Technical note

The dissolution of uranium oxides: Thermodynamic and kinetic investigations

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ABSTRACT

This work investigates the dissolution of various uranium oxides in nitric acid medium and the most predominant occurring reaction was determined on the basis of the thermodynamic and kinetic studies. Six uranium oxides were dissolved and studied. The Gibbs free energies of all the reactions $\Delta_r G°(T)$ were analyzed by Ulich model (Ulich, 1930) and the predominant dissolution reaction was found to be:

$$3U_3O_{8(s)} + 20HNO_{3(aq)} \rightarrow 9\ UO_2\ (NO_3)_{2(aq)} + 2NO_{(g)} + 10H_2O$$
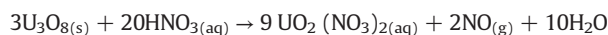
Three reaction order rate models namely the first, the second and the third order were applied on the predominant reaction reported above. According to the kinetics results, our reaction best fits the second order equation rate.

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1. Introduction

Uranium is the most representative actinide element that is of fundamental importance in the nuclear fuel cycle. Uranium dioxide powder is the starting material for the preparation of the fuel pellets used in nuclear power reactors. The nuclear fuel cycle involves several major steps consisting of the leaching of uranium ore in sulphuric acid (Guettaf et al., 2009), followed by the precipitation of uranium as yellow-cake (YC). The resulting impure material previously obtained is then purified by means of the TBP solvent extraction (Boualia and Mellah, 1989) and the precipitates obtained are identified as ammonium diuranate (ADU) or ammonium uranyl tricarbonate (AUC) (Venter and Boylett, 2009; Chegrouche and Kebir, 1992). Finally, the pure materials produced are dried, calcined and reduced to various uranium oxides.
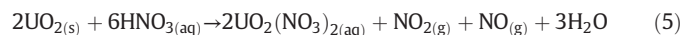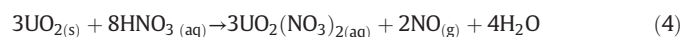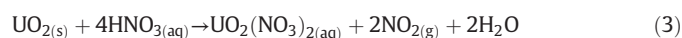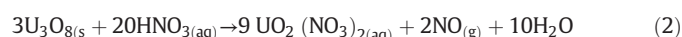
The physical properties of the oxides obtained are very important for their ultimate use as a fuel in nuclear reactors. It is now established that many of these properties are inherited from the precursor materials used (Ayaz and Bilge, 2000). Thus the method of the preparation of ammonium diuranate controls its particle size and determines the nature of the oxide obtained. This flow sheet has been studied by a number of authors (Benedict et al., 1981).

The dissolution of the different uranium concentrates by nitric acid constitutes the principal operation of the uranium refining process flow sheet (Venter and Boylett, 2009; Morss et al., 2010). The major advantage of the use of the nitric acid is its powerful oxidizing property. In fact, the nitric acid oxidizes the uranium in its different compounds

from the lower state (IV) to the highest oxidation state (VI). However, the biggest disadvantages of this reagent are respectively its high cost and its high consumption per mass unit of dissolved uranium. In addition, the dissolution of uranium oxides by nitric acid is accompanied by considerable volumes of gas emissions consisting mainly of the by-products of the nitric acid reduction such as nitrogen dioxide and monoxide (Fukasawa and Ozawa, 1986; Sakura et al., 1988; Yasuike et al., 1995; Smirnov et al., 2012).

Dyck et al. (1977) have studied the dissolution of mixed thorium–uranium oxide fuel in nitric acid/hydrofluoric acid to assist the design of equipment and procedures for reprocessing. The dissolution rate was found to depend upon the acid concentration and temperature with the optimum dissolution rate occurring at a concentration of 13 mol/L HNO_3/0.05 mol/L HF and at a boiling temperature. The dissolution of the uranium oxide with nitric acid was also addressed by Y. Ikeda et al., 1995; Homma et al., 1993).

Our study focused on the dissolution of the most important uranium oxides in nitric acid, the following reactions have been considered:

$$U_3O_{8(s} + 8HNO_{3(aq)} \rightarrow 3UO_2(NO_3)_{2(aq} + 2NO_{2(g} + 4H_2O \qquad (1)$$

$$3U_3O_{8(s} + 20HNO_{3(aq)} \rightarrow 9\ UO_2\ (NO_3)_{2(aq)} + 2NO_{(g)} + 10H_2O \qquad (2)$$

$$UO_{2(s)} + 4HNO_{3(aq)} \rightarrow UO_2(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O \qquad (3)$$

$$3UO_{2(s)} + 8HNO_{3\ (aq)} \rightarrow 3UO_2(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O \qquad (4)$$

$$2UO_{2(s)} + 6HNO_{3(aq)} \rightarrow 2UO_2(NO_3)_{2(aq)} + NO_{2(g)} + NO_{(g)} + 3H_2O \qquad (5)$$

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$$UO_{3(s)} + 2HNO_{3(aq)} \rightarrow UO_2(NO_3)_{2(aq)} + H_2O \tag{6}$$
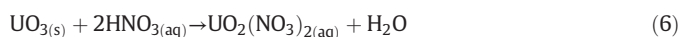
The purpose of this work was to determine the most predominant reaction during the dissolution process based on the thermodynamic analysis. The kinetics of the most predominant reaction was also investigated.

2. Experimental

2.1. Reagents and methods

Samples of the uranium oxides used in this study as raw materials: U_3O_8, UO_3 and UO_2 were supplied by Merck with more than 98% w/w purity. The uranyl nitrate solutions have been prepared by the dissolution of all the material (oxides) mentioned above in nitric acid (70% w/w) under different conditions.

The uranium was analyzed before and after dissolution process and a sensitive spectrophotometric method based on colored complexes with Arsenazo III has been used (Vucic and Ilic, 1989). All chemicals and reagents used for these experiments and analyses were of analytical grade.

2.2. Dissolution procedure

The dissolution tests of uranium oxide samples were conducted at a laboratory scale through the following procedure for each experiment: 4.0 g of various oxides have been put in contact with a volume of 25 to 30 cm^3 of nitric acid concentrate. The dissolution reaction occurred in a double jacketed dissolution vessel of 100 cm^3 capacity where both phases (solid and liquid) were mechanically agitated at 500 r·min^{-1}. Some authors found out that the dissolution reaction is not diffusion controlled, the dissolution rate was independent of the stirring speed at above 300 r·min^{-1} (Zhao and Chen, 2008).

The gas phase in the vessel was purged with air gas in order to remove NO$_X$ gases generated during the dissolution. The mixture was heated at the required temperature by means of the water running in the double jacketed vessel and all the unit was under electronic control.

3. Results and discussion

3.1. Effect of reaction time

The effect of the reaction time on the uranium oxide dissolution was studied at two temperatures 298.15 K and 353.15 K and at a constant amount of uranium. The dissolution of uranium oxide has been investigated in the time range of 30–180 min. The results obtained are shown in Fig. 1. It can be clearly seen that the increasing process time led to the increase of uranium dissolution percentage % for both temperatures. Then, it is also shown from Fig. 1 that the dissolution equilibrium was attained after 180 min which was used for further studies.

3.2. Effect of temperature

In order to study the influence of the temperature on the uranium extraction yield, a set of batch experiments were performed over the temperature range considered: 298.15 K to 353.15 K. The results are shown in Fig. 2. It can be noticed that the increasing temperature improved the dissolution process. In fact, the uranium dissolution percentage at 40 min rises from 7% to 16.5% at 298.15 K similarly the dissolution percentage increases from 62.50% to 70.2% at 353.15 K. Comparatively, our results are almost in agreement with the results obtained by (Zhao and Chen, 2008) under the conditions of temperature and time (T = 373.15 K, t = 40 min and the dissolution percentage = 60% in 4 M HNO$_3$.) (See Figs. 3 and 4).

3.3. Thermodynamic study

The Gibbs free energies derived from the Ulich model (Ulich, 1930; Mellah et al., 2007) as a function of temperature of the six dissolution reactions of the oxides studied have been considered and the values have been determined by means of the following Eqs. (7), (8), (9) and (10):

$$\Delta_r G\,(T) = \Delta_r H° - T\Delta_r S° - T(\Delta a M_0 - \Delta b M_1 + \Delta C\prime M_{-2}) \tag{7}$$

$$\Delta_r H° = \Sigma_i \delta_i\, \Delta_f H°_{298.15(products)} - \Sigma_i \delta_i\, \Delta_f H°_{298.15(reactants)} \tag{8}$$

$$\Delta_r \overset{\text{Å}}{S} = \Sigma_i \delta_i\, S°_{f298.15\,(products)} - \Sigma_i \delta_i\, S°_{f298.15(reactants)} \tag{9}$$

$$C_p = a + bT + cT_{-2} \tag{10}$$

where $\Delta_r G°(T)$ is the standard Gibbs free energy of reaction in (kJ/mo·K); $\Delta_r H°$ is standard enthalpy of reaction in (kJ/mol); $\Delta_r S°$: is the standard entropy of reaction in (J/mol·K); T is the temperature in (K); $\Delta_f H°_{298.15}$: is the standard molar enthalpy of formation at 298.15 K in (kJ/mol); $S°_{f298.15}$ is the standard molar entropy of formation at 298.15 K, (J/mol·K); C_p is the molar heat capacity at constant pressure in (J/mol/K); a, b, c′, M_o, M_1 and M_{-2} are constants; δ_i is the stoichiometric coefficients. The
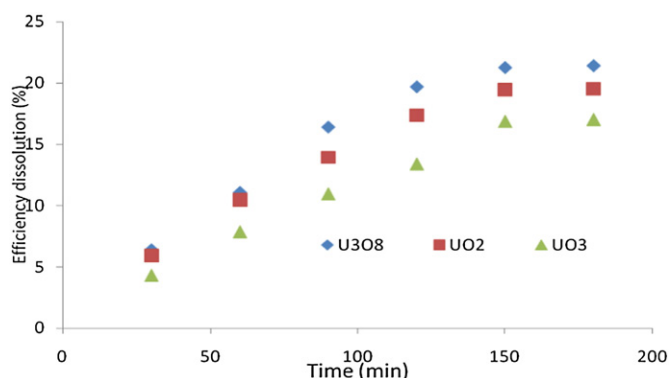

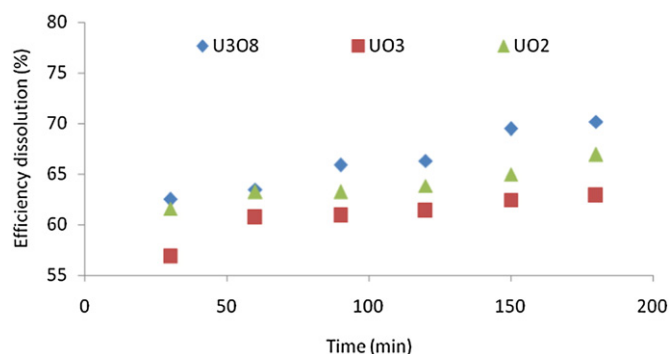**Fig. 1.** Effect of reaction time on dissolution of uranium oxide at T = 298.15 K.

Fig. 2. Effect of reaction time on dissolution of uranium oxide at T = 353.15 K.