Oxidative dissolution mechanism of uranium dioxide at 25°C

M. E. Torrero
I. Casas
J. de Pablo

Chemical Engineering Department, UPC, 08028 Barcelona, Spain

L. Duro
J. Bruno

QuantiSci S.L, Parc Tecnològic del Vallès, 08290 Cerdanyola del Vallès, Spain

The oxidative dissolution of UO_2 (s) has been important in the past to understand uranium mobility from uranium ores. Nowadays, due to the fact that uranium dioxide represents around the 98% of the spent nuclear fuel an increasing amount of experimental and modelling effort is being devoted to this type of studies.

The dissolution of this solid is largely affected by variables like pe, pH and carbonate concentration. Recently [1], we have studied the kinetics of the dissolution of UO_2 as a function of pH and oxygen partial pressure. The experimental dissolution rates obtained are shown in Fig. 1, from which the following empirical rate equation is derived:

$$r \text{ (mol m}^{-2}\text{ s}^{-1}) = 3.5 \ (\pm \ 0.8)10^{-8} \ [H^+]^{0.37}[O_2]^{0.31}$$

The fractional order in both, the proton and the oxygen concentration is an indication of the dissolution occurring via a surface mediated mechanism. On the other hand, it is important to notice the decrease of the dissolution rate with the proton activity up to pH $\approx$ 8, and the fact that rate is approximately independent of pH for more alkaline solutions.

Dissolution mechanism

The proposed oxidative dissolution mechanism can be illustrated by the following processes taking place in the system:
Step 1: Oxidation of the solid surface:

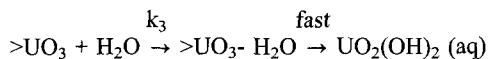$$>UO_2 + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} >UO_2{\cdot}O_2 \equiv >UO_3$$
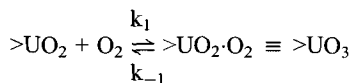
After the initial oxidation of the surface, two parallel processes may occur: Step 2, favoured at acidic pH, which implies the coordination of one proton to the surface and the subsequent fast dissolution of the surface complex. Step 3, favoured at neutral-alkaline pH, where the hydroxyl groups of water attach to the surface and the intermediate surface complex is rapidly released to the solution:
Step 2: Surface coordination of H^+:

$$>UO_3 + H^+ \overset{k_2}{\rightarrow} >UO_3\text{-}H^+ \overset{fast}{\rightarrow} UO_2(OH)^+ \text{ (aq)}$$
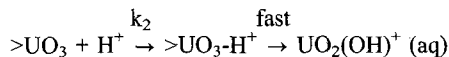
Step 3: Surface coordination of H_2O:

$$>UO_3 + H_2O \overset{k_3}{\rightarrow} >UO_3\text{-} H_2O \overset{fast}{\rightarrow} UO_2(OH)_2 \text{ (aq)}$$

From this mechanism, and after applying the stationary state approach to the reaction intermediates, $>UO_3\text{-}H^+$ and $>UO_3\text{-}H_2O$, the following rate equation is obtained

$$r = \frac{k_1[O_2][> UO_2]_{tot}(k_3 + k_2[H^+])}{k_{-1} + k_3 + k_2[H^+] + k_1[O_2]} \quad (1)$$

where $[>UO_2]_{tot} = [>UO_2] + [>UO_3] + [>UO_3\text{-}H^+] + [>UO_3\text{-} H_2O]$.

We adjusted equation (1) to the experimental data by fitting the parameters k_1, k_{-1}, k_2 and k_3. According to the average site density proposed by Davis and
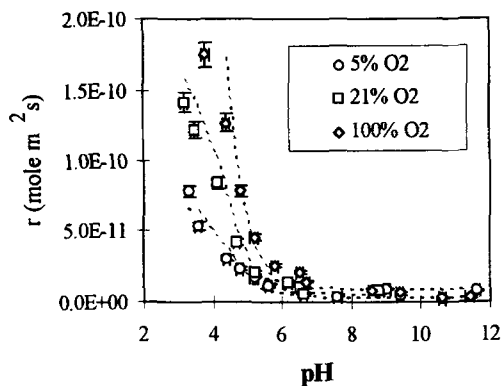

FIG. 1. Experimental dissolution rates (oxygen partial pressure: ◇ 100%; □ 21% and ○ 5%) vs pH. Dashed lines were calculated by using the rate law expressed by equation 1 (see text for explanation).

TABLE 1. Comparison between experimental and calculated dissolution rates

Reference	pH	$[O_2(aq)]$ (mol/dm^3)	$r_{exp.}$ (mol/m^2s)	$r_{calc.}$ (mol/m^2s)
UO_2 [6]	9.5	2.64×10^{-4}	10^{-11}	7.3×10^{-12}
Spent Nuclear Fuel [7]	7	10^{-5}	5×10^{-12}	9.74×10^{-13}

Kent [2] the value of $[>UO_2]tot$ was fixed at 10^{-6} moles m^2. The best fit to the experimentally determined UO_2 dissolution rates for the pH range $(3-12)$ and for the three oxygen partial pressures (5, 21 and 100%) was obtained by using the following values: $k_1 = 1.13$, $k_{-1} = 10^{-4}$, $k_2 = 5$ and $k_3 = 10^{-5}$.

The results obtained by substituting these values of the rate constants into equation (1) are plotted with dashed lines in Fig. 1, from where we can observe the good correlation between the calculated and the measured dissolution rates.

Discussion

According to equation (1), it is possible to obtain different fractional empirical reaction orders of the proton and the oxygen concentrations. The dependence of the rate of dissolution on the oxygen concentration for the oxidation/dissolution of $UO_2(s)$ has been a subject of many discussions in the literature [3] due to its importance on the safety assessment of a repository of high level nuclear waste. The same type of discussion is permanently held in the literature on the oxygen dependence on the pyrite dissolution rate [4]. Under low oxygen content, the term $k_1[O_2]$ in the denominator of equation (1) will be negligible, implying an apparent linear dependence of the dissolution rate on the oxygen concentration, what has been observed in previous published work on the dissolution of similar solid phases [5]. On the other hand, under alkaline conditions the term $k_2[H^+]$ will be negligible both, in the denominator and in the numerator of equation (1), indicating a dissolution rate independent on the proton activity at high pH values,

which in turn, can be observed from the experimental data shown in Fig. 1.

In table I, some values of the dissolution rate of similar material obtained by different authors are compared with the values calculated after the application of equation (1) to the experimental conditions reported in the references indicated.

As we can see, the calculated values are in good agreement with the dissolution rates obtained from the experiments.

Acknowledgements

References

(1) Torrero, M.E. Baraj, E., de Pablo, J., Giménez, J. and Casas, I. (1997) Int. J. Chem. Kinet., 29, 261−7.
(2) Davis, J.A. and Kent, D.B. (1990) In Mineral-Water Interface Geochemistry, Rev. Min.., 23 (M.F. Hochella and A.F.White ed.) Mineral. Soc. Am. Washington D.C., 177−260.
(3) Gray, W.J. and Wilson, C.N. (1995) Pacific Northwest Nat. Lab. Report PNL-10540. UC-802. Dec. 1995.
(4) Nicholson, R.V., Gillham, R.W. and Reardon, E.J. (1988) Geochim. Cosmochim. Acta, 52, 1077−85.
(5) Grandstaff, D.E. (1976) Econ. Geol., 8, 1493−506.
(6) Shoesmith, D.W., Sunder, S., Baley, M.G. and Wallace, G.J. (1989) Corrosion Science, 29, 1115−.
(7) Eriksen, T.W., Eklund, U.-B., Werme, L.O. and Bruno, J. (1995) J. Nucl. Mater., 227, 76−82.