The chemistry of (U,Pu)O$_2$ dissolution in nitric acid

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Abstract

The focus of this paper is the chemistry of mixed uranium plutonium oxide (MO$_x$) in nitric acid. An overview of dissolution chemistry is discussed by comparing the differences in the dissolution characteristics of uranium and plutonium oxides. An overview of batch dissolution experiments, studying the dissolution chemistry of high surface area MO$_x$ powders and low surface area MO$_x$ pellets with reference to the effects of nitrous acid, nitric acid and temperature are described. The results are discussed in terms of the autocatalytic mechanism and mass transfer limited dissolution.

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1. Introduction

The head-end of a reprocessing plant is the first step to the reprocessing of spent nuclear fuel and has two key steps, shearing and dissolution. The shearing helps to determine how the nitric acid can access the fuel and the degree of pulverization. The sheared fuel is dissolved in nitric acid followed by conditioning prior to the chemical separation process, which purifies the actinides of interest. As fuel is converted from the solid fuel matrix into solution form, any undissolved fuel is lost from the nuclear fuel cycle, increasing the long term radioactivity and radiotoxicity of the reprocessing wastes. Both the shearing and dissolution process steps are important in terms

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of minimizing fuel losses in head-end. Improvements in the understanding of MOx dissolution chemistry with optimization of the shearing step will allow the maximum recovery of fuel. The focus of this paper is to summarize the chemistry of MOx dissolution.

Figure 1 shows calculated waste radiotoxicity for various percentage recoveries of U, Pu and U, Np, Pu, Am, Cm compared with spent fuel (0 % recovery) and fission products (FP). The graphs clearly show that to maximize the benefits of future reprocessing schemes, where the minor actinides are recycled, high recoveries become increasingly important.

As part of the EU FPVII ACSEPT project, the UK National Nuclear Laboratory (NNL) has undertaken chemical studies in the area of head-end chemistry. These studies are relevant to the design of head-end processes for UK legacy non-standard fuels, support to current operations and future fuels. These studies have focused on:
- conceptual studies considering reprocessing of a variety of fuel types,
- practical studies investigating mixed uranium plutonium oxide dissolution in nitric acid
- practical studies investigating the dissolution of plutonium dioxide (simulated plutonium rich MOx residues) in the presence and absence of simulated insoluble fission products.

2. Background chemistry

Uranium dioxide (UO₂) and mixed uranium plutonium dioxide (MOx, (U,Pu)O₂) are important reactor fuels. During the reprocessing of these materials they are dissolved in nitric acid to produce a dissolver product containing typically ca. 3 mol.l⁻¹ nitric acid and 1.0-1.3 mol.l⁻¹ uranium and plutonium. This product must be suitable for the solvent extraction chemical separation process. The dissolution, is typically carried out at elevated temperature, 70-110 °C, to allow dissolution on a short timescale. During dissolution the uranium is oxidised to uranyl and nitrogen oxides (Equation 1 below) where x depends on the nitric acid concentration[1]. Depending upon the dissolver conditions the plutonium can be present in the tetravalent state or the hexavalent state.

$$3 \text{UO}_2 + 4(2+x) \text{HNO}_3 \rightarrow 3\text{UO}_2(\text{NO}_3)_2 + 2(1-x) \text{NO} + 6x \text{NO}_2 + 2(2+x) \text{H}_2\text{O} \quad \text{(where } 0<x<1) \quad (1)$$

During dissolution isotopic labelling studies have shown that the oxidation of the uranium dioxide is carried out as a solid state reaction[2, 3]. The surface oxidation and dissolution process proceeds via an autocatalytic
mechanism; that is, after a slow induction period dissolution occurs more rapidly. Early studies correlated the increase in dissolution rate with temperature and nitric acid concentration in an attempt to interpret and model the mechanism [4-7]. Due to the autocatalytic nature of the dissolution reaction the dissolution models often had gaps. A careful set of experiments studying the effect of nitric and nitrous acid (a nitric acid reduction product) showed that dissolution is dependent upon nitric and nitrous acid concentrations [8, 9]. Also, under typical dissolver conditions the nitrous acid oxidation step is much more rapid than that with nitric acid, thus providing evidence that explains the induction periods (Equation 2) and more rapid autocatalytic mechanism (Equation 3). The significance of nitrous acid in the rapid reactions and slower nitric acid reactions is supported by fundamental studies of nitric acid, e.g. [10], and the dissolution of other materials, e.g. copper metal [11].

\[
\begin{align*}
UO_2^{2+} + NO_3^- + 3 H^+ &\rightarrow UO_2^{2+} + HNO_2 + H_2O \\
UO_2^{2+} + 2 HNO_2 + 2 H^+ &\rightarrow UO_2^{2+} + 2 NO + 2 H_2O
\end{align*}
\]

(2) (3)

Unlike uranium dioxide, plutonium dioxide does not dissolve in nitric acid to an appreciable degree [2, 12]. Thermodynamic calculations have shown that the dissolution of plutonium dioxide either by reaction with acid (Equation 4) or by oxidation (Equations 5 and 6) are thermodynamically unfavourable [2]. Despite this, in MOx fuel, when the microscopic plutonium concentration is a small fraction of the uranium, the plutonium does dissolve in nitric acid [13]. The decrease in the extent of MOx dissolution for increasing plutonium content is clearly shown in Figure 2 [13]. A sharp decrease in the extent of dissolution is observed for >35% Pu (as calculated according to [Pu]/([U]+[Pu])) and little dissolution is observed for > 55–65 %Pu.

\[
\begin{align*}
PuO_2 + 4 H^+ &\rightarrow Pu^{4+} + 2 H_2O \\
PuO_2 + NO_3^- + 2H^+ &\rightarrow PuO_2^{2+} + NO_2 + H_2O \\
PuO_2 + NO_3^- + 3H^+ &\rightarrow PuO_2^{2+} + HNO_2 + H_2O
\end{align*}
\]

(4) (5) (6)

It was suggested [13] that the reduction in the extent of dissolution of MOx is due to the plutonium solubility saturation being reached. However, an alternative explanation is that at higher plutonium contents one of the reactions becomes thermodynamically unfavourable. Thermodynamic calculations in this work have shown that the nitrous acid reaction becomes unfavourable at ca. 40 %Pu. Although this result does not provide proof, it does provide an explanation based on both thermodynamics and kinetics.

![Figure 2. The percentage MOx dissolved with different plutonium contents in 5 or 10 mol.l\(^{-1}\) nitric acid at reflux for 8 hours [13]](image)
pure uranium and plutonium dioxides, the final products are not homogeneous on an atomic scale but have microscopic heterogeneities. Based on Figure 2, any plutonium rich regions will result in undissolved residues.

3. Experimental studies

Batch dissolution experiments were carried out aimed at understanding the factors that affect the dissolution of uranium dioxide and thermal reactor MOx (ca. 5% Pu). The dissolution experiments have been carried out by thermostating a volume of nitric acid, then adding the material and in some experiments sodium nitrite as a nitrous acid source. Most experiments were stirred in an attempt to minimise surface autocatalytic reactions, thereby minimising the difference between the surface and bulk solution composition. The uranium, plutonium and nitrous acid concentrations were determined by in-line and off-line UV-Vis spectrometry, either by direct measurements or by colorimetry. The solution open redox potential was also monitored using a platinum wire and Ag/AgCl reference electrode separated by a salt bridge. Analysis of powder dissolution experiments was carried out by fitting the initial linear dissolution rate to a spherical core shrinkage model, as used by other authors [9]. The results of pellet dissolution experiments will be expressed as an average dissolution rate at 30 % dissolution.

3.1. MOx powder dissolution studies

Dissolution experiments with 4.7 %Pu MOx powder (ca. 1.3 m^2.g^-1) have been used to study the effect of various nitric and nitrous acid concentrations at 40 °C. The effect of temperature and nitrous acid concentration in 4 mol.l^-1 nitric acid have also been examined. An example of the results is shown in Figure 3.

The results were used to develop a kinetic model (Equation 6), which has a similar form to the results for uranium dioxide[9].

\[
\frac{d[U]}{dt} = k_1[NO_3^-]^i + k_2[NO_3^-]^i[HNO_2]^z
\] (6)

These experiments confirm that the uranium dioxide and low plutonium content MOx dissolve via a similar mechanism and suggest that the wealth of dissolution literature available for uranium dioxide [4-7, 9] is relevant to the dissolution of bulk phase MOx.

![Figure 3. Effect of nitrous acid concentrations in 4-7 mol.l^-1 nitric acid at 40 °C upon dissolution rate of 4.7 %Pu MOx powder](image-url)
3.2. MOx pellet dissolution studies

Dissolution experiments with 5.0 %Pu MOx pellets, each with a mass of ca. 10 g, have been used to study the effect of:

- nitric acid in the absence and presence of added nitrous acid at 80 °C
- temperature
- nitric acid concentration.

An example of the effect of temperature and nitric acid concentration upon the dissolution rate is shown in Figure 4. In contrast to the results of the powder dissolution experiments at high temperature and high nitric acid concentrations, the dissolution rate becomes less sensitive to the effect of nitric and nitrous acid concentrations. Under these conditions bubbles stream from the pellet surface at a high rate and it is believed that the dissolution rate becomes mass transfer limited. Similar observations for uranium dioxide pellets have been made[4].

![Figure 4. Effect of nitric acid concentration and temperature upon the dissolution rate of MOx pellets at 30 % dissolution](image)

4. Discussion

The results of this work will allow quantitative predictions to be made about the dissolution of unirradiated MOx. This information is useful for the design of dissolver cycles. It is also important to maximize the extent of dissolution of any plutonium rich particles in MOx, as even small amounts of plutonium insoluble residues must undergo careful criticality safety case analysis. Future work to improve the understanding of the mechanism of high plutonium content MOx is needed, as this will allow the design of time efficient dissolver cycles that maximize plutonium recovery. In the dissolution of irradiated MOx the role of the fission products, in terms of the effect of solid state structure and their interaction with the dissolution mechanism, is topic for further research... This study therefore helps improve the knowledge of the dissolution of MOx by minimizing plutonium loses in the head-end dissolution step. This type of development is important to aid safety case development for U, Pu recycle schemes and to achieve the waste radiotoxicity reductions in future Np, Am, Cm recycle schemes (Figure 1).

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