Development of Zinc Decladding

Zinc Decladding. One of the uses of zinc decladding is in a single process step (without reduction) to prepare long-cooled (250-day) $\text{UO}_2\text{-PuO}_2$ fuel from early breeder reactors, such as FFTF, for aqueous processing. Eleven zinc-decladding experiments were carried out to determine operating conditions and to evaluate a design concept of a plant-scale decladder for long-cooled fuel. The decladder would replace the equipment required for sodium cleaning, some fuel-disassembly operations, shearing, and voloxidation. A tilt-pour furnace containing a graphite crucible was used to study the process on a laboratory scale.

Experimental results show that the cladding can be removed in 1-2 hr. After disintegration of the fuel assembly, mild agitation is required to achieve a relatively uniform melt. The zinc-stainless steel solution is then poured away from the oxide pellets, and the pellets are recovered from the graphite crucible. The crucible, containing a small heel, is recycled to the next decladding run. Experience acquired in these and other experiments indicates that a full-scale decladder of this type might be designed and built at the present time. A conceptual design of the decladder is presented.

Reference Flowsheet Experiments. A flowsheet for the head-end processing of short-cooled LMFBR fuel was presented in the preceding report (ANL-7871, p. 14). A small-scale experiment largely conforming to this flowsheet was carried out. No plutonium or fission products were present, and the scale of the experiment was one thousandth that shown on the flowsheet. After zinc-decladding 400 g of UO_2 pellets contained in 238 g of stainless steel tubing, the separated UO_2 and the salt-metal heel were washed with zinc, the UO_2 was reduced to metal in a liquid salt-metal system, and MgCl_2 was added to the reduction alloy to oxidize unreacted calcium metal. Distillation steps were omitted. The overall material balance accounted for all but 50 g (0.5%) of a total of 10.64 kg of salt and metal charged. Only 0.14% of the uranium was not accounted for in the decladding and wash steps.

Process Demonstration Experiments

An experiment with an irradiated stainless steel-clad $\text{UO}_2\text{-20 wt } \%$ PuO_2 fuel element was completed. The fuel element had been irradiated in EBR-II to a burnup of 3.62% and had cooled about 3.1 yr. In this experiment, the processing steps were essentially the same as those outlined at the beginning of this section. The stainless steel cladding of the fuel element was dissolved in zinc, and the oxide fuel pellets were reduced to metal in a liquid metal-salt system. In the decladding step of the experiment, 0.7% of the cerium, 0.77% of the ruthenium, and 6% of the antimony in the fuel were dissolved in the zinc decladding solution, and between one-third and one-half of the cesium was dissolved in the salt phase. About 20% of the fission gases were released during the decladding step. In the reduction step, essentially all of the plutonium was reduced, and the plutonium dissolved in the metal alloy after 330 min of agitation. This experiment was the first demonstration of the pyrochemical head-end process for LMFBR fuel with an intact irradiated fuel element.

Continuous Conversion of U/Pu Nitrates to Oxides

Studies are continuing on a fluidized-bed process for conversion of uranyl nitrate-plutonium nitrate solutions to homogeneous oxide powder suitable for LMFBR fuel fabrication. In successive steps, the mixed nitrate solutions are denitrated to $\text{UO}_3\text{-PuO}_2$ powder, and the $\text{UO}_3\text{-PuO}_2$ is reduced with hydrogen to yield $\text{UO}_2\text{-PuO}_2$ powder, the required material for fuel manufacture. An integrated program of laboratory and engineering studies is in progress. Current emphasis is on the denitration step, using pilot-scale equipment installed in a 3- by 4-module glovebox.

During the report period, the three final denitration runs in the current series with uranyl nitrate hexahydrate (UNH) solution were performed. Nominal operating conditions were denitration temperature, 300°C ; feed solution composition, 1.9M UNH in ~1M or 3.0M nitric acid; feed rate, ~90 ml/min; and fluidizing-gas rate, 1.0 ft/sec. The higher acid concentration was tested in a single run because it is the current upper limit for the forthcoming work with concentrated (~2.0M) U + Pu solutions. In these three runs, a modified startup procedure was tested satisfactorily. Reproducibility of denitrator operation was shown, and no product particle size effects were observed--i.e., no growth or diminution trends of size distribution for bed particles. About 13 kg of free-flowing UO_3 (about 1.5 bed equivalents) was produced in each 5.5-hr run.

Approval for an inventory in the pilot plant of 7 kg plutonium has been received after a lengthy period of preparation of safety and criticality hazards analysis reports and review by ANL and AEC safety committees. Pilot plant denitration studies are in progress, using an initial inventory of about 500 g of plutonium, which is sufficient for the preparation of $\text{UO}_3\text{-3 wt % PuO}_2$ material.

Two denitration runs with uranyl nitrate-plutonium nitrate feed solutions were terminated prematurely after about 2.5- and 2-hr periods. A tendency to bed agglomeration was evident, although the operating conditions used had been found satisfactory in runs with UNH solution. Although physical property data indicate that the temperatures of denitration for uranyl nitrate hexahydrate and plutonium nitrate are similar, ~250 and 220°C , respectively, these initial results in the fluidized-bed denitrator indicate a need to explore the effects of denitration parameters for U/Pu nitrate systems.

In-Line Analysis in Fuel Fabrication

The evaluation of X-ray fluorescence (XRF) as a potential on-line analytical method for determining plutonium and uranium content of $\text{UO}_2\text{-PuO}_2$ fuels has continued, using $\text{ThO}_2\text{-UO}_2$ mixtures as a stand-in. The following conclusions pertain to work during the past few quarters on the effects of variables on XRF analyses of powder and green pellets.

1. For mixed powder, heterogeneity and particle size effects have prevented demonstration of a relative standard deviation of 0.5% for XRF analysis. Earlier experiments suggest about 3% variability for analyses of powder samples of $\text{ThO}_2\text{-30 wt % UO}_2$ mixture. This 3% variability may be

largely due to mixing and sampling errors and to the unusual particle size distribution of the thorium used. This variability could probably be reduced by better mixing, control of particle size distribution, and control of the density of the examined surface. Control of these variables by a fabricator may be difficult. Application of XRF analysis to coprecipitated or homogeneous powder has not yet been explored, but should offer no problems.

2. For green pellets, the effect of density on XRF analysis is being evaluated for mixed oxides. Apparently, the particle size effect observed for powder can be largely eliminated by forming the oxide into green pellets. The effect of pellet density (or a surface effect) is now considered the primary variable governing the demonstrable precision. The effect of the $\pm 1\%$ allowable variation of pellet density (FFTF specification) on the precision of the plutonium analysis must be evaluated. At present, the relative standard deviation (RSD) caused by 1% density variation is estimated to be $\sim 0.3\%$. To attain a relative precision of 0.5%, careful control of green pellet density may be necessary.

3. X-ray fluorescence has an outstanding potential for general application as an on-line analytical method because of its speed and precision. A signal can be generated in standard equipment that is adequate to achieve a relative precision of 0.5% at 95% confidence limits within the limitations of counting statistics and with an analysis time per sample of 30 to 300 sec. Use of the XRF method assumes that the surface (to a depth of less than 100 μm) is representative of the entire pellet.

Adaptation of Centrifugal Contactors in LMFBR Fuel Processing

The performance characteristics of the long-rotor centrifugal contactor continue to be investigated. The unit, which has a 4-in.-ID separating rotor with a 12-in.-long settling zone, is being used to evaluate centrifugal contactors having critically favorable dimensions. Contactors of this type are being considered for use in plutonium partitioning and isolation steps in the Purex-type solvent extraction processing of LMFBR fuel material containing high concentrations of plutonium.

Tests have been completed to measure separating capacities at rotor speeds between 2000 and 3500 rpm. The aqueous phase consisted of 0.5M HNO_3 ; the organic phase consisted of 15 or 30% tri-n-butyl phosphate (TBP) with n-dodecane diluent. Results of these tests were substantially the same as those found in previous tests made with Ultrasene (refined kerosene) as the TBP diluent and are consistent with predictions based on evaluation of performance of other centrifugal contactors.

For all rotor speeds, minimum separating capacities were found at aqueous-to-organic (A/O) flow ratios near 1 or 2. These ranged from 5 gpm at 2000 rpm to 9 gpm at 3500 rpm. Highest capacities were found at A/O ratios of 3 or 4 and ranged from 9 gpm at 2000 rpm to 17 gpm at 3500 rpm. As was true in the tests with Ultrasene diluent, capacities at A/O ratios below 0.4 or 0.3 were lower than at A/O ratios above 2 and their patterns of variation with rotor speed were not quite as consistent as at the higher A/O ratios. This is attributed mainly to the kinds of emulsions formed at these low A/O ratios.

Flow surging was essentially eliminated by achieving a suitable compromise between mixing intensity and pumping capacity of the mixing section of the contactor.

Analysis of the hydraulic performance of the rotor indicated that pumping capacity is limited by the length-to-diameter (L/D) ratio. For contactors of this type, the maximum practical L/D ratio apparently is $\sqrt{4}$.

Preliminary tests were made with the contactor operating in the annular mixing mode. Results are promising, and the equipment is being modified to improve performance.

Electrolytic Reduction and Reoxidation of Plutonium in Purex Processes

Electrolytic reduction of plutonium is being developed as a substitute for chemical reductants in the Purex process. Earlier, an equation linking the electrolytic reduction rate to various process parameters was developed; the values of two constants, m and A , for this equation were determined from data obtained in current density experiments with a ferrocyanide-ferricyanide electrolyte.

A new electrolytic cell has been designed and built for electrolytic reduction of plutonium (IV) in nitric acid. The initial and final plutonium (IV) concentrations (determined analytically) will be compared with concentrations computed with the aforementioned equation. Good agreement will prove the validity of the equation.

I. LIQUID METAL DECLADDING OF REACTOR FUELS (W. E. Miller)

A. Engineering Development of Zinc Decladding

A head-end procedure utilizing liquid zinc solvent is being developed for processing fast breeder reactor fuel assemblies. Zinc solvent dissolves the stainless steel cladding and other structural parts of the assembly. An overlying salt layer on the zinc reduces vaporization of zinc and traps any iodine present. The resulting zinc-stainless steel solution is poured or pressure-siphoned out of the decladding vessel. The fuel oxide, which remains in the vessel, may in the case of long-cooled fuel be poured out of the decladding vessel and transported directly to an acid dissolver or may in the case of short-cooled fuel be reduced to metal by adding a Zn-Mg-Ca alloy and more salt to the vessel and agitating the melt and oxide at $>800^{\circ}\text{C}$. In the reduction step, the oxide lattice is destroyed, volatile and gaseous fission products escape from the uranium-plutonium, and uranium and plutonium metal dissolve in the reduction alloy. After reduction, the liquid salt which contains fission product iodine and calcium oxide is removed (the metal and salt phases are immiscible), and uranium-plutonium is recovered from the liquid metal solvent and charged to an acid dissolver for further processing by aqueous methods.

1. Zinc Decladding (G. J. Bernstein, J. Lenc)

Investigations are being made to evaluate the feasibility of using a simplified zinc-decladding process to prepare LMFBR fuel for aqueous processing. This process might be applied to long-cooled $\text{UO}_2\text{-PuO}_2$ fuel from early breeder operations such as FFTF. Because long-cooled fuel is being processed, no provision need be made for a high fission-product heat output or a high ^{131}I content.

Eleven experiments were carried out to determine proper operating conditions and to provide the basis for design of plant-scale equipment. Melting was done in a graphite crucible inside a tilt-pour furnace. The experimental procedure for the decladding process, which omits the reduction step, is described below. About 1 kg of high-fired UO_2 (whole and fragmented pellets), 6.2 kg of zinc, and sufficient Type 304 stainless steel tubing to give zinc containing 8 wt % SS were loaded into a 5-in.-dia graphite crucible equipped with a 2 1/2-in.-dia impeller. (No overlying salt layer was included in this simplified procedure.) The charge was heated at 860°C for 1 hr to disintegrate the stainless steel solid, and then the melt was agitated at 500 rpm for 1 hr. Agitation was stopped, the melt settled for 15 min, and then the bulk of the melt was poured slowly at 860°C by tilting the crucible so that its cylindrical axis was 2° beyond horizontal. The pour was made through a 20-mesh tungsten screen placed over the receiving vessel. (The oxide and screen would be recycled to the next decladding run. A mild steel screen also was found to be satisfactory.) The crucible was then returned to the vertical position and cooled to room temperature. After the zinc-containing receiver in the sidearm was replaced with a second vessel, the furnace was tilted 45° beyond horizontal to dump the oxide pellets from the crucible into the second receiver. In a production process, the oxide would next be charged to an acid dissolver.

It was demonstrated that 5 to 10 percent of the oxide charge will pour with the zinc-stainless steel liquid and that 90-95% of the oxide charge will dump out of the crucible in the cold pour. After the two pours have been made, very little SS-zinc residue remains in the crucible, and less than one percent of the oxide charge is trapped in the unpoured heel. The oxide in the heel is not lost but becomes part of the feed material for the next decladding cycle.

The conclusions reached as a result of this series of experiments are as follows: (1) The stainless steel cladding and shroud can be removed from oxide fuel at temperatures between 800 and 860°C, to give stainless steel concentrations in the melt as high as ~8 wt %. (2) Slight agitation of the melt is needed to rapidly complete the dissolution. (3) Zinc vaporization can be held to acceptable levels if (a) the temperature is below 890°C, (b) the time at temperature is less than 4 hr, (c) an insulated heat shield covers the crucible, and (d) pressure of the furnace inert atmosphere is held at ~15 psig. (4) Extended settling times do not prevent pouring some oxide particles with the hot zinc-stainless steel melt; however, this oxide is retained on a 20-mesh screen placed either on the crucible lip or over the receiving vessel. (5) It is not necessary to remelt the zinc-stainless steel residue remaining in the crucible after the bulk of the zinc-stainless steel has been poured in order to recover more than 90% of the UO_2 charged to the crucible. (The UO_2 not dumped would be recycled.) (6) A remotely operable system can be designed to recover fuel oxide from stainless steel-clad fuel assemblies in a form suitable for charging to an aqueous dissolver.

Conceptual design of a tilt-pour furnace suitable for zinc decladding of long-cooled FFTF fuel is shown on Fig. I-1. The procedure for decladding the reactor fuel assembly using the tilt-pour furnace is essentially the same as that described above for the experimental work. In the decladder, an FFTF core section (containing ~40 kg $\text{UO}_2\text{-PuO}_2$ and ~22 kg stainless steel) is declad with about 250 kg of zinc in a 1 1/2-ft-dia graphite crucible.

2. Reference Flowsheet Experiments (I. O. Winsch, T. F. Cannon, J. J. Stockbar)

An experiment following the flowsheet for the liquid-zinc head-end process (ANL-7871, Fig. I-1, p. 14) was carried out. The steps in the flowsheet were described in that report. The details of the experiment (DRAFS-2) are given below. In this experiment, no plutonium or fission products were present, and the scale of the experiment was approximately one thousandth that shown in the flowsheet. Distillation (concentration) steps shown in the flowsheet were not performed.

In the experiment, 400 g of UO_2 pellets contained in 239 g of stainless steel tubing was declad in zinc; the separated UO_2 and the salt-metal heel were washed with zinc; the UO_2 was reduced to metal in a liquid salt-metal system (Zn-Mg-Ca/CaCl_2), MgCl_2 was then added to the salt to oxidize unreacted calcium metal and increase the solubility of the metallic uranium in the alloy.

Figure I-2 is a diagram showing compositions and quantities for feed and exit streams of each step of run DRAFS-2. In the zinc decladding

Fig. I-1. Tilt-Pour Zinc Decladding Furnace

Fig. I-2. Laboratory-Scale Decladding-Reduction Run DRAFS-2

step and the subsequent wash with zinc, the total uranium loss was only 0.14%. Analytical results of samples taken after 1 hr and 5 hr of reduction show that 63.5 and 63% of the uranium was dissolved in the reduction alloy at these times of sampling. The remainder of the uranium was not in solution since its solubility in the calcium-rich zinc was exceeded. Calcium analysis of the reduction alloy after the 5-hr reduction period showed that the calcium concentration was 5.18% (67.2% of the calcium originally charged). The amount of the calcium expended in the reduction step was 56% of the quantity theoretically required for complete reduction of the UO_2 . This indicates that magnesium was also a reducing agent for the oxide.

After the calcium oxidation step in which $MgCl_2$ was added, the calcium concentration in the alloy dropped to 1.86 wt % and the uranium metal concentration in the alloy increased to 12.5 wt % (94.5% of the uranium charged). It is not known at present whether more time is needed for reduction or whether a lower calcium concentration is required in order to dissolve 100% of the uranium charged. Only 0.07% of the uranium charged was in the salt phase at the completion of the experiment. A total of only 50 g of salt and metal was unaccounted for out of a total of 10.64 kg of salt and metal used in the experiment.

3. Process Component Development--Crucibles (I. O. Winsch, T. F. Cannon)

A review of processing steps in the pyrochemical head-end process has indicated that crucibles 2 ft dia by 14 ft high or 3 ft dia by 6 ft high will be needed for decladding and reduction steps in the large-scale processing of LMFBR fuel. The possibility of fabricating tungsten vessels of the required size was discussed with representatives of Metallwerk Plansee. A 2-ft-dia vessel is the largest that can be fabricated by shear-forming. In addition, it would be necessary to build the 2-ft-dia tungsten crucible of cylindrical sections to provide the needed height for containing the LMFBR fuel elements. It was suggested that for larger-diameter crucibles, sections could be riveted together after which the interior of the crucible would be plasma-sprayed with tungsten to prevent seepage of liquid metal.

An alternative method suggested by Ultramet for preparing crucibles of the required size consists of vapor-depositing tungsten on cylindrical sections (2-ft dia) of SiC. The sections would be clamped together, and tungsten would be vapor-deposited over the joints. In both Metallwerk Plansee's and Ultramet's proposals, a secondary vessel would be required to support the tungsten crucible. A 5 3/4-in.-dia by 14-in.-high SiC crucible with vapor-deposited tungsten on its inside surfaces is on order from Ultramet.

Initial conversations with representatives of Norton Co. indicate some possibility that a 3-ft-dia SiC-base crucible can be fabricated in one piece for subsequent tungsten vapor deposition.

Los Alamos has used graphite crucibles on which NbC vapor was deposited to contain molten uranium-plutonium alloys in the Rover program. The possibility of using this type of crucible for the decladding and reduction steps is being investigated.

Fabricators of high-density MgO crucibles (that would be used for the containment of the Mg-Zn-U-Pu alloy in a retorting step) are being contacted. Dow-Rocky Flats reports that an oxidized tantalum crucible having a wall thickness of 90 mils is being used to retort a Mg-Zn-Ca-Pu alloy/ CaCl_2 salt for recovery of plutonium in metal buttons.

B. Process Demonstration Experiment (Irradiated Fuel)
(T. R. Johnson, W. A. Murphy, J. E. Kincinas, R. W. Clark, J. J. Stockbar)

The first experiment (CAV-9) demonstrating the ANL pyrochemical head-end process with an intact irradiated fuel element was completed in the shielded cave. The stainless steel cladding of the irradiated fuel element was dissolved in zinc, and after the oxide fuel pellets were separated from the zinc, they were reduced in a liquid metal-salt system. Sufficient analytical results are available to allow presentation of partial results. In addition to demonstration of the process with irradiated fuel, the purposes of the experiment were to confirm the behavior of the major classes of fission products and to reveal any unanticipated problems with the chemistry of the process.

The fuel element* used in the experiment had been irradiated in EBR-II to a burnup of 3.62% at a peak linear power of 13.2 kW/ft, and it had been cooled for 3.1 yr. Before irradiation, it contained (1) 37 g of natural UO_2 and (2) 80 g of mixed oxide that had an average composition of UO_2 -19.5 wt % PuO_2 ; the uranium in the mixed oxide was 91.8% enriched. The cladding was Type 316L stainless steel with an OD of 0.252 in., an ID of 0.221 in., and a length of about 35 1/2 in. The weight of the cladding, spacers, springs, and end fittings totaled about 62 g.

Because of the long cooling time, the only significant and detectable fission product activities were ^{85}Kr , ^{90}Sr , ^{106}Ru , ^{125}Sb , ^{137}Cs , ^{144}Ce , and ^{155}Eu . In addition, significant amounts of ^{54}Mn and ^{60}Co (cladding activation products) were found. From the behavior of these isotopes, the behavior in the pyrochemical process of most of the fission product elements and the elements from the steel cladding can be inferred.

1. Experimental Procedure

The furnace tube assembly used for the demonstration experiment is shown in Fig. I-3. It was heated in a resistance furnace mounted on a portable table and located in the Senior Cave Facility. The helium atmosphere of the furnace tube was circulated by a diaphragm pump through a gas manifold which was located outside the shielded cave. The gas first flowed through glass wool and silver wool filters in the off-gas port of the furnace tube to remove particulate material. The gas was next pumped through a heated CuO bed to convert tritium to water and then through a cooled bed of Molecular Sieves to remove condensable gases before the gas was returned

* The fuel element was prepared by Nuclear Materials and Equipment Corporation and was designated A-7. The preparation, irradiation, and post-irradiation nondestructive examinations have been described in NUMEC-3524 reports, e.g., NUMEC-3524-74, "Fabrication of 20 w/o PuO_2 - UO_2 Fast Breeder Fuels for Irradiation Testing in EBR-II" (June 1970).

Fig. I-3. Furnace Tube Used in Decladding Experiment with Irradiated Fuel

to the furnace tube. By analysis of the filter material and Molecular Sieves, the release of condensible fission gases could be measured.

To start the decladding step, the zinc and salt contained in the alumina crucible were melted under the helium atmosphere with the basket raised above the melt. When the melt temperature reached 800°C, the fuel and basket were immersed about 1 3/4 in. deep into the zinc. The fuel element was lowered periodically as the lower section of cladding dissolved. When sufficient cladding dissolved to ensure that the entire oxide fuel column had been exposed, the basket, containing the pellets and the remaining section of cladding, was raised out of the melt and the zinc was allowed to drain out of the basket. After the final salt and metal samples had been taken, the furnace was cooled, ending the decladding step.

In preparation for the pellet reduction step, a new tantalum crucible and stainless steel secondary containing a 2740 g reduction alloy ingot and 1060 g of salt was placed in the furnace tube. Next, the upper charging port, which contained the pellet-bearing basket, was installed. The basket was held in an inverted position by means of a rod attached to the bottom of the basket. (A tantalum rod previously attached to the top of the basket had been cut off, and a magnesium plug had been forced into the open top of the basket to prevent the loss of loose particles while the basket was inverted.)

With the basket raised in the charging port, the metal and salt were heated, and when the melt temperature reached 800°C, the basket was lowered into the melt to release the oxide fuel pellets. After 30 min, the basket was raised out of the melt and the melt was stirred at 900 rpm to reduce the oxide pellets and dissolve the uranium and plutonium. After 330 min of agitation, heating of the furnace was stopped, and the metal and salt were allowed to freeze in the tantalum crucible. During the decladding and reduction steps, filtered samples of the liquid metal phase and unfiltered samples of the molten salt phase had been obtained in tantalum tubes.

2. Experimental Results

About 0.05 g of plutonium (which is less than 0.4% of the plutonium in the fuel element) and about 0.14 g of uranium (0.16% of that in the fuel element) were found in the decladding melt after the basket had been removed. The amount of plutonium dissolved in the metal phase during the reduction step is shown in Fig. I-4, along with the plutonium reduction history for an experiment with unirradiated pellets containing UO_2 , PuO_2 , and inactive fission product elements (ANL-7871, pp. 16-19).

At the end of the reduction, 97% of the plutonium in the irradiated fuel element was dissolved in the metal alloy. It was judged that the plutonium oxide charged to the reduction alloy had been completely reduced. The 3% of the plutonium not found in solution was mostly in the basket. (No basket would be used in a plant process and hence this source of loss would not be present.)

The quantities of fission products present in the fuel element were calculated from the given burnup, the known fission yields of ^{235}U and ^{239}Pu , the time in the reactor, the cooling time, and the disintegration

Fig. I-4. Reduction of UO_2 -20% PuO_2 Pellets

System: Metal - Zn-26 at. % Mg-6.7 at. % Ca (~2700 g)
 Salt - CaCl_2 -10 mol % CaF_2 (~1000 g)

Crucible: Tantalum - 5.2 in. dia, 3 baffles

Agitator: Mo-30% W, 2 blades, 45° (pushing down)
 Dia: 2.5 in.; Height: 0.75 in.
 Speed: 850-900 rpm

Oxide Pellets: Run CAV-8 - Dia: 0.25 in.; Ht: 0.25 in.
 100 g - Unirrad. - 8.3% Fissia

Run CAV-9 - Dia: 0.22 in.; Ht: 0.25 in.
 70 g - Irrad. UO_2 - PuO_2 - 3.62% burnup
 37 g - Irrad. Nat. UO_2

rates of the fission-product isotopes. The proportion of the fissions occurring in ^{235}U or ^{239}Pu was assumed to be equal to the ratio of the numbers of ^{235}U or ^{239}Pu atoms to the total number of fissionable atoms.

The amounts of the detectable fission products in a sample were obtained by measuring the gamma activities in the sample (determined by gamma spectroscopy), using an aliquot of the solution of the total sample. Absolute disintegration rates in the samples were calculated from the count rates of identifiable gamma peaks, corrected for known geometry and efficiency factors.

The behavior of the fission products was generally as predicted. During the decladding step, the only fission product activity found in the salt phase was ^{137}Cs , and it constituted one third of the total cesium in the fuel element. The large fraction of the cesium extracted into the decladding salt is related to its mobility during irradiation. Gamma scans of the fuel element, made soon after its removal from the reactor, showed that cesium had concentrated strongly at the outer, cooler regions of the fuel element during irradiation.¹

Only small quantities of other fission products were leached from the oxide pellets by the zinc decladding alloy--6% of the antimony, 0.7% of the cerium and 0.77% of the ruthenium. In a plant-scale process, the amount of fission products removed from fuel in the decladding step undoubtedly will vary, depending on the degree of fragmentation of the fuel pellets, irradiation temperature, and linear heat rating of the fuel element. The amounts of the individual noble metals removed should be expected to differ because the individual elements migrate differently during irradiation.

Cobalt from the cladding was found only in the metal phase of the decladding step. Before magnesium was added, the manganese from the cladding was distributed in the salt-metal system with a distribution coefficient of 0.35 (wt fraction in salt/wt fraction in metal phase). The manganese in the salt phase amounted to 2% of the manganese dissolved from the cladding. In the pyrochemical head-end process, the manganese in the decladding salt will also appear in the final uranium-plutonium product because the decladding salt is fed directly to the reduction step. The manganese should not interfere with further processing of the uranium-plutonium product.

About 20% of the fission gases, xenon and krypton, was released during the decladding step, and the balance was released during the reduction step.

It was concluded that the pellets in this fuel element were not highly fragmented because (1) only a small fraction of the fission gases (20%) was released from the gas plenum of the fuel element and (2) the rate of reduction of the oxide pellets was similar to the reduction rate observed in earlier runs with intact 1/4-in.-dia UO_2 pellets in the same equipment. Also, the losses of UO_2 and PuO_2 from the basket were low, indicating that only a small fraction (<0.5%) of the fuel oxide had been present as particles smaller than the holes in the basket (1/32 in.).

REFERENCE

1. Development and Testing of $\text{PuO}_2\text{-UO}_2$ Fast Breeder Reactor Fuels. 15th Quarterly Report, October-December 1968, NUMEC-3524-62 (April 1969).

II. CONTINUOUS CONVERSION OF U/Pu NITRATES TO OXIDES (N. M. Levitz, D. E. Grosvenor, S. Vogler, F. G. Teats)

In the current nuclear fuel cycle, uranium and plutonium oxide powders suitable for the fabrication of fuel shapes (pellets) are prepared by the separate processing of uranyl nitrate hexahydrate (UNH) and plutonium nitrate solutions. The increasing demand for mixed uranium-plutonium oxides for LMFBF and plutonium-recycle fuels provide an incentive for the development of a new high-capacity process for converting uranyl nitrate-plutonium nitrate in solution to a solid oxide form. Concern about the safety of the present practice of shipping plutonium in solution form provides further impetus to this study.

A conversion process based on fluidized-bed technology developed in earlier ANL fluidization work¹ shows a high potential for meeting process requirements. Basic process steps include fluidized-bed codenitration of uranyl nitrate-plutonium nitrate solutions to $\text{UO}_3\text{-PuO}_2$ powder, followed by fluidized-bed reduction of the $\text{UO}_3\text{-PuO}_2$ with hydrogen to $\text{UO}_2\text{-PuO}_2$ powder, the required form for fuel manufacture. The process appears to be applicable over the entire concentration range of uranium-plutonium nitrate solutions and to plutonium nitrate alone. An integrated laboratory and pilot-engineering program is in progress. Initial emphasis is on the denitration step.

Earlier laboratory-scale work included the preparation and preliminary characterization of small quantities of $\text{UO}_3\text{-PuO}_2$ powders and $\text{UO}_2\text{-PuO}_2$ powders and pellets (ANL-7767, -7799, and -7841). Further laboratory-scale work on powders and pellets will be done when $\text{UO}_3\text{-PuO}_2$ materials become available from the pilot plant.

A study of the solubility limits for U/Pu nitrate solutions was made (ANL-7841, p. 24) to help in the selection of the feed composition for the pilot plant. Also, a gamma-counting method for analyzing plutonium, which avoids having to "bag out" samples from the glovebox was tested for use in the pilot plant (ANL-7871, p. 26).

Engineering investigations are being conducted in a pilot plant (ANL-7735, p. 54) housed in a 3- by 4-module glovebox that is approximately 14 ft long, 10.5 ft high, and 3.5 ft wide. The pilot plant consists of a 4-in.-dia fluidized-bed denitrator, a feed makeup system, and associated equipment and instrumentation. The feed makeup system comprises a 4-in.-dia by 60-in.-tall dissolver, a 16-in.-dia by 25-in.-tall feed-storage vessel filled with boron-glass Raschig rings as a nuclear poison, and a 3-in.-dia by 36-in.-tall feed-metering tank. The dissolver is fabricated of Pyrex pipe, and the other vessels of stainless steel. Instrumentation includes appropriate temperature and pressure sensors with local or panelboard read-outs, controllers, recorders, and an automatic data logger.

Before work in the pilot plant with plutonium materials was approved for criticality safety, experiments were done with uranium materials (see previous reports in this series). The recently modified feed makeup system was thoroughly tested, mainly for mechanical operability, in the preparation of 50-liter batches of UNH feed solution for the denitrator (ANL-7871, p. 22). A series of denitration runs of relatively short duration (5.5 hr) explored

the effects of operating variables on column operability and product (UO_3) characteristics (mainly, particle size distribution). Satisfactory performance was achieved with feed rates as high as 90 ml/min of 1.9M UNH solution in 1M HNO_3 . Denitration was carried out at 300°C, with a fluidizing gas rate of 1 ft/sec. The equipment was operated through gloves to simulate work with plutonium.

Other pilot plant work included in-place efficiency tests of the inlet and outlet filters on the glovebox itself, and of the room ventilation filters; all filters are of the AEC type. In these tests, the penetration of dioctyl phthalate (DOP) mist was measured. The results of these tests were satisfactory.

Final denitration runs with UNH solution and initial runs with mixed U/Pu feed solutions are described.

Approval for work with as much as 7 kg of plutonium was received after a rather lengthy period of preparation of safety and criticality hazards analysis reports and review by ANL and AEC safety committees. These reports contain results of Monte Carlo calculations on several equipment arrays. The calculations were made by ORNL whose assistance is gratefully acknowledged.

A. Pilot-Plant Denitration Runs with UNH Feed Solution

Three additional runs were made in the 4-in.-dia fluidized-bed denitration reactor with uranyl nitrate hexahydrate (UNH) feed solutions to test (1) a recently modified startup procedure and (2) the reproducibility of the denitration operation with respect to short-term particle-size effects. In one run, operation was with feed containing a higher HNO_3 concentration than in other runs, 3M instead of 1M. The higher acid concentration is the current upper limit for the forthcoming work with concentrated (~2.0M) U + Pu solutions. Limits on acid and actinide concentrations have been set to avoid precipitation of plutonium nitrate in the feed storage system.

The modified startup procedure involves charging a UO_3 bed into the reactor and bringing the bed to temperature while fluidizing the bed with air. During the heatup period, air is supplied to both the air and liquid side of the nozzle (a two-fluid, external-mix atomizing type) to prevent plugging of the nozzle with bed solids; air is also supplied to all pressure taps for the same reason. Water is then fed through the feed nozzle until the temperatures of the bed, reactor, and process lines become stabilized, after which UNH feed is substituted. Feeding of water during startup serves a dual function: it keeps the nozzle cool and allows the feed rate to be stabilized before switching to the actinide feed solution.

In the current runs, the liquid feed rate was not changed during the switchover from water to actinide feed nor subsequently. Nominal operating conditions were as follows: bed charge, ~8500 g of UO_3 powder (~9-in. static bed height); bed temperature, 300°C; feed composition, 1.95M UNH in 1 or 3.0M nitric acid; feed rate, 80 cc/min; fluidizing gas rate, 1.0 ft/sec at column conditions; feed atomization, 525 volumes (STP) of atomizing air per volume of liquid; nozzle position, ~9 in. above the cone bottom.

The runs were relatively short, of 5.5-hr duration, but each produced about 13 kg of free-flowing UO_3 granules equivalent to about 1 1/2 bed displacements. Product collection from the overflow point (a 1/4-in. IPS line mounted 12 in. above the cone bottom) was fairly uniform throughout the runs. Sieve analyses of hourly product samples revealed no trends with respect to the size distribution of bed particles. Some coarse (+20 mesh) agglomerates and fines (-200 mesh) were produced, equivalent to about 5 and 3%, respectively, of the total UO_3 produced. The average particle size for hourly samples from these runs was $275 \pm 25 \mu\text{m}$.

The condenser system for recovering nitric acid from the off-gas proved to be more efficient in the high-acid run; about 70% of the nitric acid was collected, as compared with about 40% in the two preceding runs. Overall, the runs were satisfactory from the standpoints of both startup and product reproducibility.

B. Pilot-Plant Denitration Runs with U/Pu Feed Solutions

To provide direct experience with plutonium materials, and yet be prudent in working with a new system (i.e., U/Pu feed solution), a single bottle of stock plutonium nitrate solution containing 479 g of plutonium was introduced into the pilot plant, rather than the multi-kilogram allowable inventory. This amount was convenient for initial tests of the denitration step.

The initial feed solution was prepared by dissolving 8230 g of UO_3 in nitric acid, and adding 15 liters of 1.4M low-sulfate UNH solution and 2.2 liters of 0.93M plutonium nitrate solution; a 30-liter batch of solution was prepared. The final U, Pu, and nitric acid concentrations were 1.7, 0.07, and $\sim 1.3\text{M}$. The starting bed material was UO_3 . At steady state, UO_3 -3 wt % PuO_2 would be produced, a material of interest for LWR plutonium-recycle fuel application.

Two runs were made; the first (Run U-16-Pu) was made under essentially the same conditions as the earlier runs with UNH solution and the second (Run U-17-Pu), at a slightly higher bed temperature, 325°C instead of 300°C .

Within minutes after startup with the U/Pu feed, the product flowing from the overflow pipe was uniformly brown (the starting bed was yellow), indicative of uniform mixing and coating of the bed particles with a layer of UO_3 - PuO_2 . After 2 hr, 35 min of apparently steady operation, bed pressure and temperature readings became erratic--generally a sign of a poorly fluidized bed or of a bed that has become agglomerated. A quick changeover was made back to water feed, and the pressure and temperature readings returned to normal. This procedure apparently avoided significant bed agglomeration since the bed material subsequently withdrawn through the bottom take-off valve was free-flowing. This technique of switching back to feeding water or alternatively cutting off all liquid feed completely when difficulties arise in the bed is a potential means of extending runs, allowing reinstituting of feed without having to draw off the bed. Further exploration of this technique is needed.

Also, examination of the inside of the reactor showed the walls to be free of any caked material. Reasons for the upset have not been determined.

A possibility is that optimum operating conditions for U/Pu feed solutions differ from those for UNH solution.

For the second run, the final bed from the first run was recharged to the reactor, with the +20 mesh fraction removed. With operation at the same feed rate (80 cc/min) but at a higher temperature (325°C), ~2 hr of smooth operation was followed by wide temperature and pressure fluctuations. Upon shutdown, approximately 80% of the bed flowed freely from the column; the remainder was a rather loosely agglomerated mass filling almost the entire cross section of the column in the region of the feed nozzle. The latter material was readily removed from the column mechanically by a probing and rapping effort. The slightly higher denitration temperature in the second run apparently is not yet in the "stable" operating region.

Sieve analyses of the product samples showed that significant particle growth had occurred even in two hours, as opposed to no observed growth in earlier runs to produce UO_3 alone. From this, the behavior of U/Pu solution during denitration is obviously different from that of UNH solution, and processing of U/Pu solutions may require different operating conditions, although decomposition temperatures for UNH and plutonium nitrate are not too different, ~250 and 220°C. Changes in feed rate, denitration temperature and fluidizing-gas rates may be needed to achieve operability. These will be tested.

A second observed difference is that the $\text{UO}_3\text{-PuO}_2$ product appears to be more spherical than the earlier UO_3 products, as determined from observations of its angle of repose through the sight glass of the product overflow line and its glass-bead-like behavior on a flat surface. This shape is advantageous for subsequent handling.

C. Miscellaneous

Glove Leak Test

A rapid in-place leak test using helium was devised for the glove-box gloves. With the glovebox maintained at about 1.8-in. negative water pressure (normal pressure is only ~0.5 in. negative), the gloves were extended fully into the glovebox. A stream of helium was directed into each glove from the outside for approximately one minute, while the helium detector probe was positioned in the ventilation duct downstream from the glovebox exit filters. No helium was detected in the course of checking the 94 gloves and glove ring areas. The sensitivity of this test has not been established, but because the test can be made quickly, it warrants further evaluation.

Venting of Shipping Containers for Plutonium Nitrate Solution

Preparations for work with plutonium materials has required the development of special handling and venting procedures for the standard shipping containers (designated L-3) in which our stock plutonium nitrate solutions are received. A L-3 container consists of a 55-gal drum fitted internally with a bird-cage and a pressure vessel that holds the primary container, a 3-liter polyethylene bottle inside a plastic bag. It is recommended that if bottles are stored for more than 30 days, they be vented to relieve any

pressure resulting from radiolytic decomposition.

Guidance in developing the procedures was obtained from Hanford personnel. Detailed written procedures were prepared and after safety and criticality reviews, approved for use.

In the procedure, the L-3 container is opened while in a walk-in hood. A survey for loose activity is made, first in the drum, then in the pressure vessel, and finally in the plastic bag around the primary bottle. Venting of the primary bottle is effected with the needle of a hypodermic syringe (fitted with a filter) which penetrates a vent hole in the cap of the primary bottle. After it is vented, the primary bottle in its plastic bag secondary is removed from the L-3 container and inserted into a second plastic bag; it is then ready for transport to the denitration pilot plant laboratory. Three bottles, which were on hand, have been safely handled by this procedure.

REFERENCE

1. A. A. Jonke, E. J. Petkus, J. W. Loeding, and S. Lawroski, Nucl. Sci. Eng. 2, 303 (1957).

III. IN-LINE ANALYSIS IN FUEL FABRICATION (J. G. Schnizlein, T. Gerding, M. J. Steindler)

A program is under way to develop rapid, precise, and accurate in-line analytical methods applicable to the fabrication of LMFBR oxide fuels. Such methods are expected to lead to decreased costs and automated procedures. The starting criteria selected for evaluation of analytical requirements are the specifications of preirradiation fuel properties and the associated precisions (ANL-7735, p. 59) for the Fast Fuel Test Facility (FFTF) project.

A. Plutonium-Uranium Ratio in Fuels

The evaluation of X-ray fluorescence (XRF) for on-line analysis of U/Pu in LMFBR oxide fuel has continued. The originally defined specification for fuel in the core zone is that the plutonium constitute $20 \pm 0.1\%$ of the actinide content, which corresponds to a relative standard deviation (RSD) of 0.5%.

An on-line analysis to establish plutonium content should be applicable at as early a step in the fabrication process as possible to offer the greatest advantage. That is, if powders can be analyzed with sufficient accuracy, the adjustment for off-specification content will be made most easily. The next most advantageous control points are the preslugging or green pellet formation steps. Finally, if the XRF method is applied to sintered pellets, it will be necessary to recycle the off-specification material to an acid solution unless the material can be recycled to the preslugging step in the process. These considerations have influenced the planning of the experimental program.

To avoid plutonium hazards and facilitate study of the important variables in the analysis, $\text{ThO}_2\text{-UO}_2$ mixtures are being utilized as a stand-in for $\text{UO}_2\text{-PuO}_2$. This substitution is practical because of the identical relationship of the atomic numbers and thus of the relevant properties (ANL-7755, pp. 45-50) for each pair of elements.

Initially in this program, instrumental and inherent limitations of the XRF method were demonstrated to be adequately low--the relative precision due to the XRF method was less than 0.5% for measurement of uranium and thorium in pellets and thoria-30% urania powder (ANL-7841, pp. 31-36). Currently, the limitations imposed by material effects (i.e., particle size distribution, density, and sample shape) for analysis of powders, green pellets, and finally sintered pellets are being evaluated in standard equipment. Use of the XRF method to analyze pellets assumes that the surface (to a depth of less than 100 μm) is representative of the entire pellet.

1. Influence of Bulk Density and Particle Size of Powders on X-ray Fluorescence Intensity

Heterogeneity and particle size effects have prevented demonstration of a relative precision of 0.5% for the XRF analysis of powder samples. For UO_2 samples with narrow particle sizes, the X-ray fluorescence signals were measured at different degrees of compaction (ANL-7871). The densities, 24 to 36% of theoretical density (T.D.), ranged from those obtained by loose packing to the tightest packing of powder obtainable by hand loading.

Fluorescence intensities (corrected for coincidence) for UO_2 of narrow density ranges and mixed particle sizes are plotted in Fig. III-1 (a revision of Fig. III-1, ANL-7871). Extrapolations of the curves representing narrow size fractions would approach the count rate of solid UO_2 or uranium metal at very high densities and would approach zero at very low densities.

Relative intensity* data for each particle size at 25, 30, 35, and 40% of theoretical density have been calculated and are plotted against the logarithm of particle size in Fig. III-2. Values calculated from fundamental parameters by J. Criss¹ are also plotted in a separate curve to allow comparison. The data indicate that for narrow particle size fractions, compaction to higher density minimizes the particle size effect. It was also observed (Fig. III-1) that compacting of powder having a wide particle size distribution to densities above 30% of T.D. results in uniformly high relative intensities.

Earlier experimental results (ANL-7871) suggest a variability of ~3% between analyses of powder samples of a ThO_2 -30 wt % UO_2 mixture. This 3% variability may be largely due to mixing and sampling errors and to the unusual particle size distribution of the thorium used. No fundamental reasons are known that would prevent this variability from being reduced with better mixing, control of particle size distribution, and control of the density of the examined surface. Application of XRF analysis to coprecipitated or homogeneous powder has not yet been explored, but should offer no problems.

It is likely that pelletizing of powder to a controlled density will be necessary to achieve the desired relative standard deviation of 0.5% for the analysis. A crude estimate suggests that a 1% variation (FFTF specification) of green pellet density (at ~60% of T.D.) will result in a change of ~0.3% in the relative intensity. The possibility is being explored that the effects of particle size and density for thorium and uranium (or uranium and plutonium) are similar enough to result in negligible errors in the Th/U (or U/Pu) ratio.

It should be noted that comparison of thorium or uranium count rates with appropriate standards may allow the fabricator to detect

* Relative intensity, I/I_{std} , is the ratio of the intensity for uranium oxide to the intensity for uranium metal at the same exciting intensity.

Fig. III-1. XRF Intensities for UO_2 of Narrow Particle-Size Distributions and Mixed Particle Sizes at Different Densities

Fig. III-2. XRF Intensity of UO_2 Relative to Uranium Metal for Various Particle Sizes and Percentages of Theoretical Density

deviations from particle size standards for fuel powder in the milling-mixing stage of fabrication; the ratio of these count rates may be a measure of homogeneity.

2. Analysis of Microspheres and Green Pellets of UO_2

The XRF intensity for urania microspheres of narrow particle size distributions (10-20 μm , 20-30 μm , 37-44 μm) at the natural packing density of about 60% of T.D. was measured (Fig. III-3). Similar XRF intensity measurements were made for irregularly shaped UO_2 particles of the three particle sizes. The relative intensity of the uranium $\text{L}\alpha$ line for UO_2 microspheres indicates that the particle size effect is similar to that for irregularly shaped powder particles although the density of the microspheres is similar to that for green pellets. To determine the effect of compaction, irregular 40- μm powder was compacted to form a pellet 64% of T.D. Its count rate relative to U metal (Fig. III-3) was 1.04. Irregular 15- μm powder compacted to a pellet 68% of T.D. showed a relative count rate of 1.003. These data suggest that both particle size and density effects may be reduced by compacting to pellets of about 65% of theoretical density. If the density effect is sufficiently small at 65% of T.D. to allow precise XRF analysis, a negligible density effect would be expected at 92% of T.D. (FFTF specification for sintered pellets).

Apparently, the particle size effect can be largely eliminated by forming green pellets, and pellet density (or a surface effect) is the primary variable governing the demonstrable precision. At present, the RSD caused by a 1% difference in density is estimated to be 0.3%. Additional experiments will be performed with green pellets of densities varying by about 10%. Results should indicate whether careful control of density prior to analysis is necessary.

3. Sintered Pellets

Application of XRF analysis to a fabrication process may require two different standards, one for sintered material (homogeneous solid solution) and the other for green pellets compressed from mixed powder, since in sintered pellets the specification that the material be homogeneous solid solution avoids the possible interference caused by heterogeneity effects observed in mixed powder. Yet to be determined is whether the acceptable density variation of $\pm 1\%$ for sintered pellets (FFTF specification) causes sufficient variability in the XRF analysis to prevent a relative precision of 0.5% being attained in plutonium analysis. The densities of $\text{ThO}_2\text{-UO}_2$ sintered pellets at three uranium concentrations previously studied (ANL-7841, pp. 31-36) deviate from the mean by as much as 2.4% of T.D. An analysis of variance was performed on the ratio of count rates of thorium to uranium for these pellets to determine whether the effects of differences in density or O/M between samples would be significantly reduced by use of this count rate ratio for analysis. Although the RSDs (which were as high as 1%) of the Th/U count rate ratio between pellets were less than one half the expected values (root mean square sums of individual count rates), the 95% confidence limits of the RSDs include the expected values. This

Fig. III-3. Relative Intensities for Microspheres, Powder, and Pellets of Urania at Different Densities

indicates that the use of the ratio of count rates of thorium to uranium does not eliminate the variation between pellets. Probably, composition errors (e.g., mixing errors) mask the influence of density on the XRF signal.

4. Optimizing Counting Time for Desired Precision

The fuel fabricator must perform the XRF analysis in a minimum time that will also satisfy the counting statistic precision. When a high-intensity excitation X-ray is used, the count rates can be high enough to perform one analysis per minute. This rate of analysis should satisfy quality assurance criteria, if the batch sizes are large enough, for a plant with a capacity of one metric ton per day. However, most counting equipment requires extensive coincidence corrections at these high rates, and the accuracy of an empirical coincidence correction is very difficult to define. Thus it will be desirable to select the lowest counting rates that provide both rapid enough analysis and the desired precision.

Mack and Spielberg² applied statistical optimization to the counting of peaks and background to the comparison of peaks. Their conclusions are (1) for a difference between two count rates, the available time should be allotted such that the ratio of times is equal to the ratio of the square roots of the count rates

$$\frac{t_C}{t_B} = \frac{\sqrt{R_C}}{\sqrt{R_B}}$$

and (2) for a ratio of two counting rates, the optimum allotment of available time is such that the ratio of the times is equal to the inverse ratio of the square roots of the count rates

$$\frac{t_A}{t_D} = \frac{\sqrt{R_D}}{\sqrt{R_A}}$$

Plummer³ extended the above relationships to allow calculation of total counting time per sample for X-ray spectrometric data with defined precisions and confidence levels. For the situation of counting two peaks and one background, Plummer's relationship was used in this work to calculate counting times for 0.5% precision at the 95% confidence level.

Optimum Total Counting Time for Sample =

$$\left(\frac{100}{P} \sqrt{ \frac{D_S R_U^{1/2} + [R_B (D_U^2 + D_S^2)]^{1/2} + D_U R_S^{1/2}}{D_U D_S} } \right)^2$$

$Z = 1.96$ for 95% confidence
 $P =$ precision desired = 0.5%
 $D =$ difference between peak and background rates
 $R =$ counting rate

Subscripts $S =$ internal standard (i.e., Th)
 $U =$ unknown (i.e., U)
 $B =$ background

The counting rates used in our calculations were from typical pellets formed from irregularly shaped powder particles, irradiated with a tungsten X-ray tube operated at 59 kVP and about 5 mA. Optimum counting times for each peak, background, and total time are presented in Table III-1 and Fig. III-4.

To obtain counting statistics with a precision of 0.5% for the Th/U ratio at 95% confidence limits, the exciting tube may be operated at 40 mA instead of 5 mA, giving a total counting time for 30-70% UO_2/ThO_2 of 29 rather than 205 sec.

Apparently, the fuel fabricator can choose analytical conditions such that a RSD of 0.5% at the 95% confidence level can be obtained with analysis times short enough (less than one minute) to match process conditions at a one metric ton per day production rate.

It is concluded from this evaluation of XRF as a potential on-line analytical method for determining plutonium and uranium content of fuels that XRF has an outstanding potential because of its speed and precision.

REFERENCES

1. J. W. Criss, U. S. Naval Research Laboratory, private communication (1971).
2. M. Mack and N. Spielberg, *Spectrochim. Acta* 12, 169-178 (1958).
3. L. N. Plummer, *Appl. Spectr.* 23, 583 (1969).

Fig. III-4. Optimum Counting Times for Urania-Thoria Pellets to Achieve $\pm 0.5\%$ Precision at 95% Confidence (59 kVP; 5 mA)

Table III-1

Optimum Counting Times for the XRF Analysis
of ThO₂-UO₂ Mixtures (59 kVP, 5 mA)

		Count Rate, cps	Square Root of Count Rate	Proportion	Difference	Optimum Time, -sec			
						Total	t _U	t _{Th}	t _{Bkg}
ThO ₂ -15 wt % UO ₂	R _U	1450	38.1	t _U /t _{Bkg} =5.8	D _U =1408	313	195	82	36
	R _{Th}	8150	90.2		D _{Th} =8108				
	R _{Bkg}	42	6.5	t _U /t _{Th} =2.37					
ThO ₂ -25 wt % UO ₂	R _U	2480	49.7	t _U /t _{Bkg} =7.65	D _U =2438	193	112.5	65	14.7
	R _{Th}	7420	85.0		D _{Th} =7378				
	R _{Bkg}	42	6.5	t _U /t _{Th} =1.71					
ThO ₂ -30 wt % UO ₂	R _U	2700	52	t _U /t _{Bkg} =8.28	D _U =2664	205	112	79.5	13.4
	R _{Th}	5600	75		D _{Th} =5564				
	R _{Bkg}	36	6.3	t _U /t _{Th} =1.44					

IV. ADAPTATION OF CENTRIFUGAL CONTACTORS IN LMFBR FUEL PROCESSING (G. J. Bernstein, N. Quattropani)

Development and testing continue on the stainless steel centrifugal contactor having a 4-in.-ID rotor with a 12-in.-long settling zone and a 15-in. length (Fig. IV-1). The ANL contactor is unique in that the settling length-to-diameter (L/D) ratio is 3, whereas in other contactors of similar type the L/D ratio is about 1.4. The contactor is being evaluated to determine its suitability for use in Purex-type solvent extraction processing of LMFBR fuel having high plutonium concentrations. Criticality hazards caused by high plutonium concentrations in the process streams will be controlled in the ANL design by limiting the diameter of the contactor to a geometrically favorable dimension. Expected advantages of centrifugal contactors are (1) reduced radiation damage to the solvent as a result of brief residence time in the contactor and (2) improved ease of operation (including rapid flushout at the end of a processing campaign).

The ANL contactor is a modification of the large centrifugal units in use in the Savannah River (SR) plant. In the application being studied, aqueous and organic phases are fed into a tee at the bottom of the contactor and then up into a mixing chamber where they are mixed with a paddle. The mixture exits through peripheral slots at the top of the mixing chamber and is then directed through a nozzle into the hollow rotor. The rotor separates the mixed phases by centrifugation as it pumps the liquids up the inside of the rotor. At the top of the rotor, weirs direct the two streams through separate discharge ports into appropriate collector rings.

The study encompasses determination of phase-separating capacity, hydraulic flow characteristics, the effects of entrained solids, effects of variations in mixing intensity, and measurements of mass-transfer efficiency. Performance of the contactor when operated with a mixing chamber at its base is being evaluated, as well as performance of a modified design of the unit (annular mixing mode) in which mixing of phases takes place by skin friction in the annulus between the spinning rotor and stationary casing.

A. Contactor Operation with Mixing in Bottom Chamber

1. Measurements of Separating Capacity

During the past quarter, tests were conducted to measure separating capacity* using 0.5M HNO_3 as the aqueous phase and 15 or 30% tri-n-butyl phosphate (TBP) in n-dodecane as the organic phase. These tests were made at the same range of rotor speeds (2000-3500 rpm) as in earlier tests with Ultrasene as the organic-phase diluent (ANL-7841).

Before capacity tests were started, a mechanical change was made to improve the operation of the equipment. Four small vanes were added to the paddle shaft to improve the transfer of mixed phases from the inlet nozzle into the rotor orifice (see Fig. IV-1). This change reduced the leakage of fluid into the casing through the annular gap between the inlet nozzle and the rotor orifice.

*Separating capacity is arbitrarily defined as the throughput with 1% cross contamination of one phase by the other.

Fig. IV-1. Centrifugal Contactor Assembly

Separating capacity was measured over a range of rotor speeds of 2000 to 3500 rpm; aqueous-to-organic (A/O) flow ratios were 0.3 to 3.0 with 15% TBP and 0.1 to 10 with 30% TBP. At all rotor speeds in the experiments with 15% TBP (Fig. IV-2), separating capacities were near their minimum values at A/O ratios of ~ 2 . As shown in Fig. IV-2, capacities at an A/O ratio of 2 ranged from 5.5 gpm at 2000 rpm to 9.5 gpm at 3500 rpm. At an A/O ratio of 3, capacity ranged from 8 gpm at 2000 rpm to 15 gpm at 3500 rpm. Performance was very nearly the same as in the Ultrasene experiments.

Test results for 30% TBP are plotted in Fig. IV-3 on a semi-logarithmic scale to accommodate the broader range of A/O ratios. Minimum separating capacities were found at an A/O ratio of ~ 1 and varied from 5 gpm at 2000 rpm to 9 gpm at 3500 rpm. Highest capacities were found at A/O ratios of 3 or 4 and ranged from 9 gpm at 2000 rpm to 17 gpm at 3500 rpm. As was true in the tests with Ultrasene, capacities at A/O ratios below 0.4 or 0.3 were lower than at A/O ratios above 2 and did not follow quite as consistent patterns of variation with rotor speed. This is attributed mainly to differences in the kinds of emulsions formed. Performance was again very similar to that found when Ultrasene was used as the diluent.

Following the runs described above, modifications of the mixing chamber and paddle were tested to determine their effects upon separating capacity and hydraulic performance. One change was the removal from the mixing paddle of the stabilizing ring (see ANL-7799, Fig. IV-2), which was originally considered necessary to increase the dynamic stability of the long rotor. A reason for questioning the need for this ring was experience showing that the rotor was very well balanced--e.g., there were no dynamic instabilities during periods of intermittent admixture of air in the mixing chamber. Also, it is possible that the ring had a deleterious effect on the mixing and pumping characteristics of the mixing chamber by shielding some of the fluid from the effects of the mixing baffles. After removal of the stabilizing ring, no significant change in the dynamic or hydraulic stability or in separating capacity was noted.

A new paddle designed to permit easy changing of the blade portion was installed. With blades that were slightly taller and of smaller radial diameter than those of the original paddle, separating capacities at an A/O ratio of 1 were approximately the same as with the original paddle; however, at the lower rotor speeds tested, separating capacities were slightly higher than with the original paddle.

The effects on separating capacity of both the stabilizing ring and a spacer ring in the mixing chamber were studied in relation to the phenomenon of flow surging (see Section 2 below). The mixing chamber in the ANL contactor had been made significantly deeper than is characteristic of the Savannah River (SR) design to permit studies with different shapes and sizes of mixing paddles and to allow evaluation of the effect of changes in mixing chamber volume and residence time. As shown in Fig. IV-1, the mixing paddle traversed only about one-half the depth of the mixing chamber rather than the full depth as in the SR design.

During earlier attempts to eliminate flow surging, it was found that more stable pumping characteristics were achieved if a doughnut-shaped spacer ring was used to fill the mixing chamber space below the paddle. More

Fig. IV-2. Separating Capacity of 4-in.-dia Rotor Centrifugal Contactor
Aqueous Phase 0.5M HNO_3
Organic Phase 15 vol % TBP in n-dodecane
1% Entrainment

Fig. IV-3. Capacity of 4-in.-dia Rotor Centrifugal Contactor

AQ-0.5 M HNO_3 ; ORG-30% TBP in n-Dodecane;
1% Entrainment

recently, separating-capacity tests were made using one paddle with a stabilizing ring, another paddle without a stabilizing ring, and with the spacer present and absent. In tests with a paddle having a stabilizing ring and with the spacer absent, separating capacities were either the same or somewhat higher than had been found when the spacer ring was used. The higher capacities were noted at the lower mixing speeds. In tests with the spacer present, the separating capacities were essentially the same whether the paddle had a stabilizing ring or not.

2. Effects of Mechanical Design and Operating Techniques on Separating Capacity, Pumping Capacity, and Operability

Further work was done to study the phenomenon of flow surging, which is attributed to the pumping capacity in the mixing chamber being substantially greater than the flow of liquid into the mixing chamber. When the mixing chamber was fully primed, its pumping capacity would become excessive, leading to a surge in the discharge of fluids into the rotor. This condition would be followed immediately by a sudden drop in pumping capacity as the chamber became air-bound, leading to a sharp drop in the discharge of fluids into the rotor. The consequent shifting of the interface at the top of the rotor increased the probability of contamination of effluent streams.

Earlier in this investigation (see ANL-7841 and ANL-7871), it was found that controlled addition of a small steady stream of air (~ 0.3 cfm) to the mixing chamber to maintain it in a semiprimed condition prevented flow surging. The simplest way to introduce air into the mixing chamber is through the casing drain line (see Fig. IV-1). The casing drain line returns to the inlet tee the excess liquid that leaks through the annular gap between the stationary nozzle and rotating orifice. (Slight leakage normally occurs here as the liquid "jumps the gap" between the vanes on the mixing paddle shaft and the rotor vanes.) It was subsequently observed that at flow rates substantially lower than the pumping capacity of the mixing chamber, there was a tendency for the mixing chamber to gulp excessive air. This condition could set off the cycle of air-bound and fully primed pumping performance noted above. At low flow rates, a semiprimed condition was maintained by throttling the valve in the casing drain line to restrict air flow into the mixing chamber. When the throughput was increased, throttling the drain line valve was not nearly so necessary since the mixing chamber then had less excess pumping capacity. The unit could run smoothly at high or low rotor speeds and high or low flowrates with the casing drain line valve partially closed.

When the input flow rates was increased to the point where the rotor could not pump at the required rate, the leakage around the nozzle tended to increase. The ultimate consequence of this leakage was to create the flooded condition discussed below but it did not lead to flow surging.

In the course of recent separating-capacity tests, it was noted that at some feed rates, the rotor reached its maximum pumping capacity before it reached its maximum separating capacity. This condition was observed at high and low A/O ratios and not at intermediate A/O ratios. Flooding resulted with the casing annulus filled with emulsion which rose until it overflowed into the organic collecting ring and contaminated the effluent organic stream. An evaluation of the pumping characteristics of the rotor was made. In addition, the relationship between pumping and separating capacity was investigated to determine if any basis exists for a practical limitation to the L/D ratio in the rotor.

In an earlier report (ANL-7841), an expression for estimating the separating capacity of a centrifugal contactor was given:

$$\text{Separating Capacity, gpm} \propto \frac{N_c^2 D_b^3 L}{10^5 N_m D_m} \quad (1)$$

where

N_c = rotor speed, rpm

D_b = rotor diameter, in.

L = settling length of rotor, in.

N_m = mixing paddle speed, rpm

D_m = paddle diameter, in.

The group includes the term 10^5 in the denominator so that the calculated value will be of the same order of magnitude as the capacity in gpm.

Although the expression indicates that separating capacity is linearly proportional to the settling length of the rotor, it is obvious that separating capacity cannot be increased without limit by increasing the rotor length. At any given rotor speed, with increased length of the rotor, separating capacity increases, but pumping capacity does not increase proportionately because of the greater lift required. Flow capacity for a very long rotor would be limited by frictional losses and hydraulic lift requirements.

As can be seen in Fig. IV-1, the mixed aqueous-organic emulsion flows through the inlet nozzle and is injected into the rotor orifice. The radial vanes quickly accelerate the emulsion to rotor speed, and the phases are separated as they are pumped up the inside of the rotor. The usual pictorial representation of a high-speed rotor shows a hollow cylindrical air-liquid interface near the axis of the rotor. However, the interface is not truly cylindrical since a small hydraulic head must be developed to overcome the static head from bottom to top and the frictional losses due to fluid flow through the internal passages of the rotor.

Examination of the hydraulic flow conditions can be simplified if one treats the problem first as involving only a single phase. If it is assumed that the rotor is completely filled with fluid, the pressure developed at any radius, r , measured from the axis of the rotor would be

$$p = 1/2 \rho \omega^2 r^2 \quad (2)$$

where

ρ = fluid density, lb/cu ft

r = radial distance from axis, ft

ω = rotor speed, radians/sec

In the conversion to hydraulic head, H , measured in feet of any fluid, the fluid density, ρ , drops out of the equation and

$$H = \frac{\omega^2 r^2}{2g} \quad (3)$$

where

g = force conversion constant, $32.2 \text{ (ft)(lb mass)/(lb force)(sec}^2\text{)}$

A plot of H vs. r is shown in Fig. IV-4 for the specific case where $\omega = 210$ radians/sec (2000 rpm). The curve is a parabola of the form $y = Kx^2$. (The horizontal scale is expanded to exaggerate the parabolic form.)

When the rotor operates with an air core along the axis (as it does in centrifugal separating rotors), the net head developed, ΔH , is given by the expression:

$$\Delta H = \frac{\omega^2}{2g} (r_2^2 - r_1^2) \quad (4)$$

where

r_1 = radius of air-liquid surface at bottom of rotor

r_2 = radius of air-liquid surface at the overflow point at the top of the rotor.

At any given rotor speed, the maximum ΔH is developed in any rotor when

r_1 = radius of the inlet orifice

r_2 = radius of the surface of the fluid flowing over the lower (organic) weir.

If two phases are present, some complexities arise from the fact that the fluid in the lowest region of the rotor has a variable effective density, depending on the A/O ratio. However, fundamentally, the evaluation is the same as for a single phase. In the contactor shown in Fig. IV-1, the flow passages for the aqueous phase are at the periphery of the rotor. If there is resistance to aqueous flow through these passages and over the circular weirs, it is automatically balanced by a movement of the aqueous-organic interface (or emulsion band) toward the axis of the rotor. The organic phase flows over the inner weir and rises radially over the weir to a level dependent on its flow rate and the rotor speed. By analogy with rise over a horizontal weir, an equation for calculating rise over a circular weir was developed at Savannah River.¹

In the recent series of tests, the maximum amount of organic phase that could be pumped through the contactor at 2000 rpm was about 5 gpm. At 5 gpm and 2000 rpm, the rise over the organic weir is 0.109 in. Since the radius of the organic weir is 1.00 in., the radius of the air-organic interface surface is 0.891 in. (0.074 ft). The radius of the rotor orifice is 0.594 in. or 0.050 ft. Using Eq. 4, $\Delta H = (210^2/64.4)(0.074^2 - 0.05^2) = 2 \text{ ft}$.

Fig. IV-4. Hydraulic Head Developed in a Rotor

In Fig. IV-4, the dotted lines show these two radii and indicate that the ΔH developed between these two points is ~ 2 ft. The actual head required to lift organic phase from the inlet orifice to its weir is 1.0 ft. The additional 1 ft of head is consumed in overcoming frictional flow through the rotor and pushing the organic-aqueous emulsion around the edge of the deflection baffle.

At higher rotor speeds, the situation would be essentially the same. A higher net pumping head would be developed, but the increased flow resulting from the increased separating capacity would result in greater frictional losses.

Although experience with the ANL contactor suggests that the limiting practical L/D ratio is ~ 3 , some benefit could still result from using a slightly higher L/D ratio, particularly if some dimensional changes are incorporated in the design. Thus, the inlet orifice (r_1) could be made slightly smaller and the organic weir (r_2) could be made slightly larger to increase ΔH . The deflection baffle could be made smaller since it probably restricts the flow of low-density emulsions around it. In addition, there are some A/O ratios near the 0.5 to 2.0 region where the separating capacity and not the pumping capacity is the flow-limiting factor. It is probable that a rotor designed for use at a more limited range of A/O ratios would show increased separating capacity if its L/D ratio were about 4 or slightly more.

It should be noted that the separating capacity limitations observed in the tests described above are not normally reached in plant operations. They were observed here because the contactor was operated at the limit of its separating or pumping capacities in the interest of defining the operating characteristics of a contactor having a high L/D.

3. Conclusions

The results of these tests demonstrate that separating capacities are not precisely determined by the parameters of paddle size, rotor speed, A/O ratio, and feed stream compositions alone. The size of the mixing chamber and baffles, solution residence time, admixture of air, and even external piping affect the nature of the emulsion formed and the ease of phase separation. To allow for the effects of all these variables, the expression, 1, is held to be valid over a range of two between high and low values. Conservative practice also would require that separating capacity be determined experimentally before a bank of contactors is used with any specific flowsheet. In addition, operating flow rates in a bank of contactors are usually limited to $\sim 70\%$ of experimentally determined separating capacity to allow for uncertainties and flow upsets.

4. Future Work

Additional tests will be made with alternative paddle designs to gain further insight into the effect of mixing intensity on hydraulic stability and phase separation. Plans are being made for measuring mass transfer efficiency in tests in which uranyl nitrate will be extracted. Other tests will evaluate the effect of entrained solids on contactor performance. A scheme is being developed that will permit these tests to be performed with relatively small volumes of feed solutions.

B. Contactor Operation in the Annular Mixing Mode

In an earlier report (ANL-7755), an alternative mode of operation of the centrifugal contactor, identified as the annular mixing mode, was described. The present contactor was designed so that it could be converted for operation in this mode (Fig. IV-5). Comparison of Figs. IV-1 and IV-5 shows that the conversion was achieved by connecting the aqueous-organic feed lines to the casing side inlets and removing the mixing chamber, the mixing paddle and shaft, and the nozzle plate. A new bottom plate was installed that had four radial baffles.

In the annular mode of operation, the feed streams flow downward through the annulus between the casing and rotor and are mixed by skin friction between the spinning rotor and stationary casing. The radial baffles on the bottom plate of the contactor convert some of the kinetic energy into pressure to force the emulsion through the rotor orifice. The phases are separated in the rotor and discharged as in the SR mode of operation.

Preliminary testing of the unit in the annular mode of operation showed excellent mixing and separating performance. However, the relatively narrow annular gap (0.27 in.) restricted flow to ~5 gpm. The contactor is being modified to permit installation of a casing providing a larger annular gap (0.55 in.).

It is anticipated that separating capacity for operation in the annular mode will be at least equal to that for the SR type of contactor. Advantages foreseen in this alternative design are (1) operation would be smoother because of the elimination of problems associated with pumping in a mixing chamber; (2) fabrication would be much easier and less costly since the rotor assembly (minus the mixing paddle and shaft) would be lighter and easier to balance, and the mixing chamber would be eliminated, as well as the requirement for close tolerance fits in the region of the rotor orifice, and (3) remote maintenance would be simplified since the entire rotor assembly could be removed through the top of the casing. This last feature is very significant in the installation and maintenance of remotely operating contactors. The design of the superstructure would be much simpler than in the SR contactor. These benefits would apply to large contactors, as well as the present ANL size.

In further testing of this type of contactor, the same kinds of separating capacity tests and extraction efficiency tests will be performed as with the SR design.

REFERENCE

1. D. S. Webster, C. L. Williamson, and J. F. Ward, Flow Characteristics of a Circular Weir in a Centrifugal Field, USAEC report DP-371 (June 1961).

Fig. IV-5. Schematic Diagram of the 4-in.-dia Rotor Centrifugal Contactor - Annular Mixer Mode

V. THE ELECTROLYTIC REDUCTION AND REOXIDATION OF PLUTONIUM IN PUREX PROCESSES

(M. Krumpelt, J. J. Heiberger, M. J. Steindler)

Electrolytic reduction of plutonium is being developed as a substitute for chemical reduction in the Purex process. In a previous report of this series (ANL-7871), two constants, m and A , for an equation linking electrolytic reduction rate to various process parameters were determined from data obtained in limiting-current-density experiments. In these experiments, limiting current densities were measured with a ferrocyanide-ferricyanide electrolyte in an electrolytic cell of large volume in which the concentration of ferricyanide was relatively constant throughout an experiment. Inclusion of the two newly determined constants in the equation for reduction rate should allow prediction of reduction rates for plutonium.

A new electrolytic cell (Fig. V-1) has been designed and built having features suitable for reduction studies with an electrolyte consisting of plutonium in nitric acid. The principal design criteria were (1) a higher ratio of electrode surface to electrolyte volume than in the cell used to determine m and A , (2) in-line monitoring of the flow rate, and (3) replaceable cell diaphragm. The high ratio of electrode surface area to electrolyte volume is dictated by the desire to increase the rate of plutonium (IV) reduction. In-line flow-rate monitoring in the new cell is achieved by measuring the pressure drop across an orifice plate. The plate and holder design are based on one described by Clark.¹ The replaceability of the diaphragm allows evaluation of various materials for the diaphragms separating the cathode and anode compartments of the cell. Initially, glass frits will be used as diaphragms. The cell voltages will be regulated potentiostatically, as in the cell used to determine m and A .

The electrolytic cell is glass except for gold-plated parts (including the impeller, the flange holding the orifice plate, and the cathode) and Teflon parts (the cathode holder, some stoppers, and the diaphragm holders). The cathode holder can hold single or multiple layers of wire cloth.

Initial tests of the new cell with a $K_3[Fe(CN)_6]$ - $K_4[Fe(CN)_6]$ -NaOH electrolyte of the previously used composition indicated agreement of limiting current densities with earlier measurements. In subsequent experiments with plutonium in nitric acid, the Pu(IV) and Pu(III) concentrations will be determined periodically, and the limiting current densities and flow rates will be recorded. Reduction rates predicted by the above-mentioned equation will be compared with these measurements. Good agreement of calculated and experimental rates will prove the validity of the reduction equation. Side reactions which could compete with or impede the plutonium reduction will also be investigated.

REFERENCE

1. W. J. Clark, Flow Measurement, Pergamon Press (1965).

Fig. V-1. Schematic Drawing of Electrolytic Cell