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Oxidation of U(IV) by atmospheric oxygen in pH 1.5–7.4 aqueous solutions

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Abstract

U(IV) oxidation by oxygen in weakly acidic and neutral solutions at pH 1.5–7.4 has been found to proceed by a pseudo-first order reaction with an induction period dependent on the accumulation of U(VI). The presence or the addition of U(VI) accelerates U(IV) oxidation. The rate constants of U(IV) oxidation by air have been determined. The oxidation mechanism involves the interaction of hydrolyzed $U(OH)_2^{2+}$ species with O_2, HO_2, H_2O_2, and $OH^\bullet$, the formation of U(V), and the reaction of U(V) with the listed oxidants. After the accumulation of sufficient U(VI), the reaction $U(VI) + U(IV) \rightleftarrows 2\,U(V)$ becomes rate-controlling. The formation of colloidal polymer solution has been observed at pH 1.5–4 during the oxidation of U(IV) by air, during photochemical reduction of U(VI), or by mixing of U(VI) and U(IV) solutions. The colloidal polymer solution has been found to be stable at 20–100 °C under anaerobic conditions. The polymer was isolated from the solution by centrifugation at $5500 \times g$. Chemical and X-ray photoelectron spectroscopy studies have shown the polymer to be a sparingly soluble mixed U(VI)–U(IV) hydroxide.

Keywords: U(IV); Oxidation; U(VI)

1. Introduction

The stability of dissolved U(IV) towards molecular O_2 has been studied in perchlorate [1–4] and sulfate [5] solutions with H^+ concentration ranging from 0.01 to 3 M. Air oxidation of U(IV) also has been studied in alkaline 1 M $NaHCO_3$ + 0.25 M Na_2CO_3 solution [6]. However, the behavior of U(IV) towards air oxidation at intermediate pH (2–8) remains not fully clear. These media are of interest in light of actinide migration in the environment, waste burial, and underwater or repository storage of irradiated uranium with defective cladding. The aim of the present work is the study of the kinetics and mechanism of U(IV) oxidation by atmospheric oxygen in pH 1.5–7.4 aqueous solution.

2. Experimental

2.1. Experimental materials

Uranium trioxide, UO_3, purified by known techniques, was used as the starting material. The UO_3 was dissolved in $HClO_4$, HCl, or HNO_3 and the resulting U(VI) solution concentrations determined gravimetrically as U_3O_8. Stock U(IV) solutions were obtained by electrochemical reduction of U(VI) in high-purity Ar-saturated $HClO_4$ solution on a mercury cathode in a cell with cathodic and anodic compartments separated by a cation-exchanged membrane [7]. In some experiments, solid Cs_2UCl_6 was used to prepare U(IV) solutions. Twice-distilled water was used in all experiments and all commercial substances were of reagent-grade. The U(IV) concentrations were determined by complexometric titration with xylenol orange and by spectrophotometry using the U(IV) absorption band at 648 nm and a Shimadzu UV-3100 spectrophotometer. Potassium phosphotungstate, $K_{10}P_2W_{17}O_{61}\cdot nH_2O$, was used to determine U(IV) concentration in solutions which also contained U(VI). This substance was synthesized and purified according to methods described by Tourné and Tourné [8].

2.2. Experimental technique

Each experiment was performed using 10–50 ml of H_2O or diluted NaOH solution in a temperature-controlled cell. Aliquots of $U(ClO_4)_4$ solution were added and the solutions bubbled with H_2O-saturated air at the rate

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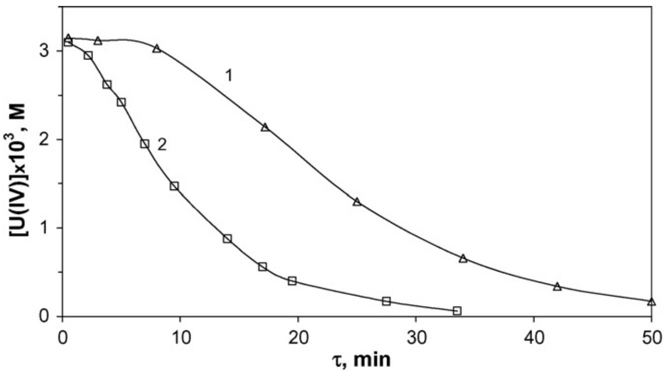

Fig. 1. The effect of U(VI) addition on the rate of U(IV) oxidation by bubbling air at pH 1.80 and 20 °C. $[U(IV)]_0 = 3.28 \times 10^{-3}$ M, $[U(VI)]_0$: (1) 0 M; (2) 3×10^{-3} M.

100 ± 10 ml/min. Periodically, aliquots were taken and analyzed for U(IV) concentrations. For 1–3 mM U(IV), the aliquot volume was 0.5 ml. The probe was introduced into a spectrophotometric cell ($l = 1$ cm) with 2.5 ml of 0.5 M $HClO_4 + 2$ mM $K_{10}P_2W_{17}O_{61}$ solution. For U(IV) concentrations ≤0.3 mM, the aliquot volume was 3.0 ml. In this case, the solution was placed into a vial or cell with 0.5 ml of 3.5 M $HClO_4 + 6$ mM $K_{10}P_2W_{17}O_{61}$ solution. A reddish-violet complex having an absorption band with maximum at 510 nm, $\varepsilon = 1000\ M^{-1}\ cm^{-1}$, forms with U(IV) and ${P_2W_{17}O_{61}}^{10-}$ according to the reaction [9].

$$U^{4+} + 2{P_2W_{17}O_{61}}^{10-} \rightarrow {U(P_2W_{17}O_{61})_2}^{16-}$$

In contrast, U(VI) forms a very weak complex with ${P_2W_{17}O_{61}}^{10-}$ in acidic media and does not hinder U(IV) determination. At the end of each experiment, the pH was measured using a combined glass electrode and "Radelkis" OP-211/1 pH-meter. The experiments were performed at 20 ± 1 °C. The experiments at higher temperatures showed very high data scatter. Each kinetic experiment was performed three times. Experimental error of the measured rate constants is estimated as ±15%.

3. Results and discussion

The decrease in U(IV) concentration from 3.28×10^{-3} M with time in pH 1.80 solution is shown in Fig. 1, curve 1. It is seen that after an induction period, the reaction accelerates. Similar observations of autocatalysis were postulated to occur by accumulation of U(VI) to interact with the hydrolyzed uranium(IV) ion, ${U(OH)_2}^{2+}$ [4]. In additional tests for the present studies, introduction of 3×10^{-3} M $UO_2(ClO_4)_2$ into U(IV) solution was observed to decrease the induction period for U(IV) oxidation with the reaction proceeding by approximately first-order kinetics (Fig. 1, curve 2). This dependence is clearly displayed for the kinetic data presented in semi-logarithmic coordinates (Fig. 2). The same phenomenon occurs at lower U(IV) concentrations – at least down to 10^{-4} M – both in the presence and absence of 3 mM $UO_2(ClO_4)_2$. At the end of the experiments, the kinetic curves in semi-logarithmic coordinates become straight lines indicating that the reaction is pseudo-first order relative to U(IV). Slopes of the initial and final sections of the kinetic curves are compared in Fig. 2 and the kinetic data are shown in Table 1.

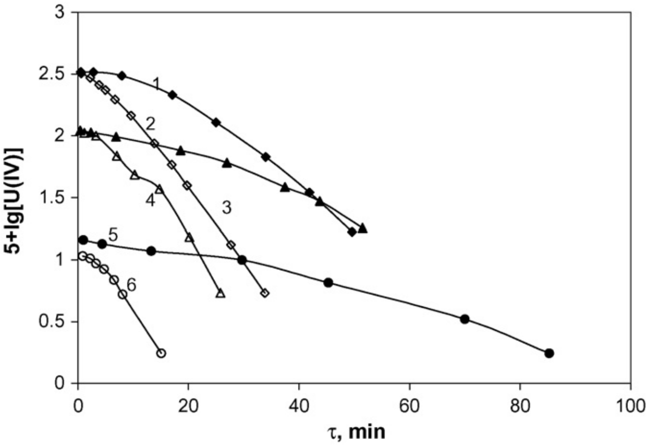

Fig. 2. Semilogarithmic kinetic curves of U(IV) oxidation by bubbling air through 20 °C, pH 1.80 solution. $[U(IV)]_0$ (mM): (1 and 2) 3.28; (3 and 4) 1.10; (5) 0.15; (6) 0.115. (1, 3 and 5) No U(VI) additions and (2, 4 and 6) addition of 3 mM U(VI).

The following conclusions are derived based on these data:

- The slopes of the final sections of the curves are the same for 5.50–6.14 and 2.86 mM U(VI) (5th column). That is, increasing U(VI) concentration beyond a certain threshold does not influence the rate of the reaction. This indicates that reacting species form a complex; after complex formation, the intramolecular transformations can proceed.
- The slopes of initial sections of curves 2 and 6 are lower than that of the final section of curve 1 at the same U(VI) concentration. This indicates that the U(IV)–U(VI) complex forms slowly.
- The slope of final section of curve 1 is lower than that of the final sections of the curves 2 and 6. This is because all of the U(IV) is complexed after 300 s (curve 6) or after 800 s (curve 2) while, in the case of curve 1, 2500 s passes until 2.95 mM U(VI) accumulates. By this time, U(IV) has partially polymerized.

Table 1
Some kinetic data of U(IV) oxidation by atmospheric oxygen at conditions indicated in Fig. 2

Curve number	$[U(VI)]_0 \times 10^4$ (M)	$[U(IV)]_0 \times 10^4$ (M)	$t_g\ \varphi_{init} \times 10^3$ (s^{-1})	$[U(VI)]_{fin} \times 10^4$ (M)	$t_g\ \varphi_{fin} \times 10^3$ (s^{-1})
1	–	32.8	–	29.5	0.657
2	30	32.8	0.364	55.0–61.4	1.053
5	–	1.5	–	1.2	0.303
6	28	1.15	0.242	28.6	1.16
Additional experiments	100 (pH 1.79)	2.48	0.325	102	0.84
	100 (pH 1.85)	1.21	0.258	101	1.1

$t_g\ \varphi_{init}$ and $t_g\ \varphi_{fin}$ are the slopes of the kinetic curves at the beginning and at the end of the reactions.

U(IV) exists as hydrolyzed species $U(OH)_n^{(4-n)-}$ in low-acidic solutions. To calculate the hydrolysis constants K' and distributions of the different $U(OH)_n^{(4-n)-}$ species ($n = 1$–4), the standard formation constants of the hydroxocomplexes, $\lg\beta_n^0$, were used given in Ref. [10]. The $\lg K'$ values were calculated according specific ion interaction theory (SIT) [11] for ionic strength $I = 0.03$ and have been found to be: -0.82 ± 0.2; -1.8 ± 1.0; -5.54 ± 1.0; -12.4 ± 1.0 for $n = 1$, 2, 3 and 4, respectively. In experiments without added U(VI), the I was not higher than indicated value 0.03. Calculations made with these values and activity coefficient $\gamma_n = 0.9$ show that at pH 1.8–1.85, up to 83.47% of the U(IV) exists as $U(OH)_2^{2+}$. The same results were obtained as well using the β_n^0 values given in Ref. [12].

Therefore, in solutions with pH 1.80–1.85, most uranium(IV) exists as $U(OH)_2^{2+}$. According to the chain reaction mechanism proposed by Halpern and Smith [1], U(IV) oxidation could occur by the following sequence of reactions:

$$U(OH)_2^{2+} + O_2 \rightarrow UO_2^{+} + HO_2 + H^{+} \quad (1)$$

$$U(OH)_2^{2+} + (HO_2,\ H_2O_2,\ OH^{\bullet}) \rightarrow UO_2^{+} + \text{products} \quad (2)$$

$$UO_2^{+} + O_2 + H^{+} \rightarrow UO_2^{2+} + HO_2,$$
$$k_3 = 31.4\,\mathrm{M^{-1}\,s^{-1}}[13] \quad (3)$$

$$UO_2^{+} + (HO_2,\ H_2O_2,\ OH^{\bullet}) \rightarrow UO_2^{2+} + \text{products} \quad (4)$$

It is known that in low-acid solutions, the following equilibrium takes place:

$$U(IV) + U(VI) \rightleftarrows 2U(V) \quad (5)$$

The equilibrium constant of reaction (5) was determined for perchloric and hydrochloric acid solutions by Nelson and Kraus [14]. It follows from our experiments that in low acidic solution, reaction (6) of complex formation proceeds before reaction (5):

$$U(OH)_2^{2+} + UO_2^{2+} \rightleftarrows U(IV)\text{–}U(VI)\ \text{complex} \quad (6)$$

Therefore, in the course of U(IV) oxidation, after accumulation of some amount of U(VI), reaction (5) becomes the rate-controlling step.

Relatively high rates of reaction (5) were demonstrated in special experiments in which weighed amounts of Cs_2UCl_6 were added to cells containing 0.1 M $UO_2(NO_3)_2$ solution. The electronic absorption spectra showed that after less than 5 min, the band at 737 nm appeared, indicating a fast equilibrium to obtain the cation–cation complex described by Newton and Baker [15]:

$$UO_2^{+} + UO_2^{2+} \rightleftarrows U_2O_4^{3+}. \quad (7)$$

Therefore, reaction (5) must occur before reaction (7). The pH of the solution during the experiment was about 1.5.

The pseudo-first order constants k' for initial sections of the kinetic curves in solutions without additional U(VI) (pH 1.80–1.85) have been obtained for various U(IV) concentrations (as determined from data given in Figs. 1 and 2):

$[U(IV)]_0$ (mM)	0.15	1.10	3.28
$k' \times 10^4$ (s^{-1})	2.92	2.90	0.27

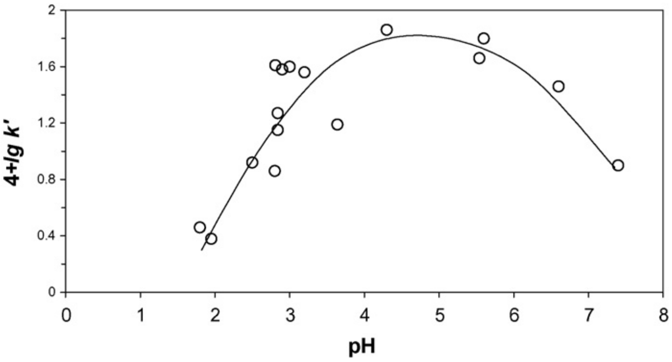

Fig. 3. Plot of pseudo-first order rate constant k' of U(IV) oxidation by air vs. pH.

The observed decrease of the constant k' with increasing U(IV) concentration is caused by polymerization of hydrolyzed U(IV). Because oxygen solubility in aerated water is 0.277 mM at 20 °C [16] and recognizing from reaction (1) that $k' = 4k_1\,[O_2]$, it is seen that $k_1 = 0.26\,\mathrm{M^{-1}\,s^{-1}}$. This value for k_1 is approximately 120-times lower than the rate constant of UO_2^{+} oxidation, k_3. This difference is plausible both by the difference in the values of standard oxidation potentials, E, for the pairs UO_2^{2+}/UO_2^{+} (0.17 V) and UO_2^{+}/U^{4+} (0.38 V) [17] and by the structural rearrangement of U(IV) ions required by reaction (1). A plot of $\log k'$ versus pH is given in Fig. 3. Despite the scattering of k' values, it is evident that $\log k'$ increases in proportion to pH in the range pH 2–3. At higher pH, the $\log k'$ value increases more slowly and decreases above pH 4.5. This variation is caused by U(IV) polymerization at higher pH.

When pH increases from 1.8 to 4, the U(IV) oxidation rate also increases and the induction period decreases as shown in Fig. 4. The acceleration of the reaction is explained by the important role of reaction (1). Disappearance of the induction period is caused by the absence of reaction (5) since at higher pH its equilibrium is fully displaced to the left. Hydrolyzed U(IV) forms polymer and the polymer incorporates the U(VI). A similar binding has been demonstrated for hydrolyzed Th(IV) and U(VI) at pH 1.5–4.0 [18]. It is seen that the U(IV) polymerization and U(VI) capture rates depend on pH. At low pH, reaction (5)

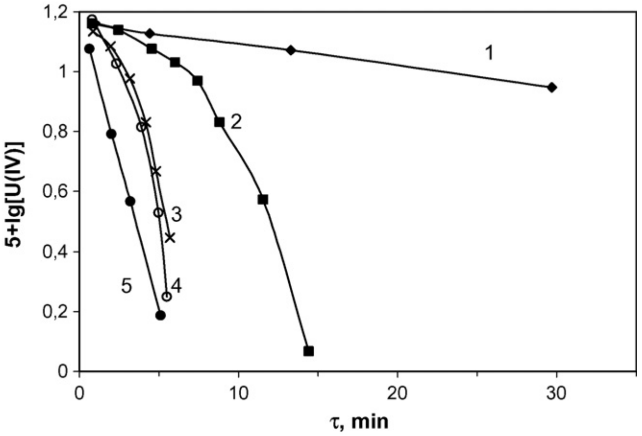

Fig. 4. Effect of pH on the oxidation kinetics of 1×10^{-4} M U(IV) by atmospheric oxygen. pH: (1) 1.80; (2) 2.48; (3) 2.83; (4) 3.20; (5) 4.14.

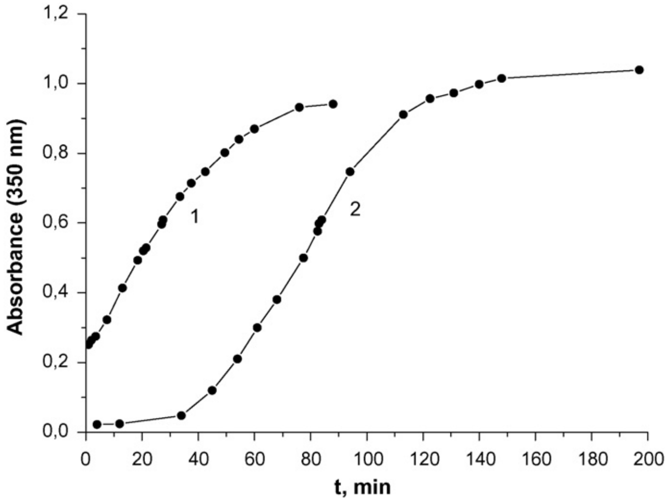

Fig. 5. Influence of pH on the formation rate of U(IV)–U(VI) mixed hydroxide in argon-saturated 25.0 °C aqueous solution. [U(IV)] = [U(VI)] = 4.38×10^{-4} M, $l = 5$ cm and $\lambda = 350$ nm. pH: (1) 2.9; (2) 2.5.

must proceed before U(IV) polymer forms. At pH 4 and higher, polymerization hinders U(V) formation.

The process of polymer formation at $\mathrm{pH} < 3$ was studied in more detail in argon-saturated solutions for reactions (5) and (7). It was found that light absorption over a wide wavelength range, especially at shorter wavelengths, increases after 1.5 h. After 24 h, the absorption spectra maxima disappear to give a structureless absorption band having higher intensity at shorter wavelengths. Though the solution becomes black, it is not turbid and the solution's light absorption remains unchanged for 1 month if kept anaerobically. Centrifugation of the solution at 1750 × *g* did not separate phases, but 1 h centrifugation at 5500 × *g* separated a black solid phase. The separated black precipitate dissolves slowly in anaerobic 1 M $HClO_4$. After 1 day, the absorption spectrum of the solution shows bands characteristic of U(IV) and U(VI) aquo ions with a [U(IV)]/[U(VI)] concentration ratio of 0.17.

Kinetic curves of increasing optical density at 350 nm are depicted in Fig. 5 for pH 2.90 and 2.50 air-free 25 °C solutions containing equimolar (0.44 mM) U(IV) and U(VI). The induction period is evident and decreases as pH increases from 2.5 to 2.9. The induction period also lengthens at 18–20 °C and decreases steeply at 80 °C. A black precipitate immediately forms and the supernatant becomes colorless and transparent upon addition of 0.07 M (pH 4.5) CH_3COONa buffer solution.

Black polymer forms also by photo-reduction of U(VI) in Ar-saturated aqueous solution containing 4.2 mM $UO_2(ClO_4)_2$ and 0.5 M C_2H_5OH at pH 2.5. After just 10-min of irradiation, the absorbance of the U(VI) band at 420 nm decreases approximately two-fold. These observations are consistent with the occurrence of reactions (8) and (9):

$$UO_2{}^{2+} + h\nu \rightarrow {*UO_2}^{2+} \qquad (8)$$

$$*UO_2{}^{2+} + C_2H_5OH \rightarrow UO_2{}^{+} \qquad (9)$$

With time, a slow increase of optical density occurs over the entire wavelength range and the solution became black, though not visibly turbid. Based on these results, it appears that in pH 2.5 solution, the U(V) completely disproportionates to form the U(IV)–U(VI) copolymer, shifting the equilibrium reaction (5) to the left.

Formation of colloidal solutions containing mixed U(IV)–U(VI) hydroxides was observed during U(VI) reduction by sodium sulfide in bicarbonate solution heated to >50 °C under inert atmosphere [19]. The product colloidal particles were studied by X-ray diffraction, photoelectronic spectroscopy, Fourier-transform IR spectroscopy, scanning electronic microscopy, and other techniques. The black particles were shown to represent mixed oxide (or hydroxide) polymers of U(IV) and U(VI). The particles did not dissolve, or at least dissolved very slowly, in weakly acidic pH 2.8 solution as shown by electrophoretic measurements performed at pH 2.8–9.5. It is noted [19] that no formation of particles of pure U(VI) hydroxo-compounds was observed at $\mathrm{pH} \lesssim 5.5$.

It is known that addition of 1 M NaOH to mixed U(IV)–U(VI) solutions under inert atmosphere forms precipitates whose color depend on the U(VI)/U(IV) molar ratio. At U(VI)/U(IV) molar ratio higher than 3:22 (12% of U(VI) in mixed uranium hydroxides), the precipitate is no longer green but black. Measurement of the magnetic susceptibility has shown that the precipitate contains a U(IV)–U(VI) hydroxide mixture [20]. Formation of such precipitates also is observed upon adding ammonia to U(VI)–U(IV) solutions at ratios ranging from 1:9 to 9:1 [21]. Beyond these ratios, the precipitates acquire the color of the prevailing hydroxide, yellow if U(VI) or green if U(IV). At a U(VI):U(IV) ratio of 1:1, the dried precipitate has a violet shade. On the basis of chemical analysis, spectrophotometry, proton magnetic resonance, and other measurements, the authors [21] concluded that the precipitate was uranium(V) hydroxide $[UO_2OH \cdot xH_2O]_n$, with $x = 2$–3.

In the present studies, several additional tests were done of the black colloid obtained at pH 1.5–2.5. It was found that the black solution is stable towards heating to 100 ± 5 °C at least for 3 days and quickly gives a grayish-black precipitate during the heating in sealed glass tube at 200 ± 5 °C. The precipitate peptizes on cooling. The precipitate's X-ray diffraction pattern shows one product, poorly crystalline uranium dioxide, UO_2. The black precipitate formed at room temperature and separated by centrifugation at 5500 × *g* was studied by X-ray photoelectron spectroscopy (XPES). Uranium(VI) hydroxide precipitated by a minimum quantity of ammonia served as a U(VI) standard in these experiments. In the XPE spectra of the black precipitate (Fig. 6), the doublet of the U4f electrons, widened in comparison with the doublet observed for uranium(VI) hydroxide, may be deconvoluted into two adjacent doublets (Fig. 6b). The binding energies of $U4f_{7/2}$ electrons (380.4 eV and 381.5 eV) correspond to U(IV) and U(VI) [22]. The slight humps at higher binding energies are due to a shake-up excitation of an electron from the O2p–U bonding band to partially occupied or unoccupied localized metal 5f levels and indicate the presence of U(IV). The increased peak intensity at 381.5 eV reveals partial oxidation on the precipitate surface.

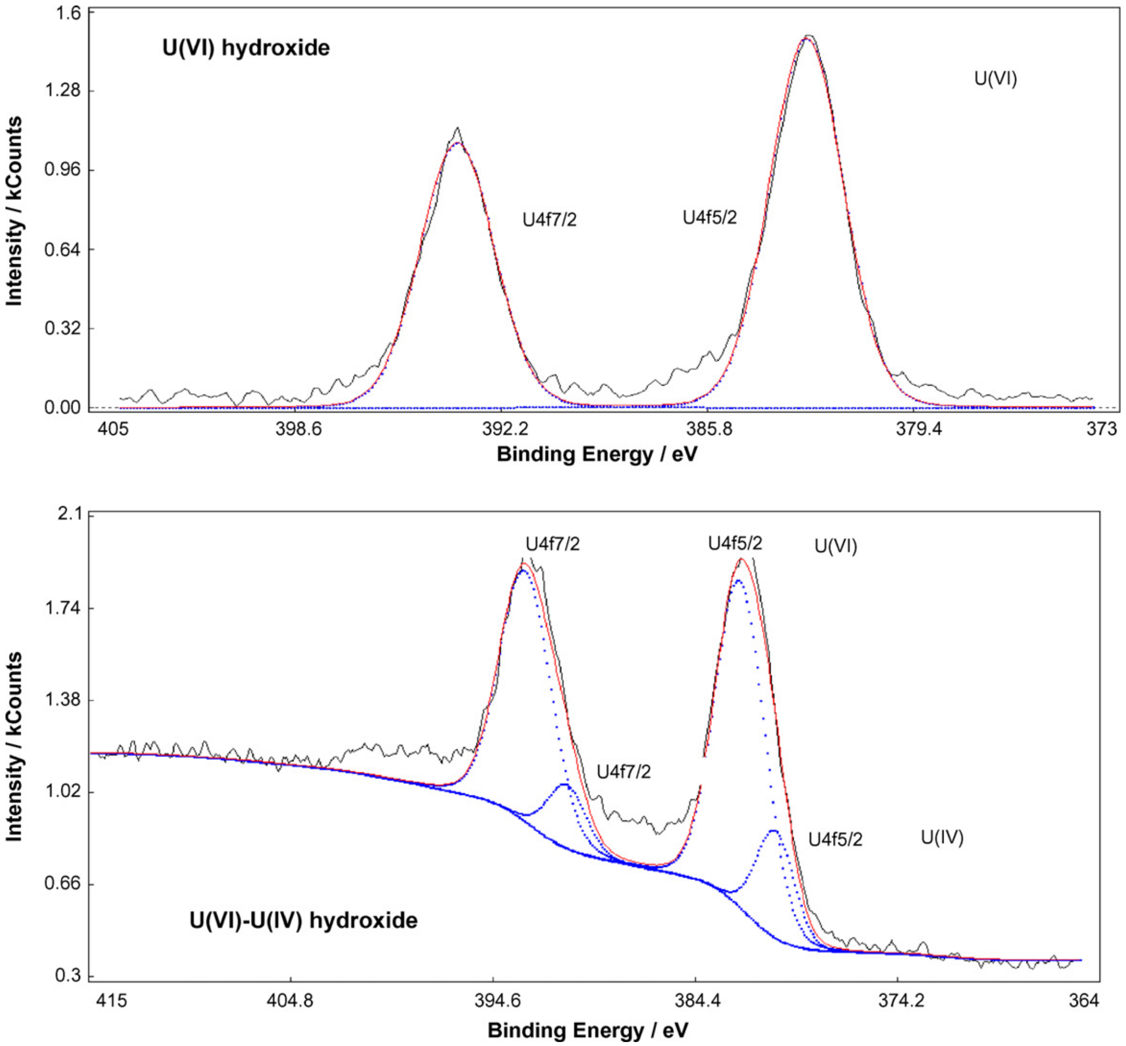

Fig. 6. XPE spectra of U(VI) hydroxide (top) and of black colloidal particles obtained by partial oxidation of U(IV) by air (bottom).

Analysis of previously published and the current experimental data shows that the polymer arising at pH 1.5–4 consist of U(IV) and U(VI) hydroxides.

4. Conclusions

1. The oxidation of U(IV) by atmospheric oxygen in aqueous solutions at pH 1.5–7.4 proceeds by a reaction that is pseudo-first order with respect to U(IV) concentration preceded by an induction period to accumulate U(VI).
2. The presence or the addition of U(VI) accelerates the oxidation of U(IV) by atmospheric oxygen in pH 1.5–7.4 aqueous solutions and decreases the induction period. The oxidation mechanism includes U(IV) hydrolysis, U(IV) and U(V) interaction with oxygen, and the equilibrium reaction $\mathrm{U(VI)} + \mathrm{U(IV)} \rightleftarrows 2\,\mathrm{U(V)}$.
3. The oxidation of aqueous U(IV) by atmospheric oxygen or by other oxidants at pH 1.5–7.4 initially yields solution containing U(IV), U(V), and U(VI). This mixture transforms into a mixed U(IV)–U(VI) hydroxide polymer as a colloidal solution (sol) stable at the studied uranium concentration range of 10^{-4} to 3×10^{-2} M and U(IV):U(VI) molar ratios ranging from 1:5 to 5:1 under anaerobic condition at 20–100 °C.

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