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Enhanced Dissolution of PuO_2 in Nitric Acid using Uranium(IV)

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The dissolution of PuO_2 is a fundamental problem in nuclear technology. In this work the effect of the U^{4+} ion on the rate of dissolution of $PuO_2(s)$ in HNO_3 was tested by experimental measurements. The U^{4+} ion greatly increases the rate of dissolution crystalline of PuO_2 powder in 5 mol dm^{-3} HNO_3 at 90 °C.

The dissolution of PuO_2 in HNO_3 has been studied by many research scientists and engineers over the past 20 years in nuclear industries all over the world.[1] Since neither the temperature nor concentration of nitric acid has much effect on the rate of dissolution of PuO_2 in HNO_3, chemical additives such as HF and Ce^{4+} have been used in order to accelerate the dissolution.[2] However, a much better alternative is required, since these reagents have a corrosive effect on the dissolution vessel. LOMI (low oxidation state metal ion) reagents are known to accelerate the dissolution of metal oxides. On the basis of these results and our theoretical considerations it was thought that the U^{4+} ion should have a positive effect on the dissolution of PuO_2 in HNO_3. In this work the effect of U^{4+} on the dissolution rate of PuO_2 in HNO_3 has been tested in preliminary experiments and is discussed theoretically.

Experimental

Materials

Crystalline PuO_2 powder (nuclear grade), which was supplied from France and characterized by X-ray diffraction method as a CaF_2-type crystal, was used for the dissolution experiments. $U^{4+}(aq)$ was prepared by the electrolytic reduction of UO_2^{2+} in HNO_3 in the presence of hydrazine with a Hg–Pt electrode at room temperature.

Apparatus

The dissolution vessel used in this experiment was a glass flask (200 cm^3) with three necks. A reflex condenser was connected to the central neck. A water-containing bottle was connected to it in order to avoid the escape of NO_x gas into the glove box. Temperature was measured with a mercury-in-glass thermometer. The vessel was placed on a hot-plate of a magnetic stirrer.

Dissolution Test

PuO_2 powder, 100–200 mg, was placed in the flask. HNO_3 solution (35 cm^3) was then poured into the vessel in the presence of $U^{4+}(aq)$ and heated to 90 °C. It was kept at this temperature for several hours under stirring.

Table 1. Effect of U^{4+} on the rate of dissolution of PuO_2 in HNO_3

composition of solution	experimental conditions	results
U^{4+}, 0.2 mol dm^{-3}; U^{4+}/UO_2^{2+}, 3 HNO_3, 5 mol dm^{-3}; N_2H_4 (H_2O), 0.5 mol dm^{-3}	90 °C, 2 h	almost completely dissolved
blank test (1) HNO_3, 10 mol dm^{-3}	100 °C, 3.5 h	no effect
blank test (2) HNO_3, 5 mol dm^{-3} $N_2H_4(H_2O)$, 0.5 mol dm^{-3}	90 °C, 1.5 h	no effect

Results

The effect of $U^{4+}(aq)$ on the rate of dissolution of PuO_2 in HNO_3 is shown in table 1. Hydrazine (N_2H_4) was added in order to prevent the oxidation of $U^{4+}(aq)$ by HNO_2 in an autocatalytic fashion. U^{4+} is stable even at 90 °C, as no change in the colour of the solution (from green to yellow) was observed. Dissolution of PuO_2 powder was detected by visual observation of the colour and transparency of the solution.

Discussion

Basic Chemistry of the Dissolution Process

Dissolution of crystalline metal oxides in aqueous solutions is often discussed from a thermodynamic view point in terms of solubility products. This is an oversimplification, as the kinetics of dissolution must also be considered. On the basis of the mechanism developed for the dissolution of UO_2 in HNO_3,[3] the reductive dissolution process can be expressed as a chemical reaction as follows on the assumption of an ionic model for PuO_2:

$$Pu^{4+}(s) + U^{4+}(aq) \rightarrow Pu^{3+}(aq) + U^{5+}(aq). \qquad (1)$$

This indicates that interfacial electron transfer from $U^{4+}(aq)$ to $Pu^{4+}(s)$ is a rate-controlling step for the dissolution. $U^{5+}(aq)$ can be converted into UO_2^+ by reaction with water and may react with the Pu^{4+} ion in solid in the same way as reaction (1) through a one-electron transfer process. However, it is not clear why $Pu^{4+}(s)$ is ejected into the solution through process (1). Sellers and Segal have discussed this mechanism for the reductive dissolution of $NiFe_2O_4$ by V^{II} in aqueous solution.[4] They claimed that the reduction of the Fe^{3+} ion in the solid results in an increase in the ionic radius of the ion and an increase in the electrostatic repulsive force between the electron clouds of the Fe^{2+} ion and the adjacent O^{2-} ion in the solid state. This theory cannot be accepted, since a fully ionic model (a hard-sphere model) for metal oxides is not justified. Presumably, electron transfer to an antibonding orbital of the metal oxides can occur, since this process will break the Pu—O covalent bond on the basis of molecular-orbital theory.

Technological Application

The use of a nitric acid–uranium(IV) solution for the dissolution of PuO_2 offers advantages over alternatives. It avoids most of the possible difficulties associated with the use of HF, such as corrosion, interference with flowsheets and glass formulation for the vitrification of HA wastes. It also avoids the addition of cerium or silver reagents, which could add to the salt burden of waste streams, and the use of electrodes in plant-handling a high level of radioactivity. Also, the resulting solution is a mixture of uranium and plutonium in HNO_3, which is suitable for direct conversion to (U, Pu) O_2.

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