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THE PREPARATION OF URANIUM DIOXIDE
FROM A MOLTEN SALT SOLUTION OF URANYL CHLORIDE

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INTRODUCTION

Pyrochemical methods are being explored for the reprocessing of nuclear reactor fuel materials. In the effort to develop processes for the dissolution of oxide fuel elements, it was discovered that uranium dioxide could be rendered soluble in molten chloride media by reaction with certain chlorinating agents among which were aluminum chloride,⁽¹⁾ chlorine and phosgene. The reaction product, when chlorine or phosgene was bubbled through a melt, open to air, and containing suspended oxides of uranium, was shown to be uranyl chloride. It was subsequently found that reduction of the uranyl chloride solution was readily accomplished and yielded uranium dioxide.⁽²⁾ This report describes the studies in the preparation of uranium dioxide from molten salt solution.

SUMMARY AND CONCLUSIONS

A dense, crystalline precipitate of pure uranium dioxide may be prepared by the reduction of uranyl chloride contained in a molten salt solution. The reduction may be accomplished by contacting the salt solution with any of several metals, by reaction with hydrogen or dry ammonia gas, or by electrolysis. Several kilograms of uranium dioxide were prepared by electrolysis using graphite electrodes. The material has physical properties which make it potentially useful as a ceramic fuel material. Further, the entire process cycle whereby an oxide of uranium is dissolved in a molten salt under the influence of chlorine, followed by reduction of uranyl chloride in the separated salt solution is of interest as a potentially useful process for irradiated oxide fuels.

EXPERIMENTALDissolution of Uranium Oxides

It has been found that uranium oxides may be chlorinated in certain molten halide salts to produce uranyl chloride which is soluble in the solvent salt. Thus, if chlorine gas is bubbled into the molten eutectic mixture of sodium chloride and potassium chloride, and uranium dioxide powder added, the uranium dioxide will be dissolved according to reaction (1):

Similarly, the other uranium oxides, U_3O_8 or UO_3 , are dissolved as uranyl chloride. However, in the case of these higher oxides, oxygen must be liberated to satisfy reactions (2) and (3):

The rate of reaction of uranium dioxide may be quite low. Using a ceramic grade UO_2 which had been sintered and ball-milled, a time of six hours was necessary to complete the reaction with chlorine in the preparation of a 0.75 molal UO_2Cl_2 solution. The rate of reaction with a 10 gram lump of massive, sintered UO_2 was prohibitively low; only about 25 per cent had dissolved after 16 hours of chlorine treatment at 800 C. On the other hand, either powdered or massive UO_2 , after ignition to U_3O_8 by roasting at 500 - 600 C for an hour, is quite readily reacted with chlorine in the salt melt. A mole of U_3O_8 could usually be completely dissolved in 2000 grams of NaCl-KCl eutectic in two hours at 800 ± 50 C. The trioxide may vary in its reactivity towards chlorination. However, its rate of reaction with chlorine is usually comparable to that of calcined U_3O_8 . The residue remaining after a period of chlorination of suspended UO_3 corresponds closely in atom ratio to U_3O_8 .

The rate of reaction when starting with any given batch of uranium oxide is quite temperature dependent, being much more rapid at 850 C than at 750 C. At 500 C, using the lower-melting KCl-LiCl eutectic solvent, the chlorination of U_3O_8 was very slow indeed.

Other chlorinating agents are effective in producing uranyl chloride. Phosgene, for example, converts the uranium oxides to UO_2Cl_2 in alkali chloride melts, although it is most likely that the phosgene breaks down to yield chlorine as the active reagent when the temperature of the experiment is above 500 C.

Aluminum chloride has previously been shown to be an effective reagent for dissolution of uranium oxides in a molten alkali chloride solution.⁽¹⁾ The products in this instance are uranium tetrachloride and alumina. Sparging the melt with air will result in the formation of UO_2Cl_2 .

The reaction of chlorine with an oxide to produce an oxygenated chloride compound appears to be unique with uranium. Plutonium oxide dissolves not at all, or only extremely slowly, under the conditions used for uranium dioxide dissolution. Plutonium dioxide does, however, react with anhydrous HCl or with aluminum chloride in molten salt solutions, the product in either case being $PuCl_3$. A separation factor of 58 was obtained in an experiment wherein a mixed crystal oxide containing UO_2 and PuO_2 in 5/1 mole ratio was subjected to the selective dissolution of UO_2 by chlorination. Thorium oxide similarly remains undissolved under the treatment by chlorine in molten chloride solutions. A separation factor of 500 was obtained in the selective dissolution of UO_2 from a ThO_2 - UO_2 mixture. Moreover, reactions similar to the reduction of uranyl chloride to uranium dioxide in molten salt solution are unknown with other actinide elements. Methods for the separation of uranium from other actinide elements, either by selective dissolution of the mixed oxides or by precipitation from chloride solutions, therefore clearly exist (see Appendix for conceptual flowsheet).

The Reduction of Uranyl Chloride to Uranium Dioxide

It was found that uranyl chloride contained in the molten solvent KCl-NaCl eutectic could be readily reduced to uranium dioxide. For example, a metal phase in contact with molten salt reacts to produce crystalline UO_2 and a metal chloride, as given by equation (4):

Several metals were found to be effective in precipitating uranium dioxide from uranyl chloride salt solutions. The metals - bismuth, lead, tin, cadmium, zinc and magnesium - each resulted in precipitates of crystalline UO_2 . The rate of reduction increased in the order that the reductants are listed, as shown by the rate curves in Figure 1. In the case of magnesium, the reduction to uranium metal would be predicted from thermodynamic considerations. However, the precipitated UO_2 has very low surface area which, together with poor wetting, undoubtedly results in unfavorable kinetics for the reduction to metal.

The reaction of uranyl chloride salt solution with aluminum metal is peculiar in that a uranium aluminum alloy is produced. This may be explained by the fact that AlCl_3 is a reagent for dissolution of UO_2 . The products in this case are Al_2O_3 solid phase and UCl_3 in equilibrium with alloyed uranium. The reduction may be driven to completion by sparging the salt phase with air.

Uranyl chloride molten salt solutions could be reduced with hydrogen gas or with anhydrous ammonia gas which decomposed to give hydrogen as the active reductant at 750 - 800 C. A very fine precipitate of crystalline UO_2 was produced in either case.

Electrolytic Reduction of Uranyl Chloride

The reduction of uranyl chloride-alkali chloride molten salt solutions by electrolysis was studied in some detail. It was found that crystalline UO_2 could be prepared when electrolysis was carried out between

FIGURE 1

Precipitation of Uranium Dioxide from $\text{KCl-NaCl-UO}_2\text{Cl}_2$ Solution with Metals

graphite electrodes at a potential of two to three volts and current densities varying from 2 to 40 amp/dm². Uranyl ions are discharged at the cathode and crystalline deposits of UO₂ are formed which adhere firmly to the cathode surface. Chlorine is liberated at the anode. The reactions are represented by equations (5) and (6):

As the electrolytic reduction of uranyl chloride nears completion, there is evidence that remaining uranium in solution is present as UCl₄. This is indicated by a change in color of the molten salt solution from red to pale green, and by a corresponding increase in the voltage required for passage of current through the cell. Further evidence is in the absorption spectrum obtained from samples of the electrolyte.

In order to explain the formation of UCl₄ in the solution, an equilibrium reaction involving uranyl chloride, uranium dioxide, and air is proposed:

The tetravalent uranium may be readily converted to uranyl ion by sparging the salt solution with air.

The current efficiency for deposition of UO₂ from uranyl chloride solutions was essentially 100 per cent in experiments done on a small scale. When the cell, later described, having a capacity of two liters was employed, current efficiencies were more often 60 to 70 per cent. This lowered efficiency was probably a result of some of the deposit sluffing from the cathode surface as a result of convective stirring and chlorine gas evolution from the anode.

SCALED-UP PREPARATION OF ELECTROLYTIC URANIUM DIOXIDE

In view of the apparent high quality of uranium dioxide which could be prepared in the molten salt medium, it was of considerable interest to prepare the material in sufficient quantity for its evaluation in fuel element fabrication operations. A goal was therefore set at five kilograms of UO_2 to be prepared for the Ceramic Fuels Development group.

Equipment and Procedures

A fused silica vessel having a working capacity of two liters was used as the cell (Figure 2). This was heated by an eight-inch length of nominal six-inch stainless steel pipe surrounding it, and used as a susceptor for the 9800 cycles/sec induction source. The electrodes were 1/2 in. x 4 in. x 14 in. slabs of pile-grade graphite, bolted to transite spacers at the top, and immersed to a depth of six inches into the bath. Direct current was supplied by two Electro Products Laboratories Model NF Universal Filtered Power Supplies connected in parallel. Current was recorded on an Esterline Angus recording ammeter, and temperature was recorded on a Brown recorder.

Approximately three kilograms of sodium chloride-potassium chloride equimolar mixture were used as the solvent salt. The uranium content was typically 10 weight per cent prior to reduction and about one per cent following a reduction cycle.

Uranium trioxide was generally used in the preparation of uranyl chloride solution. The procedure was to melt the salt at 800 ± 50 C, start a chlorine gas sparge, and slowly add one mole of UO_3 . Chlorination required two to three hours.

The electrode assembly was then introduced, the temperature adjusted to 725 ± 25 C, and current passage started. The cell voltage was observed, and the run terminated when the voltage increased beyond about three volts.

FIGURE 2

Diagram of the Molten Salt Electrolytic Cell

The electrode assembly (Figures 3 and 4) was then withdrawn and allowed to cool in air. Immersion of the cold cathode in water permitted the deposit of uranium dioxide to be easily brushed off. The product was carefully washed on a filter, dried with acetone, and finally with air.

Attrition of the graphite above the melt level was somewhat of a problem in early runs. It was found, however, that by blanketing the cell with glass wool so as to maintain a chlorine atmosphere, the graphite was protected from air oxidation.

At the end of a day's operation of the cell, it was necessary to pour the molten salt into molds so as to prevent breaking the fused silica vessel. As an alternative, it would have been necessary to maintain the salt in the molten state.

Quality of the Product

The electrolytic uranium dioxide is a coarsely crystalline material of density 10.7 - 10.9. Microscopic examination shows that it consists of small clusters of relatively large single crystals (Figure 5). The X-ray diffraction pattern shows the typical cubic UO_2 structure and no other uranium oxide impurity. Spectrochemical analyses have shown a few hundred parts per million of sodium and potassium in the product. However, chlorine found by chemical analysis was less than 10 per cent of that equivalent to the sodium and potassium. This may imply that the presence of alkali metals is due to reduction and incorporation in the lattice, rather than as occluded chloride salts. It is possible that better voltage control would minimize contamination. The tap density of the material is 6.2 ± 0.2 g/cc. A typical sieve analysis is as follows:

<u>Mesh Size</u>	<u>Per Cent Retained</u>
14	16.9
20	8.9
35	21.7
48	13.8
100	23.1
150	4.9
200	3.9
-200	6.8

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FIGURE 3
Electrode Assembly
Showing Deposit of UO_2 on Cathode

FIGURE 4
UO₂ Deposit on Cathode

FIGURE 5

Macrograph (18X) of Electrolytic Uranium Dioxide Particles

The oxygen-to-uranium atomic ratio, as determined by the ignition method, has generally been in the range 2.03 to 2.07.

Evaluation of the product as a ceramic fuel material is currently in progress. Initial results show that it compares favorably with uranium oxides which have been extensively prepared by sintering, milling, and classification.

The initial high particle density of the "as-produced" uranium oxide from molten salt solution is of great potential advantage in the refabrication of irradiated uranium dioxide into recycle fuel elements.

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FIGURE 7

Conceptual Flowsheet - Alternate Dissolution and
Reduction Steps

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