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**DEMONSTRATION OF THE SALT CYCLE PROCESS
IN A HIGH-LEVEL RADIOCHEMICAL FACILITY**

W. R. BOND, G. JANSEN, JR., AND L. K. MUDGE

DECEMBER, 1966

BATTELLE-NORTHWEST

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DEMONSTRATION OF THE SALT CYCLE PROCESS
IN A HIGH-LEVEL RADIOCHEMICAL FACILITY

by

W. R. Bond, G. Jansen, Jr., and L. K. Mudge

Chemical Development Section
Chemistry Department

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ABSTRACT

The Salt Cycle process for pyrochemically reprocessing $\text{UO}_2\text{-PuO}_2$ fuels has been studied in pilot plant equipment. The decladding, dissolution, electrodeposition, and product treatment steps of the process were integrated into a single remotely operable facility. Problem areas for future development were identified, and several kilograms of mixed oxide fuel were recycled to the Plutonium Recycle Test Reactor. The electrodeposition of $\text{UO}_2\text{-2 wt\% PuO}_2$ from molten alkali chlorides was demonstrated with feed materials irradiated up to 5000 MWd/tonne.

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DEMONSTRATION OF THE SALT CYCLE PROCESS
IN A HIGH-LEVEL RADIOCHEMICAL FACILITY

INTRODUCTION

The Salt Cycle process was developed at Hanford as part of the Plutonium Utilization Program to reprocess $\text{UO}_2\text{-PuO}_2$ fuels for recycle to thermal heterogeneous reactors. The process is based on the electrolytic deposition of crystalline, reactor-grade $\text{UO}_2\text{-PuO}_2$ solid solutions from molten chloride salts. In the recycle scheme economies are sought by processing short-cooled irradiated fuel with a minimum number of remote manipulations.

One close-coupled plutonium recycle system which has been considered for application of the Salt Cycle process is shown in Figure 1. The system is based on a zoned reactor which is fueled with unirradiated, slightly enriched UO_2 fuel elements and recycle $\text{UO}_2\text{-PuO}_2$ fuel elements containing lower enrichment uranium. A zoned reactor reduces fuel fabrication costs by minimizing the number of remotely fabricated recycle fuel elements. For this system the process should have the capability of (1) recovering the plutonium from the depleted recycle uranium in the irradiated $\text{UO}_2\text{-PuO}_2$ fuel elements, (2) combining on a molecular scale the recovered plutonium with the plutonium and a portion of the uranium from the irradiated UO_2 fuel elements, and (3) producing a $\text{UO}_2\text{-PuO}_2$ mixture that has physical properties suitable for refabrication and is relatively free of neutron poisoning fission products. An economic study of the relative merits of close-coupled, remote processing and central plant reprocessing has been made by R. W. McKee.⁽¹⁾

A simplified flowsheet, shown in Figure 2, was selected to demonstrate the remote operation of the process in the High-Level Radiochemistry Facility of the Pacific Northwest Laboratory. In this system the $\text{UO}_2\text{-PuO}_2$ is removed from fuel rods by vibratory decladding, the UO_2 is oxidized to U_3O_8 and the mixed oxide is dissolved in molten lithium chloride-potassium chloride by chlorine and hydrogen chloride gases. The uranium to be separated from the plutonium is electrodeposited as the oxide in a

FIGURE 1
Close-Coupled Plutonium Recycle System

FIGURE 2
Salt Cycle Demonstration

partition electrolysis with a hydrogen chloride gas sparge. Additional fuel is dissolved and a $\text{UO}_2\text{-PuO}_2$ mixture is electrodeposited with an oxygen-chlorine gas sparge. The mixed oxide is stripped from the electrode, crushed, washed with water, reduced with hydrogen if necessary, and sized for vibratory compaction.

The objectives of demonstrating the process were (1) to determine the feasibility of each process step in pilot plant equipment at high levels of radioactivity, (2) to define problem areas and place them in the proper perspective by operating an integrated facility containing all necessary equipment, and (3) to produce recycle product suitable for in-reactor evaluation. The emphasis was on early operation of the process without necessarily optimizing any part of the equipment.

This report is the third in a series of terminal development reports on the Salt Cycle process. Laboratory studies of the plutonium chemistry of the process are described in the first report,⁽²⁾ and the second deals with the engineering development of the unit operations necessary in the process.⁽³⁾ A fourth report is expected to detail the remote refabrication of the fuel elements and the still unfinished in-reactor performance of the mixed oxide product as a nuclear fuel.

SUMMARY

The Salt Cycle process was demonstrated in remotely operated pilot plant equipment in a high-level radiochemistry facility. The electrodeposition of $\text{UO}_2\text{-PuO}_2$ in 10- to 20-pound batches from molten equimolar lithium chloride-potassium chloride was accomplished with feed material from 75 half-length sections of fuel rods that had been irradiated up to 5000 MWd/tonne in the Plutonium Recycle Test Reactor.

The time required to declad cold-swaged half-rods by mechanical vibration increased almost directly with the fuel burnup. Vibratory-compacted half-rods, however, were declad in about 5 minutes for all cases up to an exposure level of 4300 MWd/tonne. Average waste losses were 0.6 and 0.25% for cold-swaged and vibratory-compacted half-rods, respectively, at the

higher burnups. These were greater than the 0.1% waste loss experienced in cold pilot plant tests.⁽³⁾

The dissolution of the mixed oxide feed material in the hot cell proceeded at lower rates than expected from cold pilot plant studies. The average uranium dissolution rates ranged from 0.05 to 0.5 lb/hr. The introduction of chlorine through a submerged annular gas lift instead of simple tubes improved the dissolution rate in some cases but did not do so consistently. This was partially attributed to inconsistent particle size reduction and conversion of the feed to U_3O_8 during the preceding oxidation step. The precipitation of a portion of the plutonium as PuO_2 at the gas-liquid interface on the walls of the quartz pot during dissolution resulted in incomplete recovery of the plutonium. Although a graphite liner extending just below the salt level corrected this situation, use of the liner had to be discontinued because corrosion of the graphite prevented the codeposition of plutonium with uranium. The volatilization of zirconium, ruthenium and antimony from the salt pot during dissolution of the irradiated fuel was adequately handled by the in-cell off-gas treatment system.

The degree to which the UO_2 was partitioned from the plutonium showed a strong dependence on the manner in which the salt bath was preconditioned prior to electrolysis. Plutonium decontamination factors of 120, 80, and 20 were obtained when the melt was preconditioned by (1) sparging with chlorine gas while containing particulate graphite, (2) by pre-electrolysis, and (3) by sparging with hydrogen chloride gas, respectively. Each treatment was an attempt to shift the plutonium into the non-depositing $Pu(III)$ state prior to electrolysis. Conditions for partition always became more favorable during the course of a partition electrolysis.

Controlling the enrichment of the PuO_2 in the UO_2 during codeposition was difficult. The problem was attributed to the formation of uranium (IV) which suppressed the formation of the codepositing plutonyl species. The presence of $U(IV)$ in the melt was an unpredictable function of the surface

area of the particulate graphite introduced by corrosion of various graphite pieces in the system. This variability in the reducing power not only caused variation in PuO_2 enrichment between runs but also during the course of a run. Consequently a means of process control was needed during a codeposition to maintain a proper balance of such electrolysis conditions as current density and the plutonium oxidation rate. The method developed in the laboratory for measuring the back EMF of the electrolysis cell showed promise toward this end. The back EMF is sensitive to changes in the plutonium to uranium ratio of the deposit at the deposit-melt interface. This technique should indicate off-standard conditions soon enough to allow proper action to be taken to restore proper balance of the electrolysis conditions.

Fission product decontamination factors obtained in hot cell pilot plant equipment during codeposition were lower than those obtained in the laboratory, probably as the result of poor process control. The major difficulty in removing fission products was in the rare earth and rhodium-silver region of the periodic table. The overall decontamination factor of approximately three obtained from neutron poisoning fission products during pilot plant runs was lower than the value of six desired from economic considerations and indicated processing could not be limited to a single codeposition without further process refinements.

The electrodeposited oxide was readily stripped from the pyrolytic graphite cathode without any apparent carbon contamination. Water washing of the oxide in some cases reduced the chloride content to less than 50 ppm. When the oxygen-to-uranium ratio of the material was too high it was lowered to an acceptable level by hydrogen reduction. Parallel plate crushing of the oxide resulted in 25 to 53% of the material as a coarse (-4 + 10 mesh) fraction compared to the 60% ideally desired for vibratory compaction.

A total of 13.75 kg of UO_2 -2 wt% PuO_2 codeposited in the pilot plant equipment was vibratorily compacted into fuel rods by Ceramic Research and Development personnel. At the present time, 3 fuel rods containing 4.7 kg of the recycled material are undergoing irradiation in the PRTR. The performance has been satisfactory to date.

EQUIPMENT DESCRIPTION AND OPERATION

Hot Cell

Equipment for the Salt Cycle Demonstration was installed in C-Cell of the high-level radiochemistry facility (Figures 3 and 4). The cell (6-ft-wide, 8-ft-deep, and 12-ft-high) was enclosed with 4-ft-thick walls of high density concrete. The cell was equipped with a lead glass viewing window, two master slave manipulators and a 1-ton crane. Various step plugs through the front face of the cell provided access for piping, electrical leads, and instrumentation. A small transfer mechanism through the side of the cell provided an entrance for small pieces of equipment as well as an exit for various samples. A 13-in.-diam hole through the back of the cell coupled with a sliding transfer mechanism provided an access for feed material and an exit for product material and solid waste. The exhaust air from the cell was passed through an absolute filter bank prior to discharge to a stack. To reduce the humidity of the cell air, dry air was blown past the air intake to the cell and reduced the humidity from a nominal 40% relative humidity to below 20%.

Feed Preparation

The starting material for the process was 19 rod clusters of Zircaloy-2-clad, mechanically-mixed UO_2 - PuO_2 fuel rods (Figure 5), which had been irradiated in the Plutonium Recycle Test Reactor. The clusters were first disassembled in the reactor basin and then the fuel rods were bisected in the Radiometallurgy Building with tubing cutters to give half-rods approximately 4-ft long by 1/2-in. diam. Five half-rods were loaded in an aluminum rupture can (Figure 5) and transported to the cell in a 14-ton cask.

After being loaded into the cell, the half-rods were mechanically declad. The decladder (Figures 5 and 6) consisted of a counterweighted air hammer which moved up and down a vertical anvil. A half-rod was inverted and placed against the anvil where it was held in place by an air cylinder atop the unit and an open support at the bottom. The air hammer (operated at 5000 blows per minute) was pushed along the rod with a manipulator and knocked the oxide out of the rod into a receiver which was clamped to the

Front Face Operation

Rear Face Operation

Induction Heating and Electrolysis
Station Pneumatic Control Valves and
Recording Instrumentation

FIGURE 3
Outside-Cell Equipment Arrangement

FIGURE 4
In-Cell Equipment Arrangement

Bisected Fuel Pins and Container

Oxidizer

PRTR Fuel Assembly

Remote Decladding Equipment

FIGURE 5
Feed Preparation Equipment

bottom of the decladder. To prevent release of dust to the cell atmosphere during the decladding operation, a vacuum line from the in-cell off-gas system was connected to the bottom of the decladder at the point where the oxide was discharged from the end of the rod.

The performance of the decladder during the course of the hot cell operation, which involved the decladding of 75 irradiated half-rods, was on the whole quite satisfactory. The extreme vibration experienced by the decladder during operation resulted in some minor problems. At one point the hold down cap which held the fuel rod in place became detached from the air cylinder. Because the air cylinder was welded to the decladder this could not be remedied remotely and the ease of operation of the unit was greatly impaired. The design of the decladder was later revised, making possible the removal of the air cylinder. The only other difficulty occurred when the half-rods were either cut too short or too long. It was not possible to declad the short ones and the long ones had to be sent back to be shortened.

After the desired number of half-rods had been declad, the resulting oxide was oxidized to U_3O_8 with air prior to dissolution in the molten salt. The oxidizer (Figure 5) consisted of a can with an asymmetrical funnel-slide valve outlet. In the throat of the funnel there was a sifter mechanism that promoted discharge of the U_3O_8 powder. The oxidizer outlet flange and clamp were coupled to (1) the decladder where the oxidizer received the oxide, (2) an off-gas line adapter that served as an exit for off-gas during oxidization, and (3) a salt pot lid adapter through which the U_3O_8 powder was discharged to the salt pot. A thermocouple well and an air inlet line to a gas distributor were located on the top of the oxidizer. The heat requirement for the oxidation was furnished by a resistance-wound pot furnace.

The oxidation step, being a batch operation, required a number of mechanical manipulations between batches, which was a definite disadvantage because all manipulation had to be done remotely. Furthermore, considerable difficulty was experienced with the slide valve sticking open or closed because oxide powder became wedged between the valve and the valve

block. Despite these inconveniences the oxidizer did make possible the remote oxidation of the feed material.

Salt Pot System

The salt pot system (Figure 7) included a 20-liter fused silica crucible containing 50 to 70 pounds of molten equimolar lithium chloride-potassium chloride. The salt bath was heated by radiation from an induction-heated Hastelloy B[®] susceptor which also served as a secondary container in case the silica vessel broke.

The induction heating system consisted of a 15-kilowatt, 3-kilocycle motor generator and a capacitor bank which was connected by a water-cooled coaxial cable through the cell wall to an insulated coil. A quartz-sheathed thermocouple immersed in the salt bath signalled a temperature recorder-controller which controlled the field of the motor generator. An alarm bell and automatic telephone dialling equipment were actuated by a power failure of the system.

Coupled to the susceptor was a double-lid and slide-valve assembly. Quartz sparge tubes, quartz thermowells, and graphite electrodes were inserted through the double lid into the molten salt bath. The space between the double lid was kept under a vacuum of a few hundredths of an inch of water and it was from here that the off-gases from the pot were drawn into the off-gas system. The double lid was removable from the assembly, and when its removal was necessary the slide valve provided a positive closure between the salt bath and the cell atmosphere. A perfect seal of the top lid was not achieved and as a result air leaked into the space between the double lid. To keep air away from the salt an argon purge was introduced below the lower lid to maintain a positive pressure above the salt.

To charge oxide feed to the salt pot, the oxidizer was fitted with a salt pot lid adapter consisting of a length of pipe. By inverting the oxidizer the adapter was inserted just through the double lid and a batch

[®]The Union Carbide Company

Fused Silica Pot, Susceptor, Heat Shield, and Coil

Slide Valve Assembly

Double Lid Ready for Dissolution

Oxidizer Being Discharged to the Salt Pot

FIGURE 7
Salt Pot System

of oxide could then be charged to the salt pot. After the oxide was charged to the salt pot, chlorine and hydrogen chloride gases were premixed, dried, and introduced continuously into the salt bath through quartz sparge tubes. Since the oxide was added batchwise, it formed in a pile at the bottom of the pot. Usually during the initial phase of the dissolution an annular quartz gas lift was submerged in the melt to fluidize the oxide and to increase the dissolution rate. After the oxide was dissolved the bath was conditioned with an appropriate gas sparge prior to electrolysis.

To prepare for an electrolysis two rectangular ($3/4$ in. x 4 in. x 36 in.) graphite anodes and a cylindrical (1-1/2-in. diam x 32 in.), pyrolytic graphite-coated cathode were dried and inserted through the double lid into the salt bath (Figure 8). Electrical connections to a dc power supply were made through asbestos insulated leads via nickel-plated, remotely-operable electrical couplings. The anode couplings were attached directly to the graphite anodes, but the cathode connection was made through a nickel adapter that was screwed to the top of the cathode. The dc system consisted of a 10-volt, 200-ampere rectifier with constant current or constant voltage control. Cell voltage was measured through a pair of nickel-plated battery clamps, one on the cathode and one on an anode. The instrumentation included an ampere hour meter, a voltage recorder that measured both the cell and the rectifier voltage, and a current recorder. The rectifier was provided with control of either the cell voltage, the rectifier voltage, or the current.

At the conclusion of an electrolysis, the rectifier and the gas sparges were shut off. The electrical leads and gas lines were disconnected and a transfer mechanism was positioned over the salt pot to remove the double lid and the electrodes (Figure 8). The transfer mechanism was a long stainless steel tube with three lead screws mounted around the outside. These were connected through Penton[®] bearing nuts attached to a lifting ring. Power was supplied to the lead screws through a chain drive from a small reversible air motor. By attaching the lifting ring to the salt pot lid, the

[®]The Hercules Powder Company

Double Lid Ready for Electrolysis

Salt Pot Ready for Electrolysis

Transfer Mech. Mounted on the Salt Pot

Deposit Withdrawn from the Salt Pot

FIGURE 8
Salt Pot System

lid and the electrodes could be withdrawn from the salt pot into the transfer mechanism while the salt pot remained enclosed. Once the lid was inside the transfer mechanism the slide valve on the salt pot was closed and the transfer mechanism was moved to the center of the cell. The lid was disassembled and the cathode, bearing the electrodeposited oxide, was set aside to undergo further treatment. The salt pot lid was fitted for dissolution and returned to the salt pot in reverse of the procedure above. The salt pot was then ready to receive another batch of oxide.

The design of the salt pot system was not necessarily optimum because the emphasis was on early operation of the process. In Table I quartz vessel lifetimes during the remote operations show that, once the initial problems of learning how to cushion a pot properly were overcome, there was no difficulty with pot breakage. Air inleakage into the pot represented a problem and caused concern from a process point of view. Suitable heat

TABLE I

QUARTZ SALT POT LIFE DATA

<u>Quartz Pot Number</u>	<u>Days of Operation</u>	<u>Number of Dissolutions</u>	<u>Number of Electrolyses</u>	<u>Reason for Disposal</u>
1	12	2	1	End of cold uranium runs
2	63	3	4	End of cold U and Pu runs (Pot was also broken)
3	44	4	3	Broken pot
4	147	7	14	End of particular set of runs
5	60	3	6	Put in pot without graphite liner
6	<u>233</u>	<u>6</u>	<u>12</u>	End of hot cell operations
Total	559	25	40	

and radiation resistant seals with proper electrical properties were not developed in time to be applied in the hot cell operation. The induction heating system performed well over the 1.5 years of essentially continuous operation without any maintenance being required. The in-cell circuitry of the

electrolysis system presented a problem because contact resistances at the coupling-electrode junction made it difficult to get the desired current through the system. It was found that the electrical couplings had to be cleaned prior to each electrolysis to remove what was apparently a chloride or oxide film and to ensure that the circuit functioned properly during the course of the electrolysis. Occasionally the nickel cathode adapter worked loose during the course of the electrolysis and caused the current to behave erratically. It was difficult to determine if the adapter was fastened securely to the cathode because this operation had to be performed remotely. Although the transfer mechanism performed its function of removing the lid and the electrodes from the salt pot, it was difficult to handle. Extreme care had to be taken when positioning it over the salt pot because excessive jarring could have broken the fused silica pot. Despite such difficulties the salt pot system did allow evaluation of the process in pilot plant equipment and valuable insight was gained into problem areas which would have to be corrected in order to optimize the system.

Product Treatment

Stripping of the electrodeposited oxide from the cathode and crushing to a desired particle size was accomplished by a stripper-crusher, a hydraulic press equipped with assorted die plates (Figures 9 and 10). The stripper-crusher also cut up used electrodes and spent fuel rods into suitable lengths for waste disposal. The unit consisted of a water reservoir, a pressure booster, a hydraulic cylinder, and associated high pressure valves and piping, all fastened to a heavy I beam frame. The hydraulic cylinder had either a 6-inch stroke under the supply pressure of 100 psig or a stroke of 1.5 in. under a pressure of 2500 psig. A die plate consisting of a single blade fitted to the stripper-crusher stripped the oxide from the cathode as relatively large chunks. Following this operation, a die plate consisting of a series of blades broke the large pieces of oxide into approximately 1/2-in. chunks. These were charged to a wash column where they were washed by the upflow of water to remove adhering chloride (Figure 11). At the completion of the washing step the column was placed in a resistance-wound pot furnace where the oxide was dried with an argon-hydrogen purge.

FIGURE 9
Stripper Crusher and Accessories

SCHEMATIC PIPING DIAGRAM
SEE NOTE 1

1	41	CUT OFF DIE	SH-T4
1	41	CUT OFF DIE SHIM	SH-T4
1	43	STRIPPER DIE	SH-T4
1	44	CRUSHER DIE (PRIMARY)	SH-T4
1	45	CRUSHER DIE (FINAL)	SH-T4
1	46	DIE PLATE	SH-T4
1	47	DIE PLATE	SH-T4
1	48	DIE PLATE	SH-T4
1	49	DIE PLATE	SH-T4
1	50	DIE PLATE	SH-T4
X	51	SUB ASSEMBLY	SH-T4
1	52	FRAMIE	SH-T5
1	53	BAIL	SH-T5
1	54	HAND L	SH-T4
1	55	BRACKET	SH-T5
0	56	SET SCR W/2XUNCAN 5/8" DIA 3/16" THK	SH-T5
4	57	SPRING PLUNGER 5/8" DIA 3/16" THK	SH-T5
1	58	HEX NUT 1/2" DIA 3/16" THK	SH-T5
12	59	NACH BOLT 1/2" DIA 3/16" THK	SH-T5
2	60	NACH BOLT 1/2" DIA 3/16" THK	SH-T5
1	61	GASSETT (PATENT TO PAINT)	SH-T3
1	62	DIE PLATE	SH-T4
1	63	DIE PLATE	SH-T4
1	64	HOUSING	SH-T4
1	65	PIECE CAB	SH-T4
1	66	SHUTTLE 2000 LBS W/2XUNCAN 5/8" DIA 3/16" THK	SH-T5
1	67	SHUTTLE 2000 LBS W/2XUNCAN 5/8" DIA 3/16" THK	SH-T5
1	68	SHUTTLE 2000 LBS W/2XUNCAN 5/8" DIA 3/16" THK	SH-T5
1	69	SHUTTLE 2000 LBS W/2XUNCAN 5/8" DIA 3/16" THK	SH-T5

ITEM	DESCRIPTION	UNIT
1	ASSEMBLY	
1	1. P-PIPE	SH/T 2
1	2. SUPPORT	SH/T 2
1	4. TUBE	SH/T 3
1	5. FLANGE	SH/T 3
4	6. POWER CYLINDER SHIN	SH/T 3
1	7. REMOVER ROUGH	SH/T 3
1	8. REMOVER SHIN	SH/T 3
1	9. CYLINDER ROD EXTENSION	4 SH/T 3 4 SH/T 3
4	10. SPRINGER ROD 1/2" DIA X 1/2" LG	4 SH/T 3 4 SH/T 3
1	11. SCREEN	SH/T 3
1	12. TRAY	SH/T 3
1	13. TROUGH RAY	SH/T 3
1	14. VALVE BRACKET	SH/T 3
1	15. BLOCKER	SH/T 3
1	16. SEALER #AW77 BAR 6 X 1/2" DIA SST RAM HYPAON OF DEW HOLE SEALS 1/2" DIA POSITION 1, 2, 3, 4 POSITION 4, 1 NO PISTON	MILK FLUID POWER
1	17. TANK #AW77 4 BAR 6 X 1/2" DIA HYPAON OF DEW HOLE SEALS 1/2" DIA PORT POSITION 4, 1 BOTTOM PORT POSITION 1, 1 SIGHT GLASS POSITION 1	MILK FLUID POWER
1	18. POWER CYLINDER #AW77 4 BAR 6 X 1/2" DIA SST, STROKE 1/2" ROD END VAL. SEALS 1/2" DIA POSITION 1, 2, 3, 4 CLT PORT 1/2" DIA POSITION 1	MILK FLUID POWER
1	19. CYLINDER 20" DIA 1/2" DIA 1/2" DIA P-PIPE	MILK FLUID POWER
1	20. BALL VALVE #3D101-1	MILK FLUID POWER
1	21. NEEDLE VALVE #2P 280	MILK FLUID POWER
1	22. 6 WAY VALVE #10 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	23. 4 WAY VALVE #10 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	24. 2 WAY VALVE #10 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	25. QUICK CONNECT FLG #3	MILK FLUID POWER
1	26. QUICK CONNECT FLG #3	MILK FLUID POWER
1	27. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
4	28. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	29. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	30. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
4	31. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
4	32. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	33. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	34. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	35. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
1	36. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
4	37. WASH BOLT 1/2" DIA 1/2" DIA 1/2" DIA AIR	MILK FLUID POWER
2	38. ALLEVUT 1/2" DIA 1/2" DIA	SH/T 4
1	39. DIE HOLDER	SH/T 4
1	40. DIE HOLDER	SH/T 4

FIGURE 10
Stripper Crusher Assembly Drawing

FIGURE 10

Wash Column

Sieve Shaker with Sieves in Place

Ball Mill

FIGURE 11
Product Treatment Equipment

The dried oxide was returned to the stripper-crusher where it was crushed to pass through a 4 mesh screen by using a series of recessed die plates. The oxide was then rewashed in a final attempt to reduce the chloride content. After being redried the oxide was sieved into 10, 20, 35, and 65 mesh (Tyler series) fractions. The sieve shaker (Figure 11) consisted of a platform supported by four large helical springs with vibration being supplied by a variable speed out-of-balance motor. After the initial screening the oxide was recycled between the stripper-crusher and sieve shaker until the desired particle size distribution was obtained. Minus 100 mesh oxide fines were produced in a stainless steel ball mill half-filled with 1/2-in.-diam alumina balls (Figure 11). When the oxide had been sized into the desired size fractions it was packaged and sent to the Radiometallurgy Building (327 Building) for vibratory compaction into fuel rod segments.

The stripper-crusher stripped the oxide quite readily from the pyrolytic graphite-coated cathode with essentially no carbon contamination of the oxide. Although the crushing characteristics of the unit were satisfactory, its capacity was small. A major problem was presented by the creation of oxide dust during the crushing operation. This resulted in contamination of the cell and the cell exhaust system, and required frequent changes of the absolute filters.

Off-Gas System

The off-gases from the salt pot and the oxidizer were routed to a caustic scrubber where they were treated with 4M NaOH, passed through an absolute filter and a charcoal filter in series, and discharged to the cell ventilation system. The caustic scrubber (Figure 12) consisted of a 60-gallon reservoir surmounted by a 6-ft-high, 7-in.-diam tower packed with 5 feet of 3/4-in. Raschig rings and fitted at the top with a 6-in.-long section of nickel mesh for de-entrainment. Flanged to the tower outlet just beyond a condensate drain was a removable filter assembly which consisted of a heater, a changeable dust stop, an 8 by 8-in. absolute filter, and a 6-in.-deep bed of charcoal. A vacuum was maintained on the scrubber by means

FIGURE 12
Off-Gas Treatment System Mock-up

of an air jet. The caustic was circulated from the reservoir to the tower at 3 to 5 gallons per minute by an air-driven gear pump. Attached to the scrubber reservoir was a funnel through which was added make-up caustic and 12% hydrogen peroxide to destroy the hypochlorite formed from the chlorine-caustic reaction since it would have been detrimental to the stainless steel waste storage tank. The scrubber was connected to the salt pot by a 2-in.-diam Hastelloy C[®] jumper. The jumper was trapped to prevent a blow-back from the scrubber into the molten salt pot.

The materials of construction of the scrubber presented the major problem in the operation of the off-gas system. Initially, the scrubber was fabricated from Hastelloy C because literature revealed this to be a suitable material to withstand the chemical environment presented by the off-gases from the Salt Cycle process. However, operation of the scrubber for several months revealed severe corrosion of the caustic reservoir at the liquid-gas interface. Attempts to reduce the concentrations of the hydrogen chloride and chlorine gases in the vapor space above the caustic reservoir were unsuccessful and the use of this scrubber was discontinued. A scrubber was then fabricated from polyvinylchloride with the tower of glass fiber reinforced plastic. The caustic reservoir was fitted with a stainless steel shell that provided support for the reservoir and also acted as a secondary container in case it ruptured. The PVC scrubber withstood the severe chemical environment during the course of the hot cell operation but several structural difficulties were encountered. Several broken nozzles and a crack in the top of the reservoir occurred as a result of mechanical stress and possibly the high radiation level in the cell. A dose rate of 2500 rads/hr was observed in the center of the cell during the course of operation.

The gas inlet to the scrubber often plugged with caustic, and the salt pot jumper plugged with entrained salt. These required frequent water flushes and vibrating with an air hammer to maintain the system in an operable condition. The nickel entrainment section in the top of the tower apparently failed during the course of operation because carryover of

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caustic was observed toward the end of the hot cell operation. This entrainment of caustic greatly taxed the filtering system and increased the frequency with which the filter assemblies had to be changed. Approximately every two months a brief shutdown was required to replace either a failed caustic recirculation pump or a failed filter assembly.

Sampling

Samples of the molten salt were obtained with a 41-inch-long, 8-mm-diam quartz tube sealed at one end with a vee notch located one inch from this end. When a sample was to be taken the notched end of a predried tube was introduced through the salt pot lid into the molten salt approximately 12 inches below the salt level so that salt filled that portion of the tube below the notch. The tube was withdrawn from the salt pot and the sample was allowed to freeze. The notched end of the sample tube was then inserted into a collar where a horizontal deflection of the tube broke away the portion below the notch containing the sample. The sample dropped into a small glass vial placed below the collar. The capped sample vial was then placed in a 25-pound lead sample carrier and removed from the cell to be analyzed in a shielded analytical facility.

Grab samples were taken of the oxide feed and electrodeposited product by selecting an approximately 10- to 20-gram portion of the material of interest and placing this in a plastic vial. The vial was placed in a 25-pound lead sample carrier and removed from the cell to be analyzed. In some cases the sample carrier had to be placed inside a 75-pound lead sample carrier to reduce the radiation dose rate from the sample down to an allowable level before being transported to the analytical laboratory.

Typical analysis of these samples included uranium, plutonium, and oxygen to uranium ratio by coulometry; chloride by a pyrohydrolysis technique; and various fission products by gamma energy and radiochemical analyses.

Three shielded sample ports were provided in the cell so that the radiation originating from a sample could be collimated and directed to a scintillation detector located in a removable plug in the cell wall. The

scintillation detector was connected to a 400 channel gamma energy analyzer. Collimators between the three sample ports attenuated the radiation intensity by factors of 1, 8, and 116. The equipment was used primarily for counting salt samples, which were placed in sample holders that could be inserted into the sample ports. The fission products that could be detected were zirconium, ruthenium, cesium, and cerium. Normally a sample was counted for 2 minutes followed by a 2-minute subtraction of the background. To obtain a more definitive cerium count in some cases a 30-minute count of the cerium-144 2.18 mev gamma emission was made. The main problem, as is the case when counting any solid sample, was providing a homogeneous sample and maintaining consistent geometry.

To determine the behavior of various fission products in the off-gas system the caustic scrubber was provided with gas sampling equipment. The equipment consisted of an air jet, a rotameter, and a sample filter in series with four interchangeable sample locations each accessible through a ball valve. The sample locations were at the tower inlet, the tower outlet, the absolute filter outlet, and the charcoal filter outlet. The sample filter was a linear polyethylene filter holder that was remotely inserted into the line to the sample jet and which contained a 2-in.-diam membrane filter and a 2-in.-diam activated charcoal filter paper in series. To obtain a set of gas samples the sample filter was connected between a particular sample location and the line to the sample jet. A gas sample was taken by pulling gas from the particular sample point desired via the sample jet at a given flow rate for a given time interval. After a sample was taken at each sample point the filters were loaded out of the cell and a gamma energy analysis of them was made.

Waste Disposal

During the hot cell operation various liquid and solid wastes were generated. To ensure the continued operability of the cell it was necessary to provide means for routinely removing the waste from the cell.

Depleted caustic from the caustic scrubber and water from the wash column were routed to a 4000 gallon stainless steel waste storage tank located

outside the cell. Periodically the liquid waste in this tank was trucked to the Waste Storage Tank Farms operated by the Chemical Processing Department of the General Electric Company.

Solid waste consisted of quartz tubes, graphite electrodes, fuel rod cladding, failed caustic pumps, burnt out furnaces, failed filter assemblies, and broken salt pots. The sequence of events necessary to remove solid waste from the cell is shown in Figure 13. The waste to be disposed of was placed into a 12-in.-diam by 3-ft-high aluminum waste can. A 7-ton waste cask with a 13-in.-diam by 4-ft-long bore was positioned against a hole in the back of the cell. A large scoop in the cask was pushed through the hole onto a sliding transfer mechanism in the cell. The waste can with a lid in place was laid on the scoop and the scoop along with the can was then pulled into the cask. A ball valve on the cask was closed and the cask was inverted and placed vertically over a hole on a trailer. The trailer was transported to the burial ground where the trailer was positioned over a burial pipe, the cask valve opened, and the waste can discharged to the pipe. During the course of operation about two cans of waste were removed from the cell each month.

PROCESS STUDIES

Decladding

Decladding data obtained in the Salt Cycle Demonstration is shown in Table II. Cold-swaged half-rods irradiated to 2000 and 5000 MWd/tonne

TABLE II

HOT CELL DECLADDING DATA

<u>No. of Half-Rods Declad</u>	<u>Fuel Element No.</u>	<u>Fabri- cation Technique</u>	<u>Composition of Half-Rods</u>		<u>Exposure MWd/tonne</u>	<u>Cooling Time, Days</u>	<u>Declad Time, Min</u>	<u>Waste Loss %</u>
			<u>lb U</u>	<u>gm Pu</u>				
24	5174	Vi-Pac	2.6	5.6	100	300	5	--
14	5120	Vi-Pac	2.6	5.5	400	500	5	--
15	5187	Cold Swaged	2.8	6.1	2100	200	30	--
19	5168	Cold Swaged	2.8	6.2	5300	150	60	0.6
1	5185	Cold Swaged	2.8	6.4	5100	30	60	--
2	5237	Vi-Pac	2.6	10.9	4300	150	5	0.25

Failed Filter Assembly
Being Loaded into Waste Can

Waste Can Positioned on Cask Scoop

Waste Cask Positioned on the Rear Face

Waste Cask at Burial Ground

FIGURE 13
Solid Waste Disposal

required 30 and 60 minutes respectively to be decladded. The cladding from a half-rod irradiated to 5000 MWd/tonne was sectioned and leached with hot concentrated nitric acid to determine the waste loss to the cladding. The uranium loss varied from 0.5% at the open end of the cladding to 0.65% near the end cap with an overall waste loss of 0.6%. In some of the half-rods about 2.5% of the total uranium was left in a large chunk next to the end cap because of insufficient hammering at this point.

Vibratory-compacted half-rods irradiated to 100, 400 and 4300 MWd/tonne were declad in all cases in less than 5 minutes with waste losses between 0.2 and 0.3%. Approximately 30% of the oxide adhering to the cladding was located next to the end cap. In cold pilot plant tests⁽³⁾ vibratory-compacted and cold-swaged fuel rods were each declad in less than five minutes with less than 0.1% of the fuel remaining with the cladding. There were no serious problems with irradiated cladding brittleness and airborne contamination at these fuel burnups.

Oxidation

The $\text{UO}_2\text{-PuO}_2$ was collected from the decladder in the oxidizer pot in 15- to 25-pound batches and air was passed through the oxide bed at 450 °C for 16 to 30 hr to oxidize the UO_2 to U_3O_8 in order to reduce the particle size of the material for dissolution in the salt bath. Laboratory work has shown⁽⁴⁾ that if U_3O_8 and UO_2 particles are about the same size the U_3O_8 will dissolve much faster with chlorine gas in the molten salt bath. Varying the oxygen content⁽³⁾ of the oxidizing gas resulted in air being selected as a suitable compromise between (1) overheating and sintering due to the exothermic reaction and (2) the difficulty of introducing stoichiometric oxygen in reasonable periods of time without entraining oxide in the off-gas.

Although in a large number of cases only a single oxidation was used, sometimes an oxidation followed by a reduction at 600 °C with 8% hydrogen-92% argon and a reoxidation was used to further reduce the particle size⁽⁵⁾ in an attempt to increase the dissolution rate of the material. The method of pretreating the oxide feed prior to dissolution for a number of runs is presented in Table III. During the oxidation step, which was conducted with

TABLE III

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BNWL-355

HOT CELL DISSOLUTION DATA

Run No.	Temp, °C	Gas Sparge			Feed ⁽⁷⁾ Pretreatment	Initial Melt Composition		Feed Composition		Fuel Exposure	Average Uranium ⁽⁸⁾ Dissolution Rate,		Comments
		Time, hr	Rate l/min	Vol% Cl ₂		Vol% HCl	Wt% U	Wt% Pu	lbs U	gms Pu	MWd/tonne	lb/hr	
H1	600	0-103 103-140	3 3	100 67	---	30 hr oxidation	0	0	21	45	100	0.30	(1), (2) @ 70 hr
H3	600	0-20 20-45 45-77 77-90	2 2 3 3	100 --- 67 ---	--- 100 33 100	59 hr oxidation	16	0.11	13	28	100	0.23	(1), (2) @ 29 hr
H5	600	0-6 6-23 23-117	3 2 4	100 --- 75	---	31 hr oxidation	0	0	17	35	100-400	0.08 ⁽⁹⁾ 0.32	Changed from (1) to (3) @ 40 hr, (4)
H6	600	0-18 18-44 44-62 62-90	4 4 2 4	100 50 --- 100	---	31 hr oxidation	6.1	0.13	18	38	400	0.45	(3), (4)
H11	550	0-69 69-100	4 4	12.5 100	87.5 ---	21 hr oxidation	0.8	0.02	14	30	2100	0.50	(3), (5)
H12	550	0-33 33-113 113-132	4 4 4	100 50 ---	---	14 hr oxidation	7.8	0.03	14	30	2100	0.25	(2) @ 73 hr, (3), (5)
H14	550	0-64	4	100	---	16 hr oxidation 17 hr reduction 20 hr oxidation	4.8	<0.01	13	28	2100	0.20	(3), (5)
H19	560	0-140	4	100	---	16 hr oxidation	0	0	14	31	5300	0.05	(2) @ 103 hr, (3), (4)
H25	560	0-84 84-140	4 4	100 50	---	25 hr oxidation 41 hr reduction 40 hr oxidation	2.4	0.11	17	37	5300	0.47	(3), (4), (6)

- (1) The sparge gas was introduced into the melt through two quartz sparge tubes.
- (2) The dissolution was terminated for 48 hr with a 1/2 ℓ/min HCl sparge left on the melt.
- (3) The sparge gas was introduced into the melt through a quartz gas lift.
- (4) The pot contained a graphite liner extending just below the melt level.
- (5) The pot contained a graphite liner which was corroded away and did not extend below the melt level.
- (6) One-sixth of the uranium was not added to the pot until 80 hr after the start of the dissolution.
- (7) In all cases the air or argon-hydrogen flow rate was 1-1/2 ℓ/min. The oxidations were carried out at 450 °C and the hydrogen reductions were performed at 600 °C in all cases.
- (8) Based on the dissolution of the first 50% of the uranium.
- (9) The low rate represented dissolution of first 20% of uranium and the higher one represented that of the next 30%

150- to 500-day cooled fuel, the only significant radioactivity found in the off-gas was that associated with entrained oxide particles.

Dissolution

After the completion of the oxidation step the oxide was charged into the molten salt bath in 15- to 20-pound batches. The salt bath was sparged with dried chlorine, or in some cases a premixture of chlorine and hydrogen chloride gases. The behavior of the uranium and plutonium during dissolution is illustrated in Figures 14 and 15 and pertinent dissolution conditions are given in Table III. Since the gases are relatively insoluble in the salt, good gas-solid contact is essential for rapid dissolution. The oxide must be stirred immediately and continuously after charging into the bath to prevent crust formation on the pile of oxide in the bottom of the crucible. This is illustrated in the case of Run H1 where the dissolution was interrupted for 2 days with the uranium 80% dissolved. As shown in Figure 14, the dissolution continued at a much reduced rate. During these initial dissolutions the sparge gas was introduced into the salt bath through two quartz tubes. In following runs in an attempt to promote fluidization of the oxide and thereby increase the dissolution rate, the sparge gas was introduced into the salt bath through a completely submerged annular gas lift. In Figure 14 for the case of Run H5 in which the dissolution was performed initially with sparge tubes, a fourfold increase in the dissolution rate occurred when switching to a gas lift. Higher gas rates were also possible with the gas lift because splashing of the molten salt into the gas space was decreased.

Average uranium dissolution rates based on the dissolution of the first 50% of the uranium are tabulated in Table III. Although higher dissolution rates were obtained while using a gas lift, runs with low dissolution rates were also experienced. This was attributed to the state of the oxide prior to being introduced into the melt. Detailed analysis of the degree of particle size reduction and conversion to U_3O_8 resulting from the pretreatment step was not obtained because of the radioactivity of the feed material. Particle size proved very important in determining the dissolution rates in laboratory studies.⁽⁴⁾ For this reason attempts to

FIGURE 14
Plutonium and Uranium Behavior During Dissolution

FIGURE 15
Plutonium and Uranium Behavior During Dissolution

increase the dissolution rate by further decreasing the particle size of the material by cyclic oxidation and reduction must be considered inconclusive until a more detailed study is made. The dissolution of the last 10 to 20% of the uranium proved difficult and independent of whether sparge tubes or a gas lift was used, indicating the inability of either technique for providing intimate gas-solid contact of the material on the extreme bottom of the vessel. It is therefore difficult to generalize from the uranium dissolution data beyond the conditions under which they were obtained. Better dissolution rates could probably be obtained by (1) an improved means of introducing and distributing the gas in the pot to assure intimate gas-solid contact, (2) controlled and continuous addition of the oxide to the pot to avoid buildup of the oxide into piles which make it difficult to achieve good gas-solid contact, and (3) a standardized feed pretreatment step so that a reproducible feed possessing a minimum particle size and maximum conversion to U_3O_8 is obtained.

As shown in Figures 14 and 15 a major problem during dissolution was incomplete recovery of the plutonium which resulted from the precipitation of a portion of the plutonium as PuO_2 on the walls of the quartz vessel at the liquid-gas interface. This was largely overcome by inserting a graphite liner that covered the quartz to just below the salt level and prevented the deposition of the PuO_2 at this point and allowed the plutonium to dissolve essentially at the same fractional rate as the uranium. However, it was necessary to discontinue use of the graphite liner at operating temperatures used because graphite corroded from it prevented the plutonium from being oxidized during the codeposition step. Although the graphite liner did not withstand the salt pot environment, this does not rule out the existence of a material resistant to the environment while possessing the same non-affinity for plutonium as the graphite. It might also be possible to take advantage of the beneficial effects of graphite by making controlled additions of powdered graphite to the melt during dissolution so that the melt would be depleted in graphite prior to electrolysis. As can be seen from Table IV, the plutonium recovery problem remained unsolved at the end of the hot cell tests. Better control of the atmosphere above the salt bath

TABLE IVPLUTONIUM RECOVERY DATA

<u>Quartz Pot Number</u>	<u>Pound of UO₂ Charged to Pot</u>	<u>Total Gm Pu Charged to Pot</u>	<u>Gm Pu in Solution at Disposal</u>	<u>Inventory of Pot at Disposal</u>	
				<u>Lb UO₂</u>	<u>Gm Pu</u>
1	42	---	---	20	---
2	50	137	9	1	53
3	69	130	44	22	88
4	123	262	7	0.2	99
5	51	271	78	19	130
6	<u>105</u>	<u>781</u>	<u>2</u>	<u>0</u>	<u>224</u>
Total	440	1581	140	62	594

would probably have improved the plutonium recovery, since nearly complete recovery was obtained with similarly controlled operating variables in the laboratory.⁽²⁾ Leakage of external air containing moisture into the vessel atmosphere was demonstrated in cold pilot plant equipment⁽⁶⁾ identical to that in the hot cell, but suitable heat and radiation resistant seals with proper electrical properties were not developed in time to be applied in the Salt Cycle Demonstration.

Data on the percentages of the uranium, plutonium, and various fission products in the feed present in solution at various times during dissolution of Run H1 are presented in Table V.

TABLE V

PERCENTAGE OF ELEMENT IN THE FEED PRESENT
IN SOLUTION DURING RUN H1 DISSOLUTION

<u>Time, hr</u>	<u>U, %</u>	<u>Pu, %</u>	<u>Zr, %</u>	<u>Ru, %</u>	<u>Cs, %</u>	<u>Sr, %</u>	<u>Y, %</u>	<u>Ce, %</u>	<u>Pm, %</u>
0	0	0	0	0	0	0	0	0	0
17	24	8	3	6	4	21	22	18	22
41	59	26	28	32	66	33	58	46	55
65	78	30	67	34	66	79	63	62	61
90	81	31	24	43	81	95	95	76	84
111	87	56	130	41	86	88	92	82	---
135	96	61	64	59	95	104	106	80	102
147	100	87	126	60	93	99	108	---	99

The run conditions during dissolution are presented in Table III. The constituents in the feed essentially dissolved with the uranium with the exception of the plutonium and ruthenium. The plutonium behavior was as discussed previously. Much of the ruthenium volatilized during the early portion of the dissolution with a 40% loss of ruthenium occurring while the melt was sparged with chlorine only.

The fission products ruthenium, zirconium, and antimony volatilized during the dissolution of Run H2 as shown in Figure 16. With only a chlorine sparge, the high ruthenium volatilization rate obscured the zirconium and antimony activities. The strongly oxidizing conditions in pure chlorine apparently volatilized the ruthenium as the tetroxide. Switching to a chlorine-hydrogen chloride sparge diminished the ruthenium volatilization rate to the extent that it was obscured entirely by the zirconium and antimony activities. The zirconium and antimony probably volatilized as the chlorides. Cold studies⁽⁷⁾ indicate that the bulk of the iodine charged to the salt bath volatilized almost immediately and was present in the off-gas system as a chloride.

Electrolysis - Partition

The partition of UO_2 from plutonium is accomplished by electrodeposition of the uranium with a hydrogen chloride or hydrogen chloride-chlorine gas sparge to hold the plutonium in the trivalent state which will neither react with UO_2 to form an insoluble product, nor electrolytically reduce at the cathode.^(2,8)

Data obtained from partition electrodepositions performed in the hot cell are shown in Table VI. The degree to which a partition was achieved is expressed in terms of a plutonium decontamination factor. The plutonium decontamination factor is defined as the plutonium to uranium ratio in the initial salt bath divided by the plutonium to uranium ratio of the deposited oxide.

The data show the dependence of the plutonium decontamination factors on the manner in which the bath was preconditioned prior to electrolysis. The best partition was achieved when the bath containing particulate graphite

FIGURE 16
Analysis of Off-Gas During Run H2 Dissolution

TABLE VI
HOT CELL PARTITION DATA

<u>Run No.</u>	<u>Pu DF</u>	<u>Deposit Wt., lbs</u>	<u>O/U Ratio</u>	<u>Gas Sparge During Electrolysis liters/min*</u>	<u>% Uranium Removed</u>	<u>Initial Current, amps</u>	<u>Current Eff., %</u>	<u>Temp, °C</u>	<u>Preconditioning of bath</u>
H6	120	6	2.0018	3	26	60	57	590	Carbon dust and chlorine sparge
H15	81	3	2.0068	4	97	50	90	550	Pre-electrolysis
H19	70	14	2.0087	3	89	75	55	550	Pre-electrolysis
H12	22	4	2.0130	3	21	40	56	600	HCl sparge
H1	8	13	2.0072	2	58	97	68	580	HCl sparge
H11	5	10	2.0087	3	58	50	97	540	HCl sparge

* All HCl sparge except Run H6 which was 30 vol% HCl - 70 vol% Cl₂.

was preconditioned by sparging with chlorine. The reaction of the carbon and chlorine with uranyl chloride formed some tetravalent uranium which increased the reducing power of the bath and consequently forced the plutonium into its lower valence state.⁽²⁾ The pre-electrolysis of the salt bath appeared successful in preparing the bath for a partition electrodeposition. The pre-electrolysis was carried out by reversing the electrical leads to the electrodes and electrolyzing for one to two hours with the oxide being deposited on the anodes. The electrical leads were then returned to their proper position and a partition electrodeposition was performed. The pre-electrolysis reduced any reducible plutonium species present and removed uranium oxide complexes, thus drying the bath. Lower plutonium decontamination factors were experienced when the bath was preconditioned with a hydrogen chloride gas sparge, with the decontamination factors showing a strong temperature dependence. This temperature dependence is primarily because plutonium (III) is the favored species at elevated temperatures.^(2,8)

The cross section of a deposit from one of the partition electrolyses is shown in Figure 17. The accompanying photograph shows where micro-drill samples were taken, and the autoradiograph shows the location of the principal beta-gamma emitters in the deposit. The micro-drill samples were analyzed for plutonium and uranium and the plutonium profile across the cross section was generated as shown. The plutonium content was relatively high at the beginning of the electrolysis and decreased during the course of the run. This would indicate that as the last traces of the reducible plutonium species initially present were removed the conditions for achieving a partition became progressively better. This is better illustrated by Figure 18 in which the plutonium decontamination factor from the UO_2 at each instant is shown as a function of the deposit thickness. The plutonium decontamination factor increased from an initial low value of 35 to greater than 250 at the end of the electrolysis with an overall average of 120. The run conditions during this electrolysis are presented in Table VI. Since the plutonium decontamination improved as the electrolysis proceeded, it would be expected that this electrolysis could have been continued until nearly all the uranium had been deposited with an even higher overall plutonium decontamination factor.

FIGURE 17
Distribution of Plutonium and Rare Earths Across a Deposit During
Partition - Run H6

FIGURE 18
Plutonium Decontamination Factor During Partition Electrodeposition
of UO_2 - Run H6

The fission product and transplutonium element behaviors during a partition electrolysis are presented in Table VII as decontamination factors that are averages from all the partition runs. The rare earth fission products,

TABLE VII
AVERAGE FISSION PRODUCT DECONTAMINATION FACTORS
DURING PARTITION ELECTROLYSES

	<u>Uranium Basis*</u>	<u>Plutonium Basis**</u>
Zr	0.80	---
Ru	63	---
Cs	2000	---
Y	---	1.5
Ce	---	4.5
Pm	---	3.0
Eu	---	2.5
Am	---	4.3
Cm	---	8.0

*Defined as the ratio of the element to uranium in the initial melt divided by the same ratio in the deposit.

**Defined as the ratio of the element to plutonium in the initial melt divided by the same ratio in the deposit.

which are the major removable neutron poisons in the fuel, tend to follow the plutonium. The one difference in behavior is in the relative invariance of the rare earths across the cross section of the deposit as shown in Figure 17. The zirconium codeposits with the UO_2 under all conditions. Another measure of this tendency is shown in the autoradiograph presented in Figure 17, which shows that the beta-gamma activity (largely Zr-Nb-95) concentrated in the first UO_2 deposited.

Electrolysis - Codeposition

The codeposition of UO_2 - PuO_2 involves sparging the salt bath with an O_2 - Cl_2 gas mixture which oxidizes the plutonium (III) and (IV) to the reducible plutonyl species.^(2,8) The codeposition mechanism simply involves the co-reduction of the plutonyl and the uranyl species at the cathode. To control the

FIGURE 17
Distribution of Plutonium and Rare Earths Across a Deposit During
Partition - Run H6

TABLE VIII
HOT CELL CODEPOSITION DATA

Run	EF	Deposit		O/U	l/min	Gas Sparge		Initial Melt		Final Melt		Uranium % Removed	Plutonium		CD (amps/cm ²)	Current amps	Current Eff. (%)	Time, hr	Temp, °C	Comments
		wt. lb	wt% Pu			vol% O ₂	vol% Cl ₂	wt% U	wt% Pu	wt% U	wt% Pu		% Removed	% Accounted for						
P3	1.16	10	0.40	2.0045	2	90	10	17.2	0.07	8.2	0.02	55	67	96	0.13	70	66	19	550	1
P2	0.96	17	0.73	2.0107	2	90	10	18.0	0.16	0.8	0.02	97	90	100	0.18	100	78	22	550	1
P1	0.24	14	0.14	2.0045	2	50	50	27.0	0.18	18.0	0.21	44	10	107	0.19	105	66	20	550	1
H8	1.33	8	1.65	2.0836	3	90	10	15.6	0.22	3.0	0.01	75	93	98	0.10	40	47	38	550	2,5,6
H14	1.27	18	0.14	2.0510	3	97	3	17.5	0.02	0.2	<0.01	99	100	120	0.16	85	83	31	550	2,5,6
H9	1.11	9	0.65	2.1230	3	90	10	24.2	0.16	16.8	0.02	41	45	58	0.09	40	31	60	550	2,5
H13	1.06	13	0.72	2.0621	3	90	10	16.9	0.13	5.4	<0.01	76	84	87	0.09	50	52	42	550	2,5,6
H10	0.94	14	0.65	2.0256	3	90	10	18.9	0.15	0.1	0.02	99	94	106	0.12	51	71	36	550	2,5
H2	0.84	13	0.31	2.0156	2	90	10	26.3	0.11	15.5	0.11	55	47	127	0.15	80	58	25	540	2
H3	0.66	16	0.32	---	2	90	10	25.3	0.14	10.8	0.10	69	45	99	0.17	90	83	25	550	2
H5	0.06	16	0.06	2.0043	3	90	10	22.3	0.10	6.1	0.13	84	5	102	0.18	85	94	25	550	2,4
H7	0.02	8	0.02	2.0064	3	90	10	19.2	0.22	15.2	0.24	34	9	110	---	30	48	52	550	2,4
H31	1.55	6	2.89	2.0554	3	50	50	14.7	0.31	11.0	0.20	35	58	118	---	50	30	46	560	3,6
H28	1.54	8	2.07	2.0964	4	50	50	15.4	0.24	9.5	0.02	48	76	82	---	50	40	45	560	3,6
H36	1.17	12	2.02	2.0187	3	50	50	17.0	0.35	6.4	0.09	65	70	91	0.08	45	47	59	560	3,6
H27	0.88	5	2.07	2.0410	4	60	40	9.0	0.24	4.1	0.01	66	62	66	---	30	68	26	560	3,6
H26	0.74	8	1.20	2.0190	4	60	40	15.3	0.28	9.0	0.24	53	41	117	---	50	---	17	560	3,6
H35	0.51	20	1.08	2.0142	3	50	50	18.8	0.45	2.4	0.36	90	46	105	0.06	45	58	67	560	3,6
H30	0.39	22	0.85	2.0056	3	50	50	18.4	0.45	0.1	0.27	99	42	85	---	60	58	70	560	3,6
H33	0.12	6	0.25	2.0019	3	50	50	6.3	0.15	2.1	0.17	75	11	121	0.06	30	75	22	560	3,6,7
H32	0.10	5	0.12	2.0020	3	55	45	11.3	0.15	6.3	0.15	47	4	92	---	35	72	22	560	3,6,7
H23	0.09	7	0.40	2.0072	4	90	10	12.9	0.62	6.6	0.66	58	6	101	---	55	60	23	550	3,4,6
H22	0.03	8	0.07	2.0075	4	50	50	19.5	0.534	12.9	0.62	40	1	104	0.10	55	51	28	550	3,4,6

- 1 - Feed was unirradiated UO₂-0.5 wt% PuO₂. The product was to have a PuO₂ content of 0.5 wt%.
- 2 - Feed was irradiated UO₂-0.5 wt% PuO₂. The product was to have a PuO₂ content of 0.5 wt%.
- 3 - Feed was irradiated UO₂-0.5 wt% PuO₂ plus a plutonium spike. The product was to have a PuO₂ content of 2 wt%.
- 4 - The pot contained a graphite liner.
- 5 - The pot contained a graphite liner which was corroded away and did not extend below the melt level.
- 6 - The anode surface area was reduced by a factor of 3
- 7 - The anodes had been in the melt for a period of 4 days prior to the electrolysis.

enrichment of PuO_2 in UO_2 , the rate of oxidation of the plutonium (III) and (IV) to the plutonyl species must be correlated with the rate of deposition of the UO_2 . To balance these rates in a given salt system at a given temperature involves controlling the $\text{O}_2\text{-Cl}_2$ ratio in the sparge gas and the current density.

In the codepositions performed in the hot cell the emphasis was on achieving an enrichment of one, that is, a deposit having a plutonium to uranium ratio equal to the ratio in the melt. The data obtained from these runs is presented in Table VIII where it is grouped according to the feed material used. The first group of runs were made using unirradiated $\text{UO}_2\text{-0.5 wt\% PuO}_2$ as feed. The feed material for the second group of runs was $\text{UO}_2\text{-0.5 wt\% PuO}_2$ which had been irradiated in the Plutonium Recycle Test Reactor. In the third group of runs the plutonium to uranium ratio of the melt was adjusted by the addition of irradiated $\text{UO}_2\text{-0.5 wt\% PuO}_2$ and a plutonium spike to produce an oxide product having a PuO_2 content of 2 wt%.

As can be observed from the overall enrichment factors (defined as the plutonium to uranium ratio in the deposit divided by the same ratio in the melt) determined for each of the runs, difficulty was experienced in controlling the enrichment of the PuO_2 in the UO_2 . The data show that to attain an enrichment of one required decreasing the current density and/or increasing the oxygen content of the sparge gas. It is also apparent that given run conditions did not necessarily give reproducible enrichments. This is most evident in the cases where the salt pot contained a graphite liner extending below the salt level or where the graphite anodes had been in the salt bath several days prior to the electrolysis. This difficulty was attributed to the formation of uranium (IV) in the salt bath from the reaction of the carbon and chlorine with UO_2Cl_2 . The presence of uranium (IV) suppressed the rate of formation of the plutonyl species,⁽²⁾ and lower than expected enrichments resulted. The presence of uranium (IV) was unpredictable since it was not only present in varying degrees from run to run, but varied throughout the course of a run. The rate of formation of uranium (IV) is a function of carbon surface area and consequently a function of the size and integrity of all carbonaceous materials inserted into the salt bath such as the graphite anodes. Because of the

variability in the reducing power of the salt bath, plutonium oxidation rates varied from zero to high values at which gross precipitation of plutonium as PuO_2 occurred. This resulted in wide variation of the PuO_2 enrichment across the cross section of deposits produced in pilot plant equipment as is shown in Figure 19, where the cross section of a deposit from a codeposition electrolysis is presented. The accompanying photograph shows where micro-drill samples were taken, and the autoradiograph shows the location of the principal beta-gamma emitters in the deposit. The plutonium behavior during this electrolysis was typical of those performed in the hot cell. The relatively low plutonium content at the beginning of the electrolysis was probably due to uranium (IV) being present prior to the start of the run. The uranium (IV) suppressed the rate of formation of the reducible plutonium species and the initial plutonium deposition rate was quite low. However, the uranium (IV) was apparently being oxidized away and as a result a rapid rise in the plutonium deposition rate occurred. The plutonium deposition rate reached a maximum, however, and tailed off during the rest of the electrolysis. This tailing off of the plutonium deposition rate was probably brought about by the corrosion of the anodes which introduced finely divided graphite into the melt. The resulting buildup of uranium (IV) in the salt bath suppressed the rate of formation of the reducible plutonium species and the plutonium deposition rate was progressively diminished during the latter portion of the run. The run conditions during this electrolysis are presented in Table VIII.

Since salt bath conditions during the course of an electrolysis were not invariant, it was apparent that a method of instantaneous process control was needed in which either the presence of uranium (IV) and the valence state of plutonium, or plutonium to uranium ratio of the deposit at the deposit-melt interface could be determined and used to control either the $\text{O}_2\text{-Cl}_2$ ratio or the current density. Cold pilot plant⁽⁹⁾ and laboratory work⁽²⁾ were directed with limited success toward development of spectrophotometric equipment to determine uranium (IV) content and the valence state of plutonium in the salt bath of pilot plant equipment. The most promising tool in the area of process control proved to be the measurement of the back EMF of the electrolysis cell by stopping the electrolysis for short intervals of 5 or 10 minutes.

FIGURE 19
Distribution of Plutonium and Rare Earths Across a Deposit During
Codeposition - Run H2

Laboratory data⁽²⁾ indicate the back EMF of the cell to be a strong function of the plutonium to uranium ratio of the deposit at the deposit-melt interface at a given uranium and plutonium concentration in the melt and a given temperature (Figure 20). Although the back EMF is also dependent on the absolute concentration of uranium and plutonium in the melt (increasing with increasing Pu and decreasing U concentrations), these effects are very slight if the plutonium and uranium ratio in the melt is maintained constant during the course of an electrolysis. Since this ratio should be constant when effecting a codeposition with an enrichment of one, the observation of the back EMF should be useful in determining whether this condition is actually being achieved. Laboratory data for the back EMF as a function of melt composition at an enrichment of one is presented in Table IX.

TABLE IX

BACK EMF OF $\text{PuO}_2\text{-UO}_2$ AT ENRICHMENT OF ONE
(Pyrolytic Graphite Anode: LiCl-KCl , 550 °C)

<u>Melt Composition</u>	<u>Back EMF, Volts</u>
20 wt% U - 0.4 wt% Pu	0.50
10 wt% U - 0.2 wt% Pu	0.51
5 wt% U - 0.1 wt% Pu	0.53

Consequently, if the back EMF is being observed during the course of a codeposition and it shows an increasing trend greater than that expected from uranium depletion of the bath, the oxidation rate of the plutonium is insufficient and the $\text{O}_2\text{-Cl}_2$ ratio of the sparge gas should be increased or the current density should be decreased. If the back EMF shows a decreasing trend the rate of oxidation of the plutonium is too great, PuO_2 is probably on the verge of precipitating, and the $\text{O}_2\text{-Cl}_2$ ratio of the sparge should be decreased or the current density increased.

Since the correlation of the back EMF with the plutonium behavior in the system was not known until very near the end of the hot cell runs, back EMF measurements were made only on the last few electrolyses. The back EMF data taken during the course of one electrolysis is presented along with the plutonium distribution across the cross section of the deposit in Figure 21. The

FIGURE 20
Back EMF as a Function of the Plutonium to Uranium Ratio in a
 $\text{PuO}_2\text{-UO}_2$ Codeposition

FIGURE 21

The Plutonium and Back EMF Behavior During Codeposition - Run H35

plutonium distribution was typical in that it started out relatively low, increased to a maximum when about 30% of the oxide had been deposited, and then tailed off during the rest of the run. The back EMF behaved as predicted from laboratory data with an initial decreasing trend as the result of the increasing plutonium deposition rate, followed by a rapidly increasing trend as the plutonium deposition rate tailed off. During another electrodeposition, for which the plutonium distribution and back EMF data are shown in Figure 22, the oxygen content of the sparge gas was increased temporarily from 50 to 60 vol% over a time interval during which the amount of oxide deposited increased from 20 to 30%. The plutonium distribution during this run behaved initially as the previous one by increasing to a maximum when about 30% of the oxide had been deposited, but from here on its behavior was different. Although it started to tail off as in the previous run, this was only temporary; it started increasing and passed through another maximum when about 75% of the oxide had been deposited. The sharp tailing off of the plutonium distribution as experienced in the first run had apparently been averted by the introduction of excess oxygen into the system, which decreased the reducing power of the melt by oxidizing away the uranium (IV) that would have otherwise suppressed the rate of formation of the reducible plutonium species. The back EMF proved quite valuable as an indication of what was occurring in the melt particularly when changing the oxygen content of the sparge gas. This was a first attempt at using it as a means of process control. Although the plutonium distribution of this deposit was not as uniform as desired, it was certainly more nearly constant than those of previous runs and definitely gave indication of the potential of the back EMF technique in the area of process control.

The behavior of fission products during the codeposition step was of particular interest because a close-coupled recycle system should have the capability of producing $\text{UO}_2\text{-PuO}_2$ relatively free from neutron poisoning fission products. The fission product decontamination factors obtained in hot cell pilot plant equipment and laboratory work are presented in Table X. The decontamination factors are on a plutonium basis, defined as the ratio of the element to plutonium in the initial melt divided by the same ratio in the oxide deposited from it. The data quoted for the pilot plant are the averages

FIGURE 22
The Plutonium and Back EMF Behavior During Codeposition - Run H36

TABLE X

AVERAGE PILOT PLANT AND LABORATORY
FISSION PRODUCT DECONTAMINATION FACTORS

For Plutonium Enrichment of 1

Decontamination Factors are on a Plutonium Basis

<u>Element</u>	<u>Pilot Plant DF</u>	<u>Laboratory DF</u>
Sr	400	1000
Y	1.6	---
Zr*	.8	0.2 - 1.5
Mo*	---	---
Tc	48	---
Ru*	60	20
Rh	3 - 6	3?
Pd	16	---
Ag	---	1?
I	∞	∞
Xe	∞	∞
Cs	2000	3000
Ce	3.9	4
Nd	---	4
Pm	2.6	4
Eu	1.6	3
Am	4.2	6
Cm	6.6	---

*Volatilizes during chlorine-HCl sparge.

of the data shown in Table XI. The lower decontamination factors for rare earths and the greater variability during pilot plant runs than those obtained in the laboratory probably reflect the poor process control and the air in-leakage to the salt bath. The tendency of the rare earths to follow the plutonium is illustrated in Figure 19. The significance of the decontamination factors obtained is shown better in Figure 23. The percentage of removable neutron poisons at reactor discharge for a hypothetical steady-state 10,000 MWd/tonne irradiation cycle is shown as a function of atomic number. The method of calculation and the definition of the ordinate is given in HW-72048.⁽¹⁰⁾ The neutron poisons remaining after processing with the decontamination factors shown in Table X are also shown. The major difficulty in removing neutron poisoning fission products is in the rare earth and in the rhodium-silver region of the periodic table. These results indicate that an overall decontamination factor of approximately 3 was obtained from neutron poisoning fission products during hot cell runs. It is estimated that a decontamination factor of at least 6 is required from total neutron poisoning fission products for a workable flowsheet.⁽¹⁾ It is therefore apparent that processing cannot be limited to a single codeposition in the equipment used here without further process refinements. Implicit in Figure 23 is the assumption that all of the fission products are removed from the salt bath between process batches. Pilot plant and laboratory work⁽²⁾ indicate that it may be possible to accomplish this by electrolysis or precipitation.

Electrolysis - Bath Cleanup

Because it is desirable to have the capabilities for removing neutron poisoning fission products from the salt bath prior to each batch of fuel processed, an electrolysis was performed to demonstrate the capabilities of this approach as a bath cleanup step. The salt bath was sparged with 3-liters-per-minute oxygen while passing a current of 60 amperes. The behavior of various constituents in the salt bath is shown in Table XII.

The electrolysis was carried out for 26 hours at a temperature of 560 °C with 6.2 pounds of oxide being removed from the salt bath. The data from the analysis of the deposit and final melt indicate that the bulk of the fission products were removed with the deposit at the run conditions used.

TABLE XI

FISSION PRODUCT DECONTAMINATION FACTORS DURING CODEPOSITION ELECTROLYSES

<u>Run</u>	<u>Pu EF</u>	<u>Decontamination Factors on a Plutonium Basis</u>								
		<u>ZrNb⁹⁵</u>	<u>RuRh¹⁰⁶</u>	<u>Cs¹³⁷</u>	<u>Y⁹¹</u>	<u>Ce¹⁴⁴</u>	<u>Pm¹⁴⁷</u>	<u>Eu¹⁵⁴</u>	<u>Am²⁴¹</u>	<u>Cm²⁴²</u>
H28	1.54	1.0	13.	540	---	3.1	2.4	1.3	4.3	2.7
H8	1.33	2.8	---	11,000	1.6	2.8	1.4	1.2	2.4	3.5
H14	1.27	0.3	33.	580	1.4	1.1	1.5	1.4	2.3	3.0
H36	1.17	3.3	79.	500	3.5	4.6	2.1	1.6	4.5	6.9
H9	1.11	<0.1	45.	1500	0.5	5.2	5.3	1.4	4.0	6.0
H13	1.06	1.3	180.	13,000	0.8	3.3	1.0	1.0	1.9	2.7
H10	0.94	0.8	<1.	60	0.5	0.9	0.9	1.2	0.8	0.8
H27	0.88	0.6	140.	490	---	1.6	1.2	1.0	1.4	5.2
H2	0.84	0.2	21.	570	2.5	9.4	3.0	3.1	5.5	11.0
H26	0.74	0.3	---	40	---	3.2	6.2	1.9	13.0	20.0
H3	0.66	0.4	170.	900	2.1	5.2	2.6	2.0	4.9	8.1
H5	0.06	0.1	21.	110	1.8	4.2	2.4	1.5	4.2	7.0
H7	0.02	0.6	<1.	110	1.5	6.5	3.2	2.2	5.2	8.8

FIGURE 23

Fission Product Poisons in Plutonium Recycle Reactor Fuel at Steady State Operation

TABLE XIIDATA FROM A SALT BATH CLEANUP ELECTROLYSIS

<u>Element</u>	<u>% Removal from the Salt Bath</u>
Y	98.4
Zr	85.0
Ru	86.0
Cs	< 1.0
Ce	98.1
Pm	72.3
Eu	98.7
U	99.2
Pu	85.2
Am	93.9
Cm	95.7

Plutonium Precipitation Studies

Since the precipitation of the plutonium from the salt bath as PuO_2 offered a means of separating the plutonium from the uranium, a run was performed to determine the degree of plutonium separation that could be attained in pilot plant equipment, as well as the fission product behavior. The salt bath was sparged for 94 hours with a 4-liters-per-minute 95 vol% O_2 - 5 vol% Cl_2 gas mixture at a temperature of 550 °C after which the gas sparge was changed to 100 vol% O_2 with sparging being continued for another 48 hours. During the course of the gas sparge the plutonium and fission product behavior was observed and the data that were obtained are presented in Table XIII. No attempt was made to recover the plutonium because the necessary remotely operable apparatus did not exist. The data indicate that an apparent limiting concentration of 0.01 wt% plutonium was reached and consequently only 92% of the plutonium was precipitated. Observation of the fission product behavior revealed that the cerium essentially followed the plutonium, with yttrium, promethium and europium being precipitated to a much lesser degree. A new technique recently developed in the laboratory^(2,11)

indicates that if an oxygen-chlorine sparge of the bath is immediately followed by a hydrogen sparge that 99% of the plutonium can be precipitated under these conditions.

TABLE XIII

PLUTONIUM AND FISSION PRODUCT PRECIPITATION DATA

Time, hr	Gas Sparge			Pu Conc Wt%	% Pu ppt	% Ce ppt	% Y ppt	% Pm ppt	% Eu ppt
	ℓ/min	Vol% O ₂	Vol% Cl ₂						
0	4	0	100	0.130	0	0	0	0	0
18	4	95	5	0.020	85	-	-	-	-
88	4	95	5	0.015	88	79	17	0	0
94	4	100	0	-	-	-	-	-	-
112	4	100	0	0.015	88	-	-	-	-
136	4	100	0	0.012	91	-	-	-	-
142	4	100	0	0.010	92	92	18	5	2

Off-Gas Treatment

The off-gases from the salt pot which normally contained chlorine and hydrogen chloride were routed to the previously described in-cell off-gas system which consisted of a caustic scrubber, absolute filter, and charcoal bed in series. Because of the volatilization of zirconium, ruthenium and antimony during the operation of the salt pot, particularly during dissolution, appreciable quantities of radioactive caustic waste solutions were generated. While dissolving with chlorine only, caustic waste generation rates were as high as 50 gallons per day. An alternate off-gas treatment scheme was developed in cold pilot plant studies and involved liquefaction of the chlorine⁽⁷⁾ at atmospheric pressure with the possibility of it being re-used for dissolving new fuel. Decontamination factors obtained in the hot-cell off-gas system for the volatile fission products in long-cooled fuel are given in Table XIV. The caustic scrubber removed the halogen gases and a large fraction of the activity from the off-gas stream. In the off-gas from the scrubber antimony, zirconium and ruthenium were probably in a particulate form and were completely removed by the absolute filter. The efficiency of the charcoal bed in removing iodine was not determined because of a limited supply of short-cooled fuel and mechanical difficulties experienced in the sampling system.

TABLE XIV

FISSION PRODUCT DECONTAMINATION FACTORS
FOR OFF-GAS FROM THE SALT BATH

	<u>Caustic Scrubber</u>	<u>Absolute Filter</u>	<u>Overall</u>
Zr Nb-95	14	>2900	>40,000
Ru-103, Ru-106	10	4000	40,000
Sb-125	4	>100	>400

Product Treatment

After the electrodeposited oxide was removed from the salt bath, the oxide was split off the cathode with a wedge mounted in the stripper-crusher. In cold pilot plant studies⁽³⁾ use of porous nuclear grade graphite cathodes had resulted in mechanical difficulties in removing the oxide and intolerably high (100 to 2000 ppm) carbon contents. The difficulty in removing the oxide and the high carbon content was due to mechanical interlocking of the graphite with the UO_2 . Subsequent use of graphite cathodes coated with less than 0.5 mils of pyrolytic graphite produced an oxide which was readily removed with less than 20 ppm carbon in the deposit. Pyrolytic graphite coated cathodes were used during all the pilot plant runs performed in the hot cell with no problems experienced in removing the oxide from the cathode. Analytical services for determination of carbon contamination of irradiated materials were not available. Visual examination of a cathode after a run indicated that it would have been possible to reuse a single cathode for several runs if a means for drying cathodes in the cell had been available.

The oxide was crushed to 1/2-inch chunks and washed with water to remove chloride salts from its surface. This operation reduced the chloride content to 200 to 500 ppm. Further crushing and washing apparently reduced the chloride to less than 50 ppm in some cases. Even lower chloride contents than this are desired for nuclear grade material.⁽¹²⁾ When the oxygen-to-uranium ratio was too high, the product was hydrogen-reduced with 8% hydrogen and 92% argon at 600 °C in the same apparatus used for feed oxidation. The oxygen to uranium ratio of oxide produced from one run was reduced from 2.120 to 2.005 by hydrogen reduction for 24 hours.

The final product to be used for vibratory compaction should have a particle size range approximating 60% -4 + 10 mesh, 20% -35 + 65 mesh and 20% minus 200 mesh for high density compaction. In the hot cell, parallel plate crushing produced the two large size fractions and a ball mill produced the fines. The major problem in the crushing step was attaining 60% of the oxide in the -4 + 10 mesh range. The size fraction distribution of oxide as crushed in the hot cell is presented in Table XV.

TABLE XV

HOT CELL CRUSHING DATA

<u>Size Fraction (mesh)</u>	<u>Average wt%</u>	<u>Range wt%</u>
-4 + 10	40	25-53
-10 + 35	37	33-38
-35 + 65	12	6-21
-65	11	3-18

The size distribution of the oxide as crushed was strongly dependent on the manner the oxide was loaded on the crushing plates, and as a result no correlation between the crushing characteristics and the physical properties of the oxide could be obtained. Overloading of crusher plates overcrushed the oxide and resulted in a low percentage of material in the -4 + 10 mesh range. A detailed analysis of crusher performance was made during the cold engineering studies.⁽³⁾

Product Evaluation

To meet the objective of producing material suitable for in-reactor evaluation, three batches of mixed oxide were refabricated into fuel rod segments. Production of the material consisted of charging to the salt bath 0.5 wt% PuO₂-UO₂ fuel elements irradiated in the Plutonium Recycle Test Reactor to 2000 to 5000 MWd/tonne. When the fuel had dissolved in the molten salt, additional plutonium was added to adjust the plutonium to uranium ratio in the melt so that a product containing a nominal 2 wt% PuO₂ could be codeposited. A summary of the particle size distribution and plutonium content

of the product batches is given in Table XVI and the chemical characteristics are given in Table XVII. Photographs of the cross section of the deposits that made up the respective batches are shown in Figures 24 and 25.

Batch I consisted of material from three electrodepositions (H26, H27, and H28). The run conditions during these electrolyses are presented in Table VIII. Run H27 reflected poor process control which resulted in a wide variation in the plutonium content across the cross section of the deposit as well as a high oxygen to uranium ratio. The more porous section of the deposit had a high plutonium content and as a result when the material was crushed the fine size fraction had a higher plutonium content than the coarser fractions. The increased interstitial void space of this material contributed greatly to the problem of chloride removal. The deposit produced from Run H28 was a more dense material with a much smaller variation in the plutonium content across the cross section and gave indication that a product of good quality could be obtained if proper control of the process could be maintained. The crushing of this material resulted in a more even distribution of the plutonium between the size fractions.

A total of 5.25 kilograms of material from Batch I was vibratorily compacted into ten 20-inch long fuel pins by Ceramic Research and Development personnel. The fuel density of the rods was 81 to 82% of theoretical, although the particle-size distribution was not optimum because an attempt was made to utilize as much of the material as possible. The average PuO_2 content was 2.06 wt%. However since an uncertainty exists as to the chloride content of the material (a portion of the fines was prepared in a polyvinylchloride-lined ball-mill jar), nine of the fuel pins were not charged to the PRTR. The tenth fuel pin was sent to the Material Testing Reactor of the National Reactor Testing Station at Idaho Falls where it was irradiated to about 3×10^{19} fission/cm³ (1042 MWd/tonne).⁽¹³⁾ Results of the postirradiation examination of the fuel pin revealed no unsatisfactory fuel characteristics.^(14,15)

The second batch of oxide consisted of material from two electrolyses. The quality of the material from the two deposits represented two extremes. The material from Run H30 was of very high density but contained only half of

TABLE XVIPRODUCT SIZE DISTRIBUTION AND COMPOSITIONBatch I

(5.25 kilograms)

<u>Mesh</u>	<u>Wt%</u>		<u>Wt% PuO₂</u>
-4 + 10	40	10	0.9
		12	1.1
		18	1.5
-20 + 65	40	12	1.2
		12	2.6
		16	1.9
-100	20	6	1.8
		8	6.8
		6	2.7

Batch II

(4.7 kilograms)

<u>Mesh</u>	<u>Wt%</u>		<u>Wt% PuO₂</u>
-4 + 10	55		1.0
-20 + 65	25.2	11.0	1.0
		14.2	3.7
-100	19.8	5.6	1.0
		14.2	5.1

Batch III

(3.8 kilograms)

<u>Mesh</u>	<u>Wt%</u>		<u>Wt% PuO₂</u>
-4 + 10	55		1.8
-20 + 65	25		2.0
-100	20		2.6

TABLE XVII

PRODUCT CHEMICAL CHARACTERISTICS

<u>Batch No.</u>	<u>Weight UO₂-PuO₂ kg</u>	<u>Number of Deposits Used</u>	<u>Number of Segments Fabricated</u>	<u>Wt% PuO₂ Range</u>	<u>Avg.</u>	<u>Oxygen-* to- Uranium Ratio</u>	<u>Chloride ppm</u>	<u>Oil ppm</u>	<u>Comments</u>
I	5.25	3	10	0.9-1.8 1.1-6.8 1.5-2.7	2.06	2.0190	30 - 700	---	Was not charged to the PRTR due to high chloride contamination. One segment has undergone success- ful irradiation in the MTR.
II	4.70	2	9	1.0 1.0-5.1	1.96	2.0058	63	<50	Presently under- going irradiation in the PRTR.
III	3.80	1	7	1.8-2.6	2.01	2.0050	100	<50	Possible future irradiation in the PRTR.

*After H₂ reduction.

Run H26

Run H27

Run H28

FIGURE 24
Cross-Section of Deposits in Batch I Refabricated into Fuel Rods

Run H30 - Batch II

Run H31 - Batch II

Run H36 - Batch III

FIGURE 25
Cross-Section of Deposits in Batches II and III Refabricated into Fuel Rods

the desired plutonium enrichment while the material from Run H31 contained considerable interstitial void space and a higher than desired plutonium enrichment that varied widely across the cross section of the deposit.

A total of 4.7 kilograms of oxide from Batch II was refabricated into 9 fuel pins which were screwed together to form three 60-inch-long fuel rods. These rods were then assembled into a replaceable-rod-type PRTR fuel element which was charged into the PRTR rupture loop, irradiated to 600 MWd/tonne discharged and visually examined for defects.⁽¹³⁾ It was then returned to the reactor and has been irradiated to 1450 MWd/tonne at a maximum fuel temperature of 2200 °C. Goal exposure is 5000 MWd/tonne.

Batch III was composed of material entirely from one electrolysis. The deposit was relatively dense, having the desired plutonium enrichment with much less variation than experienced in previous runs. The comparison of the properties of this material with previously produced material indicates that during this last codeposition a much closer approach to desired process control was achieved than at any other time. A total of 3.8 kilograms of this material was refabricated⁽¹⁵⁾ into 7 fuel pins that will undergo future irradiation in the PRTR.

The effect of chloride on cladding corrosion has been investigated by L. A. Pember and R. C. Smith,⁽¹⁶⁾ who irradiated mixed oxide fuels containing 200 and 300 ppm chloride as AgCl to 7000 and 4500 MWd/tonne, respectively. The fuels were operated with molten cores, but there was no apparent corrosion of the Zircaloy cladding.

The presence of localized high concentrations of $U^{235}O_2$ has been shown⁽¹⁷⁾ to be unimportant in causing local high temperatures because the enriched material was rapidly dispersed by a high rate of fuel homogenization during the early stages of irradiation. Similar behavior would be expected with PuO_2 .

CONCLUSIONS AND RECOMMENDATIONS

The mechanical decladding of irradiated half-rods was on the whole quite satisfactory. The time necessary to declad cold-swaged half-rods increased directly with fuel burn-up while for vibratory compacted half-rods it did not. The waste losses during decladding were higher for irradiated fuels than for

unirradiated fuels and were dependent on the fabrication technique. The decladder mechanism could be improved by establishing the capability for decladding rods of varying lengths and motorizing the air hammer movements to decrease manual manipulations. To achieve increased throughput, consideration should be given to decladding entire fuel assemblies at one time.

The dissolution of the oxide proceeded at slower rates than expected from cold pilot plant studies. This was due in part to the lack of intimate gas-solid contact and consistent preconditioning of the feed during the oxidation step. The following recommendations are presented as possible means of improving the dissolution rate:

- (1) Improve the manner of introducing and distributing the sparge gas in the salt pot to assure intimate gas-solid contact.
- (2) Provide continuous and controlled addition of the oxide to the salt pot to avoid the excess manipulations required in a batch transfer and the buildup of the oxide into piles on the bottom of the pot, which make it difficult to achieve good gas-solid contact.
- (3) Modify the feed pretreatment step such that a reproducible feed possessing a minimum particle size and maximum conversion to U_3O_8 is obtained. The cyclic oxidation and reduction of the feed should be investigated further as a means of further reducing the particle size of the material. Also, the use of a fluid or agitated bed concept should be investigated not only for producing a feed with uniform properties but also to provide continuous feeding.

The incomplete recovery of the plutonium during dissolution presented a problem that remained essentially unsolved at the end of the hot cell runs. The problem was attributed to the leakage of moist air into the gas space, which caused the plutonium to precipitate and adhere to the side of the quartz pot at the gas-liquid interface. The following suggestions are offered as possible solutions to the problem:

- (1) Improve atmosphere control above the melt by an improved lid design. A pressurized lid concept that was investigated⁽⁶⁾ might be applicable. A completely inert cell atmosphere, though expensive, might greatly improve process performance.
- (2) Investigate the possibility of making controlled additions of graphite to the melt during dissolution to hold the plutonium in solution so that the melt is depleted of graphite prior to a codeposition electrolysis.

- (3) Evaluate materials for a pot liner that would be resistant to the salt pot environment while possessing the same lack of affinity for plutonium as graphite.

The partitioning of the uranium from the plutonium depended on the condition of the melt prior to electrolysis and improved as the electrolysis progressed. Although a plutonium decontamination factor of over 100 was not obtained while depleting the salt bath of uranium, there is no reason to believe this could not be done if the melt were conditioned properly prior to electrolysis. Further refinement of the partition electrolysis could be adequately studied in a glove box facility with unirradiated plutonium and uranium.

The codeposition of plutonium and uranium required a delicate balance of electrolysis conditions. This balance was difficult to attain because of changes in melt conditions brought on by the introduction of particulate graphite from corrosion and poor atmosphere control as a result of the in-leakage of moist air. It is apparent that refinement of the codeposition step requires establishing a process control technique and stabilizing melt conditions by an improved salt pot design.

Improvement of the salt pot design should entail a revised lid design to prevent air in-leakage and the replacement of all graphite in the system (such as the anodes) with pyrolytic graphite or a suitable substitute to eliminate the graphite corrosion problem. The use of the back EMF technique for process control should be investigated further, along with the continued development of spectrophotometric equipment to determine the uranium (IV) content and the plutonium valence state in the melt.

It is suggested that consistent control of the codeposition step be demonstrated in optimized engineering scale equipment with unirradiated uranium and plutonium before the process is again committed to the processing of irradiated fuel. It is anticipated that improvement of the plutonium behavior in the system will also result in increased fission product decontamination factors. Since rare earth fission products are of prime concern from a neutron poisoning standpoint their behavior could also be demonstrated in conjunction with the recommended plutonium studies.

Parallel plate crushing proved to be quite slow and it is recommended that for increased throughputs that the use of a roll-crusher or similar equipment be investigated. Considerable release of radioactivity to the cell as a result of dusting during crushing of the product was experienced and indicates the need for containment for this operation. This is also true for any transfers of the crushed product between containers.

In future development of this process consideration should be given to the following factors that were not investigated in the Salt Cycle Demonstration.

- (1) Off-gas treatment by chlorine liquefaction to trap radioiodine and reduce caustic waste by recycling chlorine.
- (2) The processing of fuel values from occasional broken crucibles.
- (3) The recovery of cesium and strontium from the salt bath after they have accumulated for many processing cycles.
- (4) The problems associated with process scaleup to service a 1000 MW(e) reactor (about 1 ton per week).
- (5) The process limitations imposed by criticality.

In regard to the question of criticality, the precipitation of plutonium in the salt bath can result in the buildup of PuO_2 in the system. The minimum critical mass of plutonium as PuO_2 when fully reflected and unmoderated is about 12 kg.⁽¹⁸⁾ Geometry control requirements based on a plutonium density of 10 g/cc are very strict with a maximum safe cylinder diameter of <3.8 in.⁽¹⁹⁾ Water or other moderating materials must be rigorously excluded from the salt pot system to allow these limits. However, in the product treatment steps such as washing, which must be separated from the salt pot system, equipment can be designed to meet geometry control limitations for aqueous systems containing UO_2 - PuO_2 .

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REFERENCES

1. R. W. McKee. Economic Evaluation of Close-Coupled Fuel Processing with Plutonium Recycle. BNWL-28. January, 1965.
2. G. E. Benedict, L. G. Morgan, and R. A. Nixon. Plutonium Chemistry of the Salt Cycle Process, in preparation, December, 1966. Pacific Northwest Laboratory, Richland, Washington.
3. G. Jansen, Jr., L. K. Mudge, and P. W. Smith. Engineering Development of the Salt Cycle Process, BNWL-354. December, 1966.
4. "Research and Development on Fuel Processing," Reactor Fuel Processing Quarterly, vol 3, no. 4, p 34. October, 1960. Argonne National Laboratory.
5. S. Strausberg and T. E. Luebben. Chemical Pulverization of Sintered Uranium Dioxide Bodies-Part I, NAA-SR-3910. August 1, 1959.
6. G. R. Bloom. Melt Atmosphere Control Studies for the Salt Cycle Process, BNWL-CC-372. Pacific Northwest Laboratory, Richland, Washington. April 26, 1966.
7. L. K. Mudge and J. R. Lundquist. Chlorine Recovery and Radioiodine Behavior in the Salt Cycle Process, BNWL-279. June, 1966.
8. G. E. Benedict and R. A. Nixon. Hanford Salt Cycle Process I. Plutonium Chemistry, HW-SA-3622. General Electric Company, Richland, Washington. July 17, 1964.
9. G. R. Bloom. Detection and Oxidation Rate Studies of U(IV) in the Salt Cycle Process, BNWL-CC-373. Pacific Northwest Laboratory, Richland, Washington. April 26, 1966.
10. G. Jansen, Jr. Fission Product Poisoning in a Model Plutonium Recycle System with Close-Coupled Reprocessing, HW-72048. January 2, 1962.
11. G. E. Benedict, W. R. Bond, G. Jansen, Jr., L. G. Morgan and J. R. Lundquist. Status of the Salt Cycle Process for Processing Oxide Fuels. BNWL-SA-205. Pacific Northwest Laboratory, Richland, Washington. September 3, 1965.
12. H. J. Anderson. Specifications for Nuclear Grade Mixed Oxides (UO_2 - PUO_2), Hanford Salt Cycle Compactible Powder, HW-84512-RD. November 16, 1964.
13. Ceramics Research and Development Quarterly Report, January-March 1965, Pacific Northwest Laboratory, Richland, Washington, BNWL-91.
14. Ceramics Research and Development Quarterly Report, April-June, 1965, Pacific Northwest Laboratory, Richland, Washington, BNWL-150.
15. Ceramics Research and Development Quarterly Report, July-September, 1965, Pacific Northwest Laboratory, Richland, Washington, BNWL-198.
16. L. A. Pember and R. C. Smith. The Effect of Chloride Contamination on Zircaloy-2 Clad Mixed Oxide Fuel, in preparation, December, 1966. Pacific Northwest Laboratory, Richland, Washington.

REFERENCES Continued

17. Quarterly Progress Report, Research and Development Programs Executed for the Division of Reactor Development, October-December 1961, p 58, General Electric Company, Richland, Washington, HW-73100. May 1, 1962.
18. C. L. Brown. Unpublished data, Pacific Northwest Laboratory, Richland, Washington, 1965. Personal communication.
19. Physics Research Quarterly Report, July, August, September, 1965, Pacific Northwest Laboratory, Richland, Washington, BNWL-193. October 15, 1965.

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