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The kinetics of dissolution of UO_2 under reducing conditions and the influence of an oxidized surface layer (UO_{2+x}): Application of a continuous flow-through reactor

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Abstract—We have studied the kinetics of dissolution of uranium dioxide, $UO_2(s)$, under strongly reducing conditions ($H_2(g)/Pd$). We have investigated the dependence of the rate of dissolution as a function of critical geochemical parameters: pH, pCO_2 , and carbonate concentration. By using a stirred batch reactor, the kinetics of dissolution of an UO_{2+x} surface layer and the subsequent precipitation of UO_2 have also been studied. Although the initial UO_2 is pretreated before starting the experiments, it seems to be very difficult to avoid the formation of the oxidized surface layer. For this reason we have developed a thin layer continuous flow-through reactor in order to study the kinetics of dissolution of pure $UO_2(s)$.

The dependence of the rate of dissolution of these solids on the proton concentration of the solution may be expressed according to the following equations:

$$r_{diss}(UO_2)(mol\ sec^{-1}\ m^{-2}) = 1.4(\pm 0.3) \times 10^{-8} [H^+]^{0.53 \pm 0.08} \quad (3 \leq pH \leq 7)$$

$$r_{diss}(UO_2)(mol\ sec^{-1}\ m^{-2}) = 1.9(\pm 0.8) \times 10^{-12} \quad (7 \leq pH \leq 11)$$

$$r_{diss}(UO_{2+x})(mol\ sec^{-1}\ m^{-2}) = 1.1(\pm 0.3) \times 10^{-12} [H^+]^{-0.30 \pm 0.02} \quad (3 \leq pH \leq 9)$$

The mechanism of dissolution of these solids is surface controlled.

The rate of dissolution of UO_2 in acidic solutions may be described in terms of an integer dependence on the activity of the protonated surface complexes:

$$r_{diss}(UO_2)(mol\ sec^{-1}\ m^{-2}) = 1.11 \times 10^{13} \{>UOH_2^+\}^4 \quad (2 \leq pH \leq 6)$$

INTRODUCTION

URANINITE IS ONE of the most common uranium minerals. What is often reported as uraninite in the geochemical literature covers a wide range of $UO_{2+x}(s)$ uranium oxides with UO_2 and U_3O_8 as endmembers. Uranium oxide minerals of higher O/U ratio between 2.3 and 2.7 are usually called pitchblende (MAYNARD, 1983).

The presence of the pure endmember UO_2 in uranium oxide mineralizations is rare and is usually associated with strongly reducing or very anoxic genetic conditions. The presence of pure crystalline U_3O_8 has been observed in the vein-type deposits at Key Lake (DAHLKAMP, 1978).

The cycle of uranium in natural waters and consequently the formation of uranium ore deposits is connected to the oxygen cycle, and consequently to the iron and sulfur ones. Uranium is mobilized from the source (e.g., granites, interbedded volcanic ashes) under oxic conditions as uranium (VI) and precipitates in anoxic conditions (MAYNARD, 1983). The precipitation in anoxic media occurs in the form of either uraninite (UO_2) or coffinite ($USiO_4$), depending on the silicate concentrations (LANGMUIR, 1978). The transformation of uraninite to coffinite occurs in the concentration range of SiO_2 from 17 to 140 ppm.

Access to oxygen or to other oxidants has been assumed

to be a requisite in order to mobilize uranium. The kinetics of uraninite (UO_2) dissolution under oxidizing conditions has been extensively studied. A comprehensive review has been recently prepared (GRAMBOW, 1989). The most extensive investigation of the kinetics of uraninite dissolution (GRANDSTAFF, 1976) included the dependence on pO_2 , $[HCO_3^-]$, and pH.

The average uranium concentrations in natural waters under reducing conditions are between 10^{-7} – 10^{-8} mol dm^{-3} (3 to 30 ppb). This is consistent with equilibrium with $UO_2(s)$ (BRUNO et al., 1988). Nevertheless, most uraninites show under reducing conditions O/U ratios larger than two. The solubility of UO_{2+x} solid phases is normally higher than that of pure UO_2 under reducing conditions (BRUNO et al., 1988). This indicates that, under these conditions, uranium is initially dissolved from the primary sources and it reprecipitates as UO_2 . This would suggest a mechanism of mobilization of uranium under reducing conditions which is different from the one commonly accepted. The understanding of this possible mobilization mechanism is obviously very relevant in the case of the disposal of UO_2 spent nuclear fuel in granitic geological formations. In this case it is important to know to what extent and how fast the high grade UO_2 is dissolved under reducing conditions. Such a study is not available to our knowledge.

The overall reaction for mineral dissolution and secondary phase precipitation can be expressed as

$$r_{overall} = r_{diss} - \sum r_{prec} \quad (1)$$

where the summation expands over all possible precipitation



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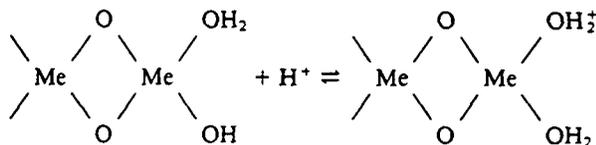
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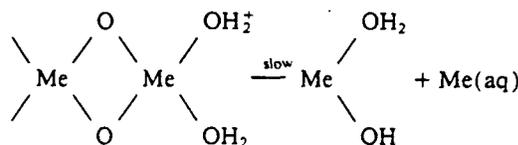
reactions of secondary phases for the individual components of the mineral phase.

The kinetics of dissolution of metal oxides have been extensively studied. Stumm and coworkers have proposed a generalization of the surface controlled mechanism (WIELAND et al., 1988). For metal oxides the overall dissolution reaction (r_{diss}) is the result of a series of sequential steps:

- 1) the mass transport of solutes (H^+ , OH^- , in the absence of other complexing ligands) to the mineral surface, $>\text{MOH}$;
- 2) the adsorption of the solutes (H^+ , OH^-) to the hydrated mineral surface:



- 3) the detachment of the reactants from the surface:



- 4) the mass-transport of the reactants to the bulk of the solution.

Normally, the transport of solutes and reactants is faster than the detachment of the reactants from the surface. In this case the dissolution reaction is surface controlled and the rate of dissolution is proportional to the activity of the adsorbed species (WIELAND et al., 1988):

$$r_{\text{diss}} = k_{\text{H}} \{>\text{MeOH}_2^+\}^p \quad (2)$$

The aims of this work are to present a general study of the kinetics of dissolution of UO_2 as a function of

- 1) the redox state of the surface;
- 2) the proton concentration (pH) of the solution in contact;
- 3) the pCO_2 and the bicarbonate concentration;

and to discuss the results of the investigation in terms of the dependence of the degree of surface protonation as a function of the pH. Consequently, to establish the mechanism of dissolution of pure UO_2 and an oxidized, UO_{2+x} , surface layer under anoxic natural waters conditions is intended.

EXPERIMENTAL

The preparation and purification of all chemicals and gases used has been previously described (BRUNO et al., 1985a). The oxidation state of the uranium in solution was ensured to be U(IV) by a constant $\text{H}_2(\text{g})$ flux in the presence of a palladium catalyst. This method has previously proved to be successful (BRUNO et al., 1985b, 1987). The uranium content in the solution was determined by a spectrophotometric laser fluorescence method using a Scintrex UA-3 apparatus (ROBBINS, 1978).

The solid phase used was an uranium dioxide supplied by ASEA ATOM Co. The mean particle size was approximately $50 \mu\text{m}$. The bulk composition of the solid was characterized by X-ray powder diffraction (XPD) as $\text{UO}_{2.001}$. The surface area was determined by the BET method to be $0.201 \pm 0.002 \text{ m}^2 \text{ g}^{-1}$. The two different

experimental devices that were applied for the kinetic determinations, using for both the same solid phase described above, were as follows.

Batch Reactor

A pre-treatment of the solid phase was necessary in order to remove both the possible oxidized layer formed on the surface and fine particles. The presence of fine particles would make the interpretation of the results obtained very difficult (PETROVIC et al., 1976; PETROVIC, 1976). Several methods have been proposed to eliminate those contributions. Among them, the most drastic one uses HF to clean the solid surface (HOLDREN and BERNER, 1979). However, this method has been seriously criticized due to the fluorination of the surfaces (PERRY et al., 1983) and because of the possibility of change in the properties of the solid creating kinks and edges of high reactivity (CHOU and WOLLAST, 1984). For these reasons, a less vigorous treatment was used in our case. A weighed amount of the solid was kept for not less than 24 h in a dilute HClO_4 solution under $\text{H}_2(\text{g})$ atmosphere and in the presence of a palladium catalyst. The solid was washed afterwards several times with degassed bidistilled water and transferred to the experimental vessel under $\text{H}_2(\text{g})$ atmosphere to prevent oxygen contamination.

Experimental methodology

We performed two different series of experiments in order to determine separately the influence of pH and $[\text{HCO}_3^-]$ on the rate of dissolution. The determination of the pH influence was carried out in a $0.008 \text{ mol dm}^{-3}$ sodium perchlorate medium to simulate the average ionic strength of granitic groundwaters. The hydrogen ion concentration was adjusted and kept constant by using either HClO_4 or NaOH.

In the investigations concerning the effect of HCO_3^- on the rate of dissolution, we used different mixtures of $\text{HCO}_3^-/\text{ClO}_4^-$ to obtain a constant ionic strength of $0.008 \text{ mol dm}^{-3}$. This set of experiments was carried out under a constant $\text{CO}_2(\text{g})$ partial pressure obtained by bubbling different mixtures of H_2/CO_2 of well-known composition. The volume of the test solution was 200 mL, and 2.0 g of solid were used. In all cases the stirrer was in direct contact with the solid phase. In addition, we checked the influence of a high bicarbonate concentration on the rate of dissolution by carrying out an extra experiment at 100 mM in HCO_3^- .

Both types of experiments, in perchlorate and bicarbonate media, were carried out in the following way. A known volume of the test solution was previously degassed, and the pH was adjusted to the required value. The solution was transferred to the reaction vessel, and aliquots (4 mL) for the uranium analysis were taken at intervals of time. The pH and the Eh of the test solution were continuously monitored by means of a combined glass electrode and a platinum wire, respectively. The samples were filtered through $0.22 \mu\text{m}$ MILLIPORE filters to ensure that only dissolved uranium contributed to the analysis. Constant high-speed stirring ensured the homogeneity of the bulk solution and avoided mass-transport control within the solution.

Flow Reactor

A second experimental approach was developed in order to compare and validate the results obtained when using a batch reactor. Continuous flow reactors of different characteristics have been widely used for this kind of kinetic determinations (CHOU and WOLLAST, 1984, 1985; KNAUSS and WOLERY, 1986; RIMSTIDT and DOVE, 1986; WOLLAST and CHOU, 1985). The experimental system selected by us is based on a continuous flow-through/thin solid layer reactor. In this system, the solid phase is contained in a reactor through which the test solution is continuously pumped. Using a thin layer of solid one ensures an optimum contact between both solid and liquid phases and minimizes the diffusion through the solid that can arise when a thicker layer is used. Since the reactor was unstirred, this is an important statement that was initially assumed in the experiments carried out. Anyway, the absence of a mass-transport influence in the dissolution rates determined with this system is shown below in the light of the results obtained.

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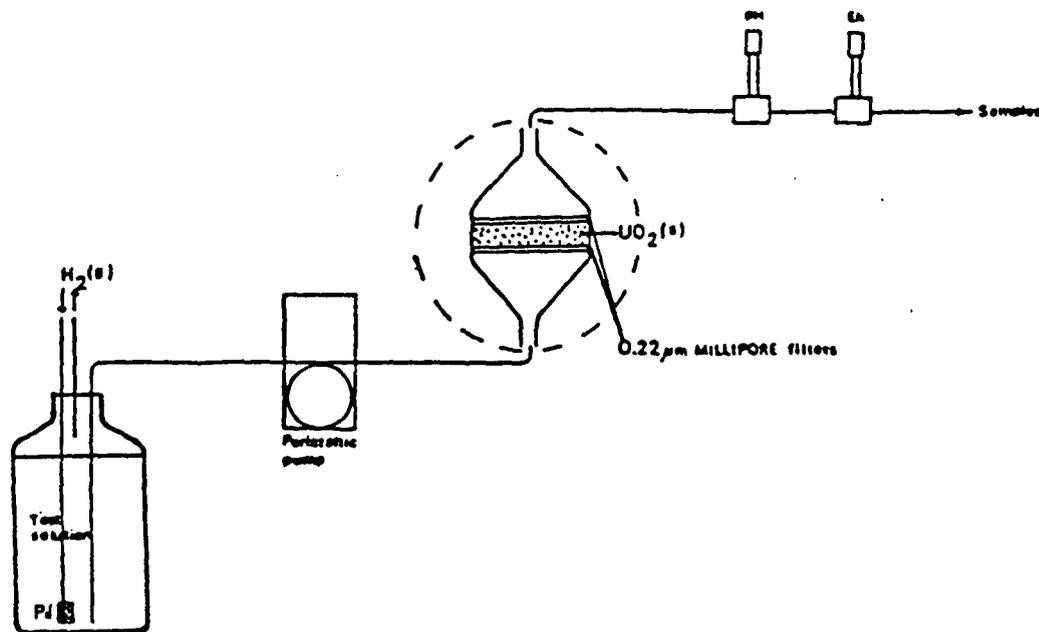


FIG. 1. Experimental scheme of the thin-film continuous flow reactor.

Once the solid is enclosed into the reactor, no further manipulation is required, because a new experiment is started just by changing the conditions of the input test solution. Redox potential measurements were used to quantify that the reducing conditions remained throughout the experiments.

The solid was enclosed into the reactor without any pre-treatment. The problems concerning the presence of highly reactive phases different from the bulk uranium dioxide are eliminated during the first hours of the experiment. The more soluble phases are dissolved out of the reactor in the initial stage, giving a high initial concentration of the dissolved products in the output solution. Finally, only dissolution due to the bulk solid phase under study is obtained (RJMSTIDT and DOVE, 1986).

The dissolution rate depends only on the aqueous phase composition in the absence of secondary solid phases and if the surface area remains constant. Under these conditions, the system evolves to a steady state and dissolution rates can be determined by multiplying the flow rate by the concentration of the dissolved ion in the output solution.

Furthermore, the possible contributions to the measured reaction rates of either the products of the reaction or the secondary phases formed are avoided because they are dissolved out of the reactor before saturation is reached (WOLLAST and CHOU, 1985).

Experimental methodology

A known weight of $\text{UO}_2(\text{s})$ (≈ 0.5 g) was enclosed into the reactor between two MILLIPORE filters (diameter: 13 mm) with a pore size of $0.22 \mu\text{m}$ to ensure that only the concentration of dissolved uranium was measured. The ionic strength of the feed solution was adjusted to $0.008 \text{ mol dm}^{-3}$ by using sodium perchlorate, and either sodium hydroxide or perchloric acid were used to adjust the pH to the required value. The reducing conditions of the feed solution were obtained by bubbling $\text{H}_2(\text{g})$ in the presence of a palladium catalyst. The hydrogen flux was maintained a minimum of 24 h before starting the experiment.

A variable flow rate peristaltic pump was used to circulate the test solution through the reactor. The values of pH and Eh were continuously monitored by means of an on-line combined glass-electrode and a platinum wire, respectively. The experimental device is shown in Fig. 1.

We took samples of the effluent at regular time intervals. Their uranium content was analyzed to monitor the attainment of steady

state. At this point, we readjusted the pH of the test solution and a new experiment was started. Once the conditions of the feed solution were changed, a new steady state was reached in approximately 24 h except for the first experiment, where we detected a high initial uranium concentration in the effluent (see Fig. 2). We assume that this was due to the dissolution of the more reactive phases, as explained above.

The dissolution rates determined using continuous-flow reactors are based on the uranium concentration of the effluent at steady state. One must ensure that the uranium concentrations measured actually correspond to steady state instead of solubility equilibrium. The amount of uranium dissolved depends on the reaction time, which is related to the residence time of the test solution in the reactor, given by

$$t = V/Q \quad (3)$$

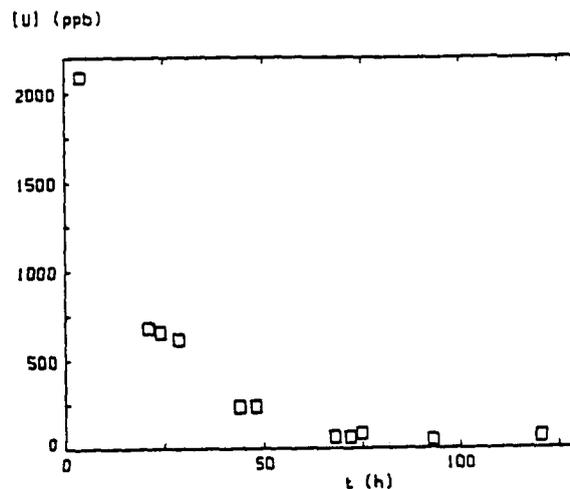


FIG. 2. Uranium concentrations as a function of time obtained in the effluent of the thin-film continuous flow reactor after a new experiment is started.

where V is the volume of solution in contact with the solid phase and Q is the flow rate (CHOU and WOLLAST, 1985). Since the volume is constant, the uranium concentrations of the effluent must be inversely proportional to Q , if steady state is reached. Therefore, the effect of pumping rate on the uranium concentration of the effluent was checked. Ideal behaviour was found up to $Q = 0.5 \text{ mL min}^{-1}$, approximately. Hence, the flow rate normally used on the subsequent experiments was in the range $0.1\text{--}0.5 \text{ mL min}^{-1}$.

The dissolution rate values were calculated using the following equation:

$$r_{\text{diss}} = Q(\text{dm}^3 \text{ sec}^{-1})[\text{U}]_0(\text{mol dm}^{-3}) = \text{mol sec}^{-1} \quad (4)$$

where $[\text{U}]_0$ stands for the uranium concentration of the effluent. These values were normalized with respect to the total surface area of the solid phase.

Determination of the pH_{zpc}

Acid-base titrations of an inert electrolyte were carried out in our lab by Forsgren in the presence and in the absence of a known amount of a solid phase suspension (FORSGREN, 1987). From both mass and charge balances the total surface charge can be calculated. From the values obtained, the pH corresponding to a net surface charge equal to zero (pH_{zpc}) can be determined (STUMM and MORGAN, 1981; SCHINDLER and STUMM, 1987).

Two different solid phases were used. A solid previously in contact with the air and another one pretreated under reducing conditions were titrated in order to compare the results obtained. The solid in contact with the air is assumed to develop an oxidized surface layer, with a composition likely to be U_3O_7 according to previous investigations (ALLEN et al., 1986; SHOESMITH et al., 1989).

The value obtained by FORSGREN (1987) for U_3O_7 was $\text{pH}_{\text{zpc}} = 3.4 \pm 0.4$, to be compared with an earlier determination $\text{pH}_{\text{zpc}}(\text{U}_3\text{O}_7) = 3 \pm 1$ found in the literature (SUNDE et al., 1986). For UO_2 , FORSGREN (1987) gives a $\text{pH}_{\text{zpc}} = 6.7 \pm 0.3$.

RESULTS

Batch Reactor

Some sets of data in the form $[\text{U(IV)}]$ in solution versus time (hours), obtained using different bicarbonate concentrations in the test solutions, are shown in Fig. 3. The behaviour of the system shows a fast initial increase of the uranium in solution followed by a decrease after a few hours until a final steady state is reached. The same trend was observed in our previous studies when working with sodium perchlorate as ionic media (BRUNO et al., 1988). The results from the most significant experiments, with and without bicarbonate, are presented in Table I. The behaviour observed indicates an initial dissolution of a surface layer of UO_{2+x} , which could not be eliminated with the pretreatment used, followed by the precipitation of a more stable phase, UO_2 , under reducing conditions. This oxidized surface layer has not been specifically identified in our experiments. However, the surface of UO_2 is oxidized very rapidly to $\text{UO}_{2.3}$ in solutions in contact with air at low temperatures. This oxidation requires extremely high potentials ($\geq 300 \text{ mV}$) in order to proceed further than U_3O_7 (SHOESMITH et al., 1989). Hence, on the basis of this electrochemical reasoning, we assume that this is the composition of the oxidized surface layer.

The mechanism presented is in agreement with previous observations on the reduction of U(IV) in the presence of $\text{UO}_2(\text{s})$ (FORWARD and HALPERN, 1953, 1954; BUNJI and ZOGOVIĆ, 1958; BALACEANU et al., 1958). In order to achieve fast and complete U(VI) reduction and UO_2 precipitation, these authors studied the effect of several catalysts (Ni, Ni-

Raney, and UO_2), hydrogen pressure, temperature, and $\text{HCO}_3^-/\text{CO}_3^{2-}$ concentrations.

The work by BUNJI and ZOGOVIĆ (1958) is of special interest because it shows that $\text{UO}_2(\text{s})$ is in fact capable of accomplishing complete reduction of a U(VI) from solution. Their results also imply that the active surface area was in fact changing during the experiments of FORWARD and HALPERN (1953) and BALACEANU et al. (1958).

BALACEANU et al. (1958) observed that sodium bicarbonate decreases the rate of U(VI) reduction, while the effect of Na_2CO_3 in their experiments was negligible. BALACEANU et al. (1958) concluded that HCO_3^- prevents the formation of an initial carbonate precipitate of intermediate oxidation degree by keeping U(IV) in solution. An inspection of the data for 70°C in Fig. 14 of BALACEANU et al. (1958) gives a dependence of the precipitation rate as a power of ≈ -1.1 on the activity of the bicarbonate ion.

In our experiments the dissolution rate was determined from the slope of the initial linear segment of the uranium concentration versus time (Fig. 3). The values obtained were normalized with respect to both the total surface area of the solid used and the volume of the test solution. In Fig. 4 we present the data obtained in both series of experiments (perchlorate and bicarbonate media) in the form $\log(r_{\text{diss}}/S)$ versus pH. The logarithm of the initial dissolution rate shows a linear dependence on the proton concentration of the test solution in the pH range 3 to 9 (see Fig. 4), while the datum at pH = 12 shows a behaviour which cannot be correlated to the rest of the data probably due to the formation of uranates at this high pH value and, thus, affecting the rate of dissolution measured. In the pH range 3 to 9 the dependence can be described in terms of the following equation:

$$r_{\text{diss}}/S(\text{mol sec}^{-1} \text{ m}^{-2}) = k_{\text{H}}[\text{H}^+]^{-0.32 \pm 0.05} \quad (5)$$

with $k_{\text{H}} = 1.1(\pm 0.3) \times 10^{-12}$ as the rate constant.

From these results it is concluded, as it was noticed above, that even if care is taken during experimental procedures to keep an oxygen-free atmosphere around $\text{UO}_2(\text{s})$, an oxygen-enriched coating (U_3O_7) is always formed on the surface of $\text{UO}_2(\text{s})$. POSEY-DOWDY et al. (1987), for example, had to use a preleaching treatment to reduce initial uranium dissolution (in absence of oxygen) to less than 0.01 mg dm^{-3} . In our experiments the total amount of uranium dissolved varied between 0.1 and 1.4 mg dm^{-3} . Taking into consideration the actual surface area in our experiments (which varied between 0.24 and $2.06 \text{ m}^2 \text{ dm}^{-3}$) and the cubic crystal lattice parameter ($a_0 = 5.470 \text{ \AA}$, four UO_2 units in the unit cell, IAEA 1965), we calculate that the depth of UO_2 dissolved, i.e., the UO_2 thickness equivalent to the U_3O_7 coating initially present in the experiments, was always less than 4 \AA (i.e., less than one unit cell deep). In addition, the influence of the pH on the rate of precipitation of the final solid phase (UO_2) was also determined to define its influence in Eqn. (1).

The values obtained in the pH range from 3 to 12 show no significant influence in either the proton or bicarbonate concentrations on the precipitation process, if the ionic strength is kept constant to $0.008 \text{ mol dm}^{-3}$ (Fig. 5). On the other hand, at higher bicarbonate concentrations (0.1 mol dm^{-3}), the precipitation rate has been found to be slower in

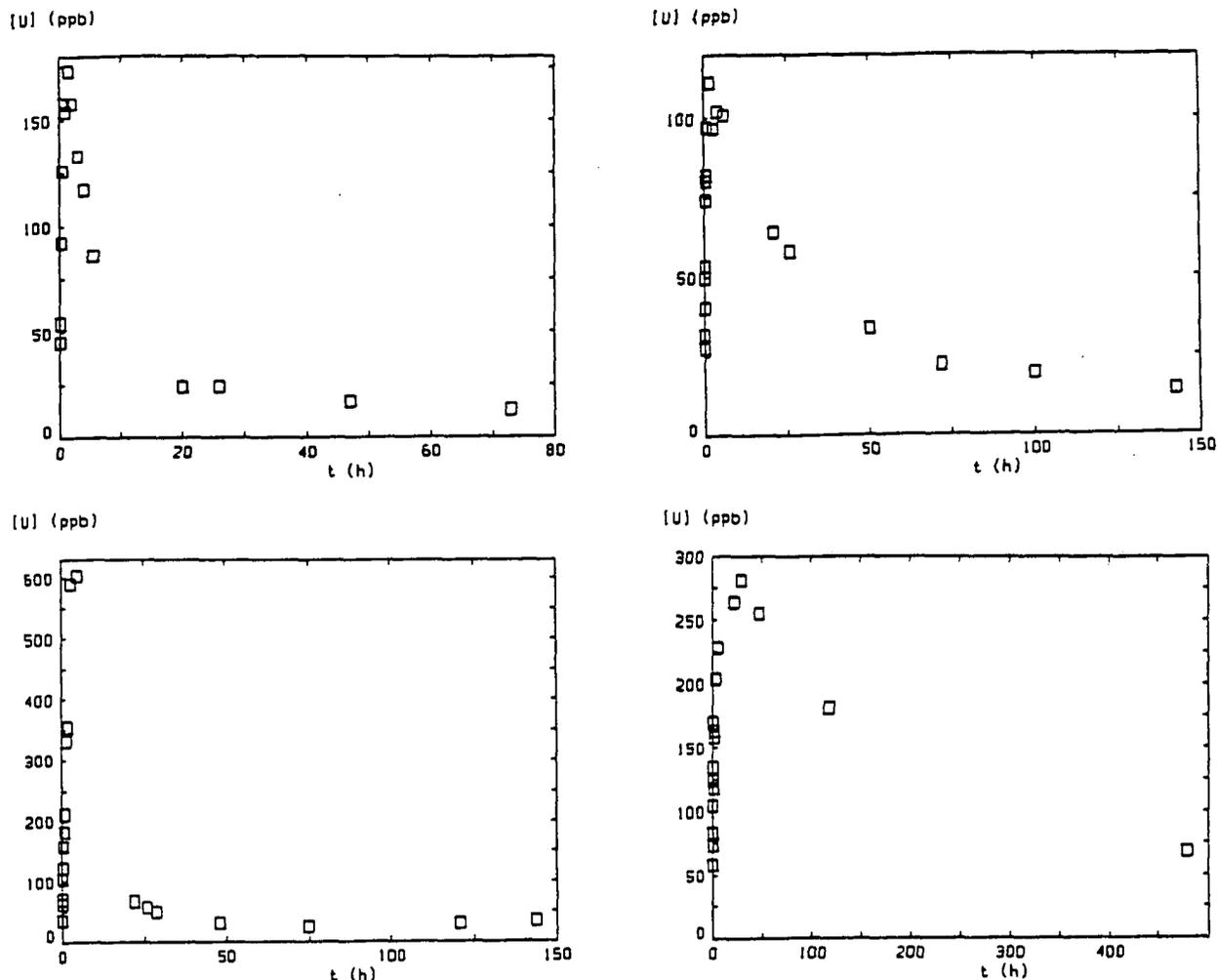


FIG. 3. Total dissolved uranium concentration as a function of time obtained in batch reactor experiments for the dissolution of U₃O₇(s) in bicarbonate media. (a) [HCO₃⁻] = 1 mM, CO₂(g) 1%; (b) [HCO₃⁻] = 1 mM, CO₂(g) 5%; (c) [HCO₃⁻] = 5 mM, CO₂(g) 5%; (d) [HCO₃⁻] = 100 mM, CO₂(g) 5%.

agreement with previous observations (BALACEANU et al., 1958). More experimental work is necessary in order to present a complete description of the influence of high bicarbonate concentrations on the precipitation rate.

Flow Reactor

The results obtained in 0.008 mol dm⁻³ perchlorate media are presented in Table II as the total uranium concentration of the effluent as a function of both the flow rate of the feed solution and the pH. In Fig. 6 the values of log (r_{diss}/S) calculated with Eqn. (4) are plotted versus pH. The data show two different trends. In the pH range 3 to 7, log (r_{diss}/S) is nearly dependent on pH. The dissolution rate can be related to the hydrogen ion concentration in the form

$$r_{\text{diss}}/S \text{ (mol sec}^{-1} \text{ m}^{-2}\text{)} = k_{\text{H}^+} [\text{H}^+]^{0.53 \pm 0.01} \quad (6)$$

with $k_{\text{H}^+} = 1.4 (\pm 0.3) \times 10^{-8}$ as the rate constant.

The data obtained between pH 7 and 11 show no clear dependence of the rate of dissolution with the proton con-

centration. Consequently, the rate expression can be adjusted to the equation

$$r_{\text{diss}}/S \text{ (mol sec}^{-1} \text{ m}^{-2}\text{)} = k_{\text{H}_2} \quad (7)$$

with $k_{\text{H}_2} = 4.4 (\pm 3.9) \times 10^{-12}$.

The possible influence of the precipitation reaction on this value is discussed in the next section.

DISCUSSION

Dissolution of U₃O₇

The dependence of r_{diss} for U₃O₇(s) on [H⁺] can be explained in the following terms:

- The negative dependence indicates that the dissolution rate is favoured by the presence of OH⁻ ions in solution.
- Fractional reaction orders are observed for different type of minerals including oxides, bicarbonates, and silicates. Several investigators (LASAGA, 1981; GRAUER and STUMM, 1982; STUMM and FURRER, 1987) have shown that this can be described in terms of surface complexation as the

TABLE I.- Total concentration of uranium in solution ($\mu\text{g dm}^{-3}$) versus time (hours) for the most significant experiments carried out in the stirred batch reactor

EXPERIMENT:	A	B	C	D	E	F	G	H	(*)
t	[U]								
0.02	45	580	134	70	--	--	--	--	
0.033	--	---	---	---	--	28	35	58	
0.083	--	---	---	---	45	32	--	73	
0.117	--	---	---	---	--	--	62	--	
0.167	--	---	---	---	54	40	70	104	
0.25	--	---	---	---	--	50	--	---	
0.333	--	---	---	---	92	53	104	83	
0.5	--	---	---	---	126	74	122	125	
0.667	--	---	---	---	--	80	157	169	
0.75	--	---	---	---	158	--	---	---	
0.833	--	---	---	---	--	82	182	134	
1	50	580	264	105	154	97	211	118	
1.5	--	---	---	---	173	--	331	158	
2	50	600	305	130	158	111	355	163	
3	51	680	314	145	133	97	589	204	
4	54	700	305	150	117	102	---	---	
5	--	700	---	150	86	---	603	229	
6	59	700	321	---	---	101	---	---	
7	62	650	261	160	---	---	---	---	
8	62	650	---	---	---	---	---	---	
9	64	680	316	160	---	---	---	---	
10	71	---	---	---	---	---	---	---	
11	--	---	---	170	---	---	---	---	
19	--	680	---	---	---	---	---	---	
20	--	700	---	---	24	---	---	---	
21	--	---	232	---	---	64	---	---	
22	--	750	---	---	---	--	67	264	
23	79	600	177	135	--	--	--	--	
25	83	600	203	135	--	--	--	--	
26	--	---	---	---	24	58	58	---	
27	--	580	207	130	--	--	--	--	
29	85	560	170	---	--	--	50	281	
30	--	---	---	135	--	--	--	--	
31	87	---	187	---	--	--	--	--	
33	86	---	---	130	--	--	--	--	
43	--	550	---	---	---	---	---	---	
45	--	580	128	---	--	--	--	--	
47	--	500	116	110	17	--	--	255	
48	--	---	---	---	--	--	32	---	
49	--	---	163	100	--	--	--	--	
50	115	500	---	---	--	34	--	---	
52	---	---	---	91	--	--	--	---	
54	125	---	---	---	--	--	--	---	
55	---	---	146	---	--	--	--	---	
56	125	---	---	89	--	--	--	---	
69	---	---	145	---	--	--	--	---	
71	---	---	---	65	--	--	--	---	
72	---	---	---	---	--	22	--	---	
73	---	---	---	---	13	--	--	---	
74	---	380	---	65	--	--	--	---	
75	155	---	97	---	--	--	25	---	
77	---	---	---	58	--	--	--	---	
79	---	---	85	---	--	--	--	---	
80	---	---	---	51	--	--	--	---	
93	---	---	76	---	--	--	--	---	
95	175	---	---	---	--	--	--	---	
96	---	280	---	---	--	--	--	---	
100	---	---	---	---	--	19	--	---	
103	205	---	43	---	--	--	--	---	
116	---	240	---	---	--	--	--	---	
119	230	---	---	---	--	--	--	181	
120	---	230	---	---	--	--	--	---	
121	240	---	36	---	--	--	31	---	
123	240	---	---	---	--	--	---	---	

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-8:
Fig:
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natio:

Table 1. (Continued)

EXPERIMENT:	A	B	C	D	E	F	G	H	(*)
t	[U]								
125	245	---	---	---	---	---	---	---	---
143	---	---	---	---	---	14	35	---	---
165	---	---	21	---	---	---	---	---	---
189	---	---	19	---	---	---	---	---	---
192	---	---	---	11	---	---	---	---	---
479	---	---	---	---	---	---	---	68	---

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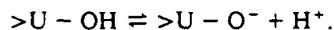
(*)

- A: 8mM NaClO₄, V₀=500 ml, 0.74 g UO₂, pH=3
- B: 8mM NaClO₄, V₀=500 ml, 0.60 g UO₂, pH=5.3
- C: 8mM NaClO₄, V₀=500 ml, 0.65 g UO₂, pH≈9
- D: 8mM NaClO₄, V₀=500 ml, 0.63 g UO₂, pH=12
- E: 7mM NaClO₄+1mM NaHCO₃/1% CO₂, V₀=200 ml, 2.05 g UO₂, pH=7
- F: 7mM NaClO₄+1mM NaHCO₃/5% CO₂, V₀=200 ml, 2.05 g UO₂, pH=6.3
- G: 3mM NaClO₄+5mM NaHCO₃/5% CO₂, V₀=200 ml, 2.05 g UO₂, pH=6.9
- H: 100mM NaHCO₃/5% CO₂, V₀=200 ml, 2.05 g UO₂, pH=7.9

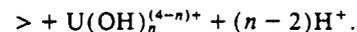
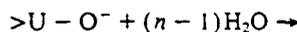
controlling step for the mineral dissolution, because the ion detachment will depend on the number of adjacent bound sites. The fractional rate order can be transformed in this case to an integer dependence on the concentration of surface species. This is in agreement with the low pH_{zpc} = 3.4 of U₃O₇. We can assume that the surface charge $\sigma \approx \{>UOH_2^+\} + \{>UO^-\}$. Hence, at pH > 4, $\sigma \approx \{>UO^-\}$ and $r_{diss} \propto \{>UO^-\}$.

The mechanistic steps proposed for the dissolution process are

- 1) The fast deprotonation of the oxidized surface layer (U₃O₇)



- 2) The rate determining step, the slow detachment of the metal ion



- 3) In the presence of bicarbonate on the test solution, the formation of carbonate complexes. This is assumed to be a fast step reaction since no dependence of the rate of dissolution on this anion has been found.

On the other hand, the lack of dependence on the rate of precipitation of UO₂(s) on the proton concentration, can be explained by surface growth of the UO₂(s) crystals. This type

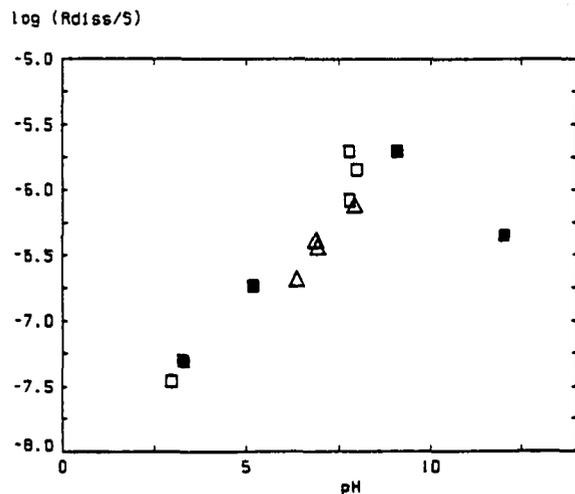


FIG. 4. Values of the rate of dissolution of U₃O₇(s) calculated for batch reactor experiments in both perchlorate (□) and bicarbonate media (Δ) as a function of pH. (■) corresponds to earlier determinations (BRUNO et al., 1988).

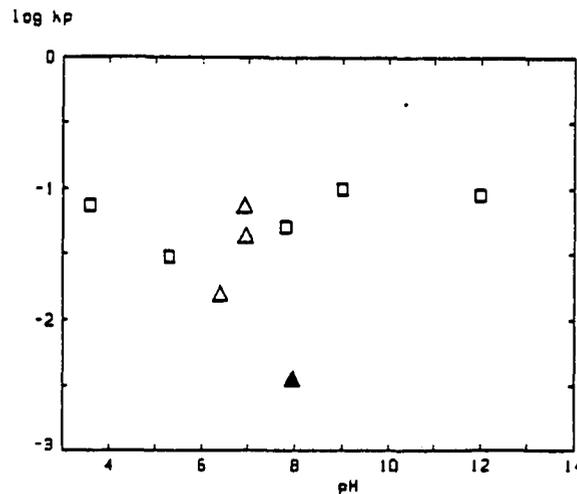


FIG. 5. Calculated values of the precipitation constants of UO₂(s) obtained for batch reactor experiments for both perchlorate (□) and bicarbonate (Δ) media as a function of pH. The full triangle corresponds to the value obtained at 100 mM bicarbonate.

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TABLE II.- Total concentration of uranium ($\mu\text{g dm}^{-3}$) on the effluent of the continuous flow-through reactor versus both the flow rate (ml min^{-1}) and the pH

Flow rate	[U]	pH
0.175	1920	3.4
0.181	2003	3.5
0.241	962	3.8
0.191	1237	3.9
0.180	1335	4.0
0.172	1390	4.0
0.158	397	4.5
0.169	523	4.5
0.160	80	5.9
0.169	79	6.0
0.336	37	6.1
0.352	40	6.1
0.544	163	6.5 (a)
0.544	178	6.5 (b)
0.415	71.4	6.7
0.275	65.4	6.7
0.278	84.6	6.7
0.276	50	6.7
0.402	67	6.7
0.246	25	6.8
0.255	27.5	6.8
0.266	22	6.8
0.596	6.7	8.4
0.537	21	8.6 (a)
0.537	25	8.6 (b)
0.509	23	9.5 (a)
0.509	25	9.5 (b)
0.527	30	9.6 (a)
0.527	32	9.6 (b)
0.480	33	9.6 (a)
0.480	38	9.6 (b)
0.467	28	9.7
0.547	25.5	9.8
0.503	28.5	9.9
0.469	78	10.0 (a)
0.469	87	10.0 (b)
0.520	24.3	10.0
0.512	22.6	10.0
0.464	8.5	10.1 (a)
0.464	9.8	10.1 (b)
0.515	60	10.3 (a)
0.515	61	10.3 (b)
0.517	79	10.4 (a)
0.517	79	10.4 (b)
0.453	14	10.6 (a)
0.453	15	10.6 (b)
0.449	17.4	10.8 (a)
0.449	19.5	10.8 (b)
0.443	21.4	10.9 (a)
0.443	22.9	10.9 (b)

=====

Each pair marked as a and b indicates the same determination but taken the samples at different distances of the reactor showing no significant adsorption of uranium into the walls of the system.

Weight of uranium enclosed into the reactor: 0.56-0.63 g

of process is typically controlled by a surface reaction and, thus, depends on the topography of the mineral surface. Crystal growth normally takes place preferentially at kinks

(STUMM et al., 1983), often caused by screw dislocations having higher surface energy than the atoms in the plain surface.

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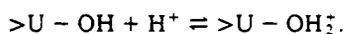
Dissolution of UO₂

The fractional reaction order obtained for the UO₂(s) dissolution indicates, as discussed for the dissolution of U₃O₇, the surface complexation as the controlling step for the mineral dissolution.

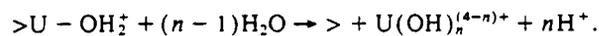
The positive dependence on [H⁺] between pH 3 and 7 (cf. Fig. 6) shows that the dissolution rate of UO₂ is favoured in this pH range by the presence of H⁺ ions in solution. The sign on the proton dependence indicates a completely different surface behaviour than the one observed for U₃O₇ in the same pH range. This indicates that the surface oxidation of UO₂ to U₃O₇ was avoided by working with the flow system.

Hence, we propose the following mechanism for the dissolution of UO₂ under reducing conditions:

- 1) Fast protonation of the surface layer



- 2) The rate determining step, the slow detachment of the metal ion



- 3) As in the previous case, the formation of bicarbonate complexes.

The uranium concentrations of the effluent measured in the flow reactor experiments are sometimes close to the equilibrium concentrations predicted from the reaction (for pH ≥ 5):



with $[U(OH)_4(aq)]_{eq} = 9(\pm 4) \times 10^{-8}$ (from BRUNO et al., 1988) where $[U(OH)_4]_{eq}$ is the concentration at equilibrium.

Because of this, when studying the kinetics of dissolution under these conditions, the precipitation reaction should also be considered. In this case, according to Eqn. (1)

$$r_{diss} = r_{meas} - r_{prec} = d[U(IV)]/dt - k_p[U(OH)_4] \quad (8)$$

in the pH range 7 to 11, $[U(IV)] \equiv [U(OH)_4]$, and

$$r_{diss} = d[U(IV)]/dt - k_p[U(IV)] \quad (9)$$

where k_p was determined in independent batch reactor experiments under the same conditions (cf. Fig. 5). The value obtained in perchlorate media is

$$k_p = 1.9(\pm 0.8) \times 10^{-5}$$

The rate constant for the dissolution of UO₂ corrected according to Eqn. (9) is, therefore,

$$k_{diss} = 1.9(\pm 0.8) \times 10^{-12}$$

By applying the relation $K_{eq} = k_{diss}/k_{prec}$, we obtain $K_{eq} = 1(\pm 0.6) \times 10^{-7}$, which results in

$$\log K_{eq} = -7.10 \pm 0.30$$

to be compared with the value determined in previous solubility measurements of the same phase (BRUNO et al., 1988):

$$\log K_{eq} = -7.08 \pm 0.17$$

for the reaction: $UO_2(s) + 2H_2O = U(OH)_4(aq)$.

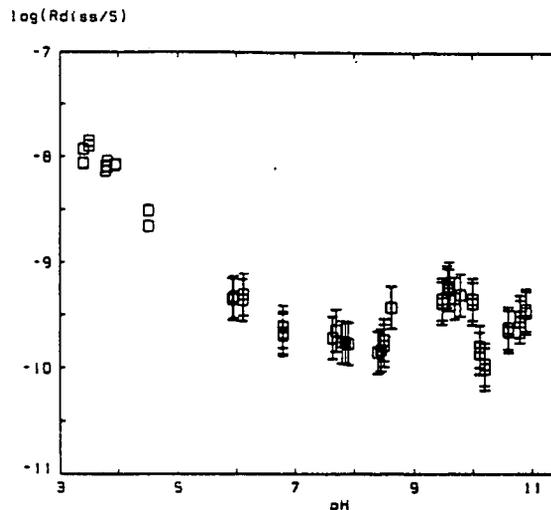


FIG. 6. Rates of dissolution of UO₂(s) obtained in the thin layer continuous flow-through reactor as a function of pH.

The agreement between the values indicates that the rate constants obtained for both the stirred batch reactor and the unstirred flow-through reactor are consistent. This implies that no significant influence of a mass-transport contribution is found in the rates of dissolution determined.

In addition, the results obtained in both continuous and discontinuous systems, and the mechanisms proposed, are compatible with previous observations on dissolution processes of different oxides (FURRER and STUMM, 1983; STUMM, 1986; STUMM et al., 1987) and aluminosilicates (CARROLL-WEBB and WALTHER, 1988; BLUM and LASAGA, 1988).

Correlation Between Surface Charge Determinations and Rate of Dissolution

There is a clear correlation between the pH_{zpc} of UO₂ and U₃O₇ and the dependence of their rates of dissolution on pH. The rates of dissolution of both UO₂ and U₃O₇ have their minimum at the corresponding pH of zero charge.

As we have previously discussed in the introduction, STUMM and coworkers (WIELAND et al., 1988) have found that the surface protonation equilibria of different minerals can be approximated to a Freundlich isotherm of slope recalculated by us as 0.14 ± 0.03 . These authors proposed that at pH values lower than the pH_{zpc} the activity of the protonated surface $\{>MOH_2^+\}$ can be calculated by the following expression:

$$\{>MOH_2^+\} = (K_F/[H^+]_{zpc}^m)[H^+]^m \quad (10)$$

with $K_F = 10^{-6.5 \pm 0.1}$ and $m = 0.14 \pm 0.03$.

By applying Eqn. (10) to our data on UO₂ suspensions, we can calculate the activity of the protonated UO₂ surface in the pH range 2 to 6. A plot of $\log r_{diss}$ versus $\log \{>UOH_2^+\}$ can be approximated by a straight line of slope 3.93 and an intercept of 16.6 (see Fig. 7). Hence, we can write the rate equation for the dissolution of UO₂ in acidic solutions as

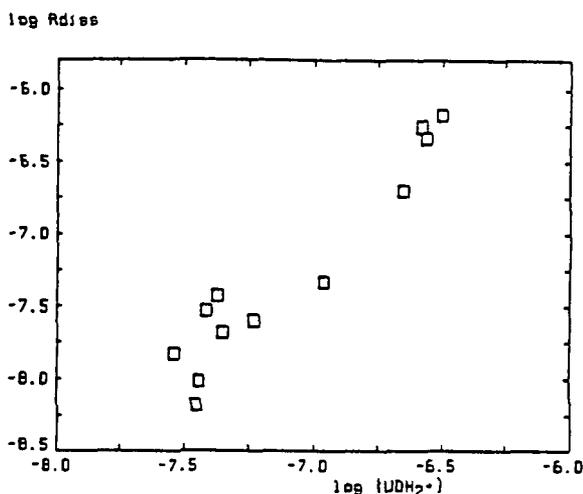
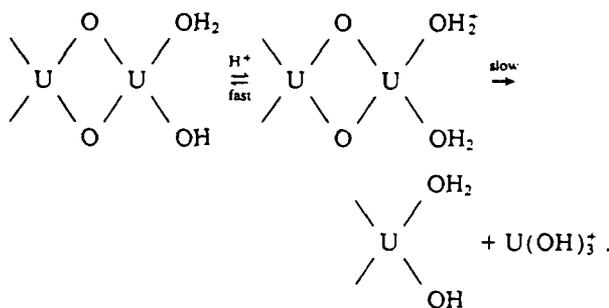


FIG. 7. Dependence of the rate of dissolution of UO_2 on the activity of the protonated surface complexes.

$$r_{\text{diss}} = k_{\text{diss}} \{>\text{UOH}_2^+\}^4 \quad (11)$$

with $k_{\text{diss}} = 1.11 \times 10^{13}$.

We can, thus, propose a mechanism for the dissolution of UO_2 in the pH range 2 to 6 as



By applying the general rate law on the dissolution of minerals derived by WIELAND et al. (1988), the proton promoted dissolution rate can be written as

$$r = kx_a P_j S \quad (12)$$

where r is the proton promoted dissolution rate ($\text{mol sec}^{-1} \text{m}^{-2}$), x_a denotes the mole fraction of active sites, P_j represents the probability to find a specific surface site in the coordinative arrangement of the precursor to the activated complex, and S is the concentration of sites at the surface.

P_j may be expressed in general as

$$P_j \propto \{>\text{MOH}_2^+\}^j \quad (13)$$

where the exponential j is ideally correlated to the oxidation state of the central metal ion M (STUMM and WIELAND, 1991). This is also the case for UO_2 , where we find

$$P_j \propto \{>\text{UOH}_2^+\}^4. \quad (14)$$

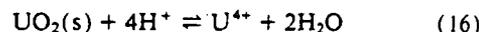
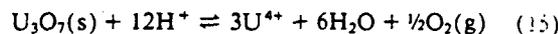
Geochemical Modeling

The consistency of both the rate and the equilibrium constants obtained in this work were checked by performing calculations with a general purpose computer program package,

the EQ3/6 geochemical reaction path codes. These programs are a convenient tool that may be used to calculate the evolution of geochemical systems that might be of interest for a nuclear repository assessment (WOLERY, 1980, 1983). The EQ6 code is able to solve kinetic rate laws for reactions included in its data base (DELANY et al., 1986).

In the aqueous model of the EQ3/6 package, each chemical reaction includes a product (mineral or aqueous complex) and any number of defined basis species. For the reactions considered in this work, the basis species are U^{4+} , H_2O , H^+ , $\text{O}_2(\text{g})$, and HCO_3^- .

In order to simulate the dissolution of U_3O_7 and the precipitation of UO_2 , we have used the following heterogeneous reactions:



together with the aqueous speciation model described by BRUNO and PUIGDOMÈNECH (1989). Therefore, new expressions for the net dissolution and precipitation reactions must be written for the EQ3/6 codes. For this purpose we have used the transition state expression (LASAGA, 1981; DELANY et al., 1986). Thus, for precipitation

$$d[\text{U}]/dt = -k_p S q_- [1 - (Q_-/K_-)] \quad (17)$$

where q_- is the kinetic activity product for the reaction products, Q_- is the ion activity product of the mineral precipitation reaction, and K_- is the equilibrium constant for the precipitation reaction (cf. DELANY et al., 1986).

We have simulated some of the experimental data reported in the present work with the EQ3/6 code and Eqn. (17) (and its complement for dissolution reactions). The input parameters are as follows: for the reaction of the solubility of UO_2 expressed above in Eqn. (16), we need the values of $\log K_- = -2.44$ (equivalent to a UO_2 -solubility of $0.0043 \text{ mg dm}^{-3}$) and $k_p = 1.95 \times 10^{-9} \text{ sec}^{-1} \text{ cm}^{-2}$. For the reaction of the solubility of U_3O_7 [15], we used the value of $(k_d[\text{H}^+]^{-0.3}) = 1.93 \times 10^{-13}$ and an initial amount of $\text{U}_3\text{O}_7(\text{c})$ equal to $0.4414 \mu\text{mol dm}^{-3}$.

The results are presented in Fig. 8, which illustrates the potential of the EQ3/6 codes to simulate problems related with uranium geochemistry. The results also corroborate the validity of the assumptions made in the numerical methods used to extract rate constants from the experimental data. Unfortunately, the EQ6 code incorporates an integration procedure which performs poorly on stiff kinetic systems, and computer execution times for this kind of problems might be very large in small computers (e.g., the run to draw Fig. 8 takes several days of CPU time on a VAX-750, whereas on a CONVEX C210 it takes only some minutes of CPU time).

Temperature Dependence

In order to obtain the temperature dependence of the precipitation rate, we have fitted a first degree kinetic expression and Arrhenius equation to the data of FORWARD and HALPERN (1953) and BUNJI and ZOGOVIC (1958). The calculated activation energy is $E_a = 98.7 \text{ kJoules mol}^{-1}$ from the data

of BUNJI and ZOGOVIC (1958) using UO_2 catalyst on solutions probably containing 20 g dm^{-3} of Na_2CO_3 and 32 g dm^{-3} of NaHCO_3 , and $E_a = 45.6 \text{ kJ mol}^{-1}$ from the data of FORWARD and HALPERN (1953) using Ni catalyst on solutions probably containing 50 g dm^{-3} of Na_2CO_3 . This can be compared with values between 50 and 63 kJ mol^{-1} obtained by BALACEANU et al. (1958) using Ni-Raney catalyst.

Using Arrhenius equation and the activation energy of $E_a = 98.7 \text{ kJ mol}^{-1}$ for the data of BUNJI and ZOGOVIC (1958), we obtain a rate constant for the reduction of U(VI) and UO_2 precipitation at 25°C of $8.9 \times 10^{-12} \text{ sec}^{-1} \text{ g}^{-1} \text{UO}_2 \text{ atm}^{-1}$. The surface area was increasing during the experiments of BUNJI and ZOGOVIC (1958). Furthermore, specific surface areas for UO_2 vary with the degree of crystallinity from 80 to $0.2 \text{ m}^2 \text{ g}^{-1}$ (GREILING and LIESER, 1984; BRUNO and PUIGDOMÈNECH, 1989). If a value of $80 \text{ m}^2 \text{ g}^{-1}$ is used, a rate constant of $k_p = 7.2 \times 10^{-10} \text{ sec}^{-1} \text{ m}^{-2} \text{ atm}^{-1}$ is obtained for solutions containing about 0.2 mol dm^{-3} Na_2CO_3 and 0.4 mol dm^{-3} NaHCO_3 . Taking into account that the presence of bicarbonate slows down the reaction (BALACEANU et al., 1958), this rate constant agrees qualitatively well with the values of $1.9(\pm 0.8) \times 10^{-5}$ in 0.008 M NaClO_4 and $9.3(\pm 0.1) \times 10^{-7}$ for our 0.1 mol dm^{-3} NaHCO_3 experiment (cf. Fig. 5).

CONCLUSIONS

We have studied the kinetics of dissolution of UO_2 and UO_{2+x} in a wide pH range (3 to 11). The dependence of the rate of dissolution on the hydrogen ion concentration has been established. The following rate equations have been determined for $\text{UO}_2(\text{s})$ in the acidic pH range $3 \leq \text{pH} \leq 7$:

$$r_{\text{diss}}(\text{UO}_2) (\text{mol sec}^{-1} \text{ m}^{-2}) = 1.4 (\pm 0.3) \times 10^{-8} [\text{H}^+]^{0.53 \pm 0.02}$$

For UO_{2+x} the dependence of the rate of dissolution on pH in the range $3 \leq \text{pH} \leq 9$ is given by the expression

$$r_{\text{diss}}(\text{UO}_{2+x}) (\text{mol sec}^{-1} \text{ m}^{-2}) = 1.1 (\pm 0.3) \times 10^{-12} [\text{H}^+]^{-0.30 \pm 0.02}$$

In all cases the mechanism of dissolution is surface controlled. In the acidic pH range the dissolution of UO_2 is proton promoted, while for UO_{2+x} it appears to be hydroxo promoted already at $\text{pH} \approx 3$. This is explained by the different surface protonation properties of the two solids. The UO_2 surface is positively charged up to $\text{pH} = 6.8$ ($\text{pH}_{\text{zpc}} = 6.8 \pm 0.3$) and, consequently, the surface charge $\sigma \approx \{>\text{UOH}_2^+\}$. The rate of dissolution of UO_2 in the acidic pH range has been shown to be proportional to the activity of the protonated surface species, according to the expression

$$r_{\text{diss}}(\text{UO}_2) (\text{mol sec}^{-1} \text{ m}^{-2}) = k_{\text{H}} \{>\text{UOH}_2^+\}^4$$

This confirms the ideal correlation found between the oxidation state of the central ion and the order with respect to the activity of the protonated surface complex (STUMM and WIELAND, 1991). On the other hand, UO_{2+x} has a $\text{pH}_{\text{zpc}} = 3.4 \pm 0.4$, consequently at $\text{pH} > 3.4$, the surface charge σ

$[\text{U}]_{\text{tot}} / (\text{mg/l})$

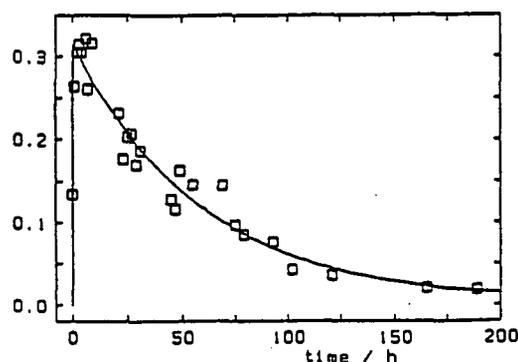


FIG. 8. Results from EQ3/6 calculations (continuous line) simulating the experimental data (squares) obtained in the present work for $\text{pH} = 8.5$, 8 mM NaClO_4 , $p(\text{H}_2) = 0.97 \text{ atm}$, amount of UO_2 : 1.2 g dm^{-3} (surface area: 0.2412 m^2).

$\approx \{>\text{UO}^-\}$ and the rate of dissolution should be proportional to the activity of the deprotonated surface.

In the neutral to alkaline pH range (7 to 11), we found that the rate of dissolution of UO_2 is independent of pH. As we have already discussed, the measurements have been performed in conditions close to equilibrium and the measured rates have to be taken as limiting ones. However, the non-dependence of the rate of dissolution with pH is confirmed even for the selected data obtained far from equilibrium. The rate of dissolution of UO_2 in the pH range 7 to 11 is of zeroth order:

$$r_{\text{diss}}(\text{UO}_2) (\text{mol sec}^{-1} \text{ m}^{-2}) = 1.9 (\pm 0.8) \times 10^{-12}$$

This rate constant indicates that the half-time for the dissolution reaction of UO_2 in the pH range of most natural waters and under reducing conditions is in the order of days. If we compare that with the range of residence times of undisturbed groundwaters ($\tau: 10^2$ – 10^5 a), we can conclude that the dissolution of UO_2 and, consequently, the mobility of uranium under these conditions will be thermodynamically and not kinetically controlled.

The development of the continuous flow-through reactor, using a thin layer of solid inside it, has proved to be useful for the study of pure dissolution reactions without the interference of surface impurities or secondary phases formation.

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