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By

G. E. Benedict and R. A. Nixon

Chemical Research
Chemical Laboratory
Hanford Laboratories

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HANFORD SALT CYCLE PROCESS I. PLUTONIUM CHEMISTRY

By

G. E. Benedict and R. A. Nixon*

The Salt Cycle Process is an outgrowth of exploratory research on pyrochemical reprocessing approaches initiated about five years ago at Hanford Laboratories in behalf of the Plutonium Recycle Program. It is a concept which shares the objectives of all close-coupled reprocessing schemes in that it seeks to achieve economies by effecting conversion of short-cooled irradiated fuel to workable recycled fuel with a minimum number of simple remote manipulations. It is aimed specifically at the reprocessing of UO_2 - PuO_2 based fuels for recycle to thermal heterogeneous reactors.

The principle steps in the Salt Cycle Process are (Figure 1): 1) fuel-clad separation; 2) oxidation of the UO_2 to U_3O_8 ; 3) dissolution of the U_3O_8 - PuO_2 material in a molten chloride salt by reaction with chlorine and HCl ; 4) recovery of UO_2 by electrolysis, partly decontaminated from fission products, either freed of plutonium oxide or enriched with it; and/or 5) recovery of PuO_2 by precipitation, partly decontaminated from fission products and uranium.

Crystalline UO_2 separated from PuO_2 is electrodeposited from a molten chloride solution of uranyl chloride and plutonium III chloride by maintaining a dry, oxygen free, chlorine gas blanket in the cell vapor space.

Crystalline UO_2 - PuO_2 solid solutions are prepared by electrolyzing a solution of their chlorides in molten alkali chlorides while sparging the melt with oxygen-chlorine gas mixtures.

Plutonium dioxide is precipitated as dense black crystals, relatively free of uranium oxides by oxygen-chlorine sparging if conditions are properly adjusted.

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All electrolytic reactions may be carried out at a temperature of 550° C, which is far below the melting points of the oxides, but the products are crystalline and have near-theoretical densities.

The electrolytic reaction was reported as early as 1888 by Hampe⁽³⁾ who obtained UO_2 by the electrolysis of molten uranyl chloride. Extensive studies of this reaction, as it occurs in molten chloride salt solutions of uranyl chloride, have been reported in recent years by Robins⁽⁴⁾, Wilks⁽⁵⁾ and Chalkley⁽⁶⁾ in England; Van Lierde and co-workers⁽⁷⁾ in Belgium; and by Stromatt⁽⁸⁾ and Scott and Widge⁽⁹⁾ at Hanford Laboratories. Therefore, the preparation of uranium dioxide by electrolysis of uranyl chloride in a molten chloride media will be discussed here only as it pertains to UO_2 - PuO_2 separation and co-deposition. The primary function of this paper is to describe the recovery of plutonium in the Salt Cycle Process and provide a progress report on known chemistry of plutonium in molten chloride media.

EXPERIMENTAL

Equipment

Quartz or vycor tubes fitted with lavite caps were used as the melt containers in all experiments. The furnaces used in these investigations were designed and constructed at Hanford (Figure 2). They were conventional nichrome-wound resistance furnaces with windows added for viewing and illumination. This feature allowed continuous observations to be made during electrolyses and precipitations.

A glove box equipped with inlet and outlet air flow control valves and operated with an atmosphere of dried compressed air, provided an environment in which plutonium bearing, hygroscopic melts could be used. The majority of the electrolyses were made with an Electro Laboratories Model PS-2 D.C. power supply. In some cases a Ag/AgCl reference electrode was used to control cathode potential, but most electrolyses were made at constant current.

Salt Systems

Early salt cycle studies were made in the equimolar NaCl-KCl melt, but its high melting point (667°C) allowed experimentation only in a limited temperature range ($700^{\circ} - 800^{\circ}\text{C}$). Other lower melting alkali chlorides were investigated in order to use temperature as a process variable.

The salt systems studied, arranged in the order of increasing ease of PuO_2 dissolution, are: 2.5 LiCl-NaCl, 2.5 LiCl-KCl, LiCl-KCl, and more briefly, LiCl-CsCl and pure CsCl. The increase in ease of dissolving PuO_2 in these melts is ascribed to the increase in stability of the plutonium chlorides in KCl and CsCl melts.

The majority of these laboratory scale electrolysis and precipitation studies were made using about 150 grams of total melt containing 20 weight per cent uranium and 0.2 weight per cent plutonium. In one method of melt preparation, the proper amounts of U_3O_8 and PuO_2 were added to the selected molten salt and dissolved in Cl_2 and HCl. A sparge of HCl was continued for at least two hours after all solids had dissolved, before the melt was considered ready for experimentation.

Melts possessing the same properties may be prepared in less time by melting $\text{UO}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ with the salt flux in an HCl gas stream and then adding PuCl_3 after the melt reached the desired temperature. The two-hour HCl sparge must still be used to bring the melt to a constant starting condition.

In larger equipment, the HCl sparge time necessary to dry the melt and remove excess oxide is much longer than two hours. The humidity in the surrounding air also seems to be a factor if the system is not properly sealed.

Plutonium Chemistry

Before discussing processing steps in detail, a brief description of the known chemistry of plutonium in molten chloride media is necessary. The following spectra (Figure 3) were measured by J. L. Swanson⁽¹⁰⁾ at Hanford Laboratories.

Plutonium(III) is the stable valence when the melt is sparged with HCl. Plutonium(III) is oxidized to a mixture of (III) and (IV) by chlorine gas, the IV/III ratio depending on the temperature, salt system, and the partial pressure of chlorine.

Plutonium(III) and (IV) are oxidized to plutonyl(VI) by oxygen-chlorine gas sparging. Removal of chlorine from the solution of plutonyl(VI) by sparging with helium results in a spectrum which is predominately plutonyl(V). The remaining plutonyl(VI) peaks are subtracted and the spectrum of pure plutonyl(V) is obtained.

UO₂ Deposition Free of PuO₂

Plutonium was first successfully separated from uranium in the Salt Cycle Concept using the NaCl-KCl melt system. The UO₂ was removed by cathodic deposition while maintaining a moisture-free, chlorine gas blanket over the melt, but this separation (D.F. = 200) was more a function of the operating temperature than the melt system. High separation of plutonium from the electrodeposited UO₂ depends on holding the plutonium in the trivalent state which will neither react with UO₂ to form an insoluble product, nor electrolytically reduce at Salt Cycle cathode potentials. Plutonium(III) becomes the predominant valence at elevated temperatures in chlorine-saturated melts, and the UO₂-PuO₂ separation improves for this reason with increased temperature as shown in Figure 4.

Higher valences of plutonium are more stable in melts prepared from the higher weight alkali chlorides and therefore the UO₂-PuO₂ separation drops when using these melts as shown in Figure 5.

PuO₂ Precipitation

The addition of SnO₂ to a chlorine saturated Salt Cycle melt was the first successful method found to carry plutonium without precipitation of gross amounts of the uranium (Figure 6). It was then discovered that oxygen-chlorine gas mixtures would precipitate PuO₂ directly, producing dense, black PuO₂ crystals. The PuO₂

precipitation mechanism at the time was thought to be a simple exchange of oxide for chloride in the Pu(IV) chloride to form PuO_2 . Since Swanson obtained the spectrophotometric evidence for plutonyl(V) and (VI) in 1963, the mechanism is now believed to involve decomposition of these higher oxidation state chlorides to PuO_2 and Cl_2 .

Codeposition of UO_2 - PuO_2

Codeposition of UO_2 - PuO_2 was first accomplished by sparging an electrolysis cell containing NaCl-KCl melts at 750°C with moist air. The mechanism of this codeposition is not understood, but it seems to have involved an electrophoretic migration of the finely divided PuO_2 precipitated by the moist air. The codeposits prepared in this manner were porous, had low density and the O/U ratio was greater than 2.1.

Codeposition was next attempted in chlorine sparged LiCl-KCl melts at lower temperature. It was hoped the UO_2 - PuO_2 would codeposit in a manner analogous to the UO_2 - ThO_2 deposition where the ThCl_4 was known to react with UO_2 to give ThO_2 and UCl_4 . Plutonium(IV) chloride was shown to exist in chlorine saturated LiCl-KCl melts at temperatures below 675°C by Gruen and coworkers at Argonne⁽¹¹⁾. However, codeposition of PuO_2 with UO_2 could not be obtained by chlorine sparging the electrolysis cell at 550°C . The Pu(IV) chloride - UO_2 metathesis reaction only goes well enough to be an annoyance when trying to separate PuO_2 from UO_2 .

Oxygen-chlorine mixtures were first used in codeposition attempts as a sparge gas in an attempt to produce plutonium(IV) oxychloride which hopefully could be reduced at high potential to codeposit plutonium suboxide with UO_2 . However, cathode voltage made little difference on the amount of codeposition obtained.

The major part of the codeposition work cited here was done before the mechanism of the codeposition was explained. Plutonyl(V) and Plutonyl(VI) chlorides were believed to be unstable in molten alkali melts because of the thermal instability of the pure compound. Swanson's spectrophotometric evidence for plutonyl(V)

and (VI), plus our observation that PuO_2 can be obtained by electroreduction of the plutonium in $\text{O}_2\text{-Cl}_2$ sparged solutions, shows the codeposition mechanism to be simply electroreduction of the plutonyl and uranyl species at the cathode.

To control the codeposition enrichment of PuO_2 in UO_2 , the rate of oxidation of plutonium(III) and (IV) to the plutonyl species must be balanced against the rate of deposition of UO_2 .

Important variables in the codeposition then are temperature, $\text{O}_2\text{-Cl}_2$ ratio in the sparge gas, salt system, starting current density, and rate of cell current flow. The effect of some of these important variables are shown in Figures 7, 8, 9, and 10.

In the laboratory, enrichments as high as 170 and deposits containing up to 70 weight per cent PuO_2 have been prepared by this codeposition technique.

Fission Product Decontamination

The rare earth fission products were the only group studied extensively in the laboratory-scale salt cycle work. The rare earths account for about fifty per cent of fission product nuclear poisoning.

The rare earths separate from UO_2 in partition electrolyses by factors as high as 2000. The rare earth decontamination factors from plutonium in the PuO_2 precipitations are greater than 100. However, the rare earth decontamination factors in the codeposition of solid solutions of $\text{UO}_2\text{-PuO}_2$ (Pu basis) are only 3 to 6. The low rare earth decontamination in codeposition electrolyses may be caused by a reducible species of rare earth giving a solid product, or the UO_2 product may be altered enough by $\text{O}_2\text{-Cl}_2$ sparging that a reaction occurs between the uranium oxide and rare earth chloride giving a solid rare earth product.

Figure 11 shows the present laboratory flowsheet for salt cycle, which would give satisfactory rare earth decontamination and involves using a partition UO_2 electrolysis and PuO_2 precipitation step followed by either mechanical mixing or a second codeposition cycle.

Chloride Problem

The chloride contamination in washed partition type UO_2 has been measured as low as 10 ppm. Chloride contamination in precipitated PuO_2 is not a problem since the product can be heated to high temperatures in oxygen gas to remove chloride.

The codeposits of washed UO_2 - PuO_2 containing 0.5 to 3.0 weight per cent PuO_2 were contaminated with 80 to 100 ppm chloride. Hydrogen reduction and vacuum outgassing lowered the chloride contamination to the 15-20 ppm range.

Conclusion

The plutonium recovery methods in the Hanford Salt Cycle Process have been improved considerably since earlier publications^(12, 13). The process now can produce UO_2 , PuO_2 , and UO_2 - PuO_2 solid solutions. The most pressing problem remaining could be solved by improving the decontamination for fission product nuclear poisons.

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HANFORD SALT CYCLE - SUMMARY FLOWSHEET

FIGURE 1

SEE-THROUGH FURNACE ARRANGEMENT

FIGURE 2

ABSORPTION OF Pu IONS

LiCl-CsCl Eutectic - 400 C

0.0089 Molar Pu - 3.3 cm Cell

Carry 14 H Spectrophotometer

FIGURE 3

PARTITION AS A FUNCTION OF TEMPERATURE C
LiCl-KCl Melt - Cl₂ Sparge

<u>Temperature C</u>	<u>Plutonium Separation Factor</u>
475	19
550	13
625	45
700	130

FIGURE 4

PARTITION VS MELT SYSTEM
550 C - Cl₂ Sparge

<u>Melt System (Mole Ratios)</u>	<u>Plutonium Separation Factors</u>
2.5 LiCl-NaCl	130
2.5 LiCl-KCl	100
LiCl-KCl	13
LiCl-CsCl	2

FIGURE 5

PuO₂ PRECIPITATION
575 C

Salt System (Mole Ratios)	Carrier (1 gm SnO ₂ /40 mg. Pu)		50% O ₂ - 50% Cl ₂ Sparge	
	% Pu ppt	U Sepn. Factor	% Pu ppt	U Sepn. Factor
2.5 LiCl-NaCl	90	500	85	600
2.5 LiCl-KCl	28	140	90	1100
LiCl-KCl	10	40	No ppt	----

FIGURE 6

UO₂ - PuO₂ CODEPOSITION

Plutonium Enrichment - V. S. Oxygen Content of Sparge

LiCl - KCl; 550 C; Starting Current Density (0.75 amp/cm²)

32 to 48 Percent of U Deposited

<u>Percent O₂ in O₂ - Cl₂ Sparge</u>	<u>Enrichment Factor $\frac{\text{Pu/U (Deposit)}}{\text{Pu/U (Starting Mel)}} \frac{\text{Pu/U (Deposit)}}{\text{Pu/U (Starting Mel)}}$</u>
0	0.077
20	0.067
40	0.91
60	1.1
80	1.2
100	1.5

FIGURE 7

UO₂ - PuO₂ CODEPOSITION
PuO₂ Enrichment V. S. Starting Current Density
LiCl-KCl, 550 C, 50% O₂ - 50% Cl₂ Sparge
40 to 48 Percent of U Deposited

<u>Starting Current Density</u> amps/cm ²	<u>Enrichment Factor</u>
0.75	1.1
0.38	1.7
0.19	2.0

FIGURE 8

UO₂ - PuO₂ CODEPOSITION

PuO₂ Enrichment vs Cell Temperature

LiCl-KCl; 60% O₂ - 40% Cl₂ Sparge; 0.75 amp/cm² Starting Current Density
40 to 48 Percent U Deposited

<u>Temperature, C</u>	<u>Plutonium Enrichment Factor</u>
475	0.37
550	1.1
625	1.7
675	0.53

FIGURE 9

UO₂ - PuO₂ CODEPOSITION

PuO₂ Enrichment V. S. Salt System

LiCl-KCl; 550 C; 50% O₂ - 50% Cl₂ Sparge; 0.2 amp/cm²

4 to 10 Percent of U Deposited

<u>Salt System (Mole Ratios)</u>	<u>Enrichment</u>
1.5 LiCl - KCl	3
LiCl - KCl	6
LiCl - CsCl	13

FIGURE 10

PRESENT LABORATORY FLOWSHEET FOR MAXIMUM RARE EARTH DECONTAMINATION

FIGURE 1A

II-4A-362