



OXIDATIVE DISSOLUTION OF TRIURANIUM OCTAOXIDE IN HYDROXIDE-PEROXIDE MEDIA

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Abstract. The article presents the results of a kinetic study of oxidative dissolution of powdered triuranium octoxide samples in the aqueous mixture NaOH – H₂O₂. It was found that the concentration of the oxidant/complexing reagent (H₂O₂) in 1.0 mol/L NaOH solution determines the chemistry of the process and influence on the kinetic of U₃O₈ oxidative dissolution. The rate and completeness of U₃O₈ dissolution have also been shown to depend on the physical properties of the initial oxide powder and alkaline solution temperature. Process rate constant values for all studied conditions are calculated. The calculated value of the apparent activation energy was 47 kJ/mol (U₃O₈ powder sample obtained at 480°C) and 33.8 kJ/mol (U₃O₈ powder sample obtained at 600°C), which corresponds to the limitation of the process by a chemical reaction. Based on the results obtained, the conditions for the quantitative dissolution of U₃O₈ in NaOH – H₂O₂ solutions were determined.

Keywords: triuranium octoxide, uranium dioxide, oxidative dissolution, hydrogen peroxide, sodium hydroxide

1. INTRODUCTION

The direction of spent nuclear fuel (SNF) reprocessing in carbonate or alkaline media is related to oxidative dissolution step and further partitioning of carbonate/bicarbonate or carbonate-alkaline multi-component radioactive solutions and considered as an alternative to nitric acid-based hydro-chemical reprocessing in various options of the PUREX process [1]–[7].

Hydrogen peroxide (H₂O₂) is considered as the most suitable oxidizer of U(IV) when UO₂-based or voloxidized SNF (in the U₃O₈ form) is dissolving. The applying of H₂O₂ in the oxidative dissolution process makes it possible to quickly and quantitatively dissolve uranium dioxide (UO₂) or triuranium octoxide (U₃O₈) in carbonate media due to effective oxidation and the formation of highly soluble mixed uranyl(VI) peroxo-carbonate species [8]–[10].

The potential for application of H₂O₂ to dissolve metallic uranium [11]–[14], UO₂ and uranium mononitride (UN) [15,16] in solutions of alkali-metal hydroxides (LiOH, NaOH, KOH) was confirmed.

In the presence of CO₃²⁻ or OH⁻ ions, stable soluble mixed peroxo-carbonate(hydroxide) species and anionic uranyl(VI) peroxide cage clusters are formed. The high solubility of these species makes it possible to develop alternative non-acidic approaches to SNF reprocessing and also has a significant effect on the migration of uranium in groundwater during the storage of high-level nuclear waste.

In the ternary U(VI) – OH⁻ – O₂²⁻ system monomeric species [UO₂(OH)(O₂)]⁻ (predominant in the region from 9.5 to 11.5), [(UO₂)₂(OH)(O₂)₂]⁻ (found in significant amounts at pH < 10.5) [17,18], [UO₂(OH)₂(O₂)₂]²⁻, [UO₂(OH)(O₂)₂]⁴⁻ (pH = 12) [19],

[(UO₂)(H₂O)₂(O₂)₂]²⁻, [(UO₂)(H₂O)(OOH)(O₂)₂]³⁻, and [(UO₂)(OOH)(O₂)₂]³⁻ (pH = 11.62) [20] were identified. In solutions with high concentrations of MOH (where M is Li⁺, Na⁺, K⁺) and H₂O₂, negatively charged U(VI) peroxide aqueous macroanions [(UO₂)(O₂)_{1.5}]₂₀²⁰⁻, [(UO₂)₂₈(O₂)₄₂]²⁸⁻, [(UO₂)(O₂)(OH)]₂₄²⁴⁻, [(UO₂)₃₂(O₂)₄₀(OH)₁₆]³²⁻ are formed [15,16,21].

The concentration of H₂O₂ directly affects the formation and decomposition of highly soluble uranyl(VI) peroxide cage clusters existing in the solutions as aqueous macroanions. Uranyl(VI) peroxide cluster formation cannot proceed without an excess of H₂O₂.

Lower concentrations (less than 0.1 mol/dm³) of H₂O₂ and hydroxide reduce the effectiveness dissolution of UO₂ and UN and tend to form less soluble simple uranyl(VI) peroxide species ([UO₂(O₂)₃]⁴⁻, [(UO₂(O₂)₂)₄]⁸⁻, or [(UO₂(O₂)₂)₅]¹⁰⁻) rather than highly soluble peroxide clusters [15].

In the absence of a sufficient concentration of alkali cations, the interaction of peroxide with UO₂ can lead to the formation of insoluble secondary phases such as studdite ([UO₂)(O₂)(H₂O)₂·2(H₂O)] or metastuddite ([UO₂)(O₂)·2(H₂O)] [22]–[25]. The interaction of studdite with H₂O₂ may be accompanied by the formation of uranyl(VI)–peroxide complexes [UO₂O₂]⁰, [UO₂(O₂)₂]²⁻ and [UO₂(O₂)₃]⁴⁻ [26].

Thus, H₂O₂ affects the release of uranium from SNF by forming solid phases and/or soluble uranyl(VI) peroxide species. In this case, the fundamental importance for the development of oxidative dissolution processes of uranium oxides (UO₂, U₃O₈) in hydroxide systems is redox reactions, complexation, and polymerization processes involving peroxide ion.

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The study of the kinetic characteristics of U_3O_8 oxidative dissolution processes in hydroxide-peroxide solutions is an important current task and particular importance for the development of safer and simple systems for the extraction of uranium from SNF and radioactive waste.

The purpose of this research was to study the features of powdered U_3O_8 oxidative dissolution process and determine the conditions for its complete dissolution in sodium hydroxide solution in the presence of hydrogen peroxide.

2. MATERIALS AND METHODS

Solid NaOH and 30 % (9.8 mol/L) aqueous solution of H_2O_2 of the chemically pure grade were used.

Uranium dioxide powder as a starting material was used. The composition of the initial UO_2 powder, according to the X-ray diffraction (XRD) analysis corresponded to $UO_{2.25}$ (PDF–2/2010 № 20–1344). The specific surface area (SSA) value, calculated using the Brunauer, Emmett, and Teller (BET) method for the $UO_{2.25}$ powder sample was $3.3 \text{ m}^2/\text{g}$. Powdered

samples of U_3O_8 , were obtained by heat treatment of the powdered $UO_{2.25}$ in the air atmosphere for 120 min in the calcinations temperature (t) range from 480 to 1200°C . The heat treatment mode was as follows: 120 min of heating – 120 min of isothermal exposure – slow cooling together with the furnace. The heat treatment products were fine crystalline powders, whose colour, depending on the treatment temperature, ranged from olive green to black. In all cases, the final heat-treated product for $UO_{2.25}$ from 480 to 1200°C was U_3O_8 (PDF–2/2010 № 76–1850). Table 1 shows the SSA values for U_3O_8 powder samples.

Table 1. Data on the specific surface area of U_3O_8 powder samples.

$t, ^\circ\text{C}$	480	600	800	1000	1200
$SSA_{BET}, \text{m}^2/\text{g}$	3.8	3.7	1.8	0.8	0.1

Figure 1 shows the micrographs for the UO_2 (1,2) and U_3O_8 (3–12) powder samples obtained with a scanning electron microscope (SEM).

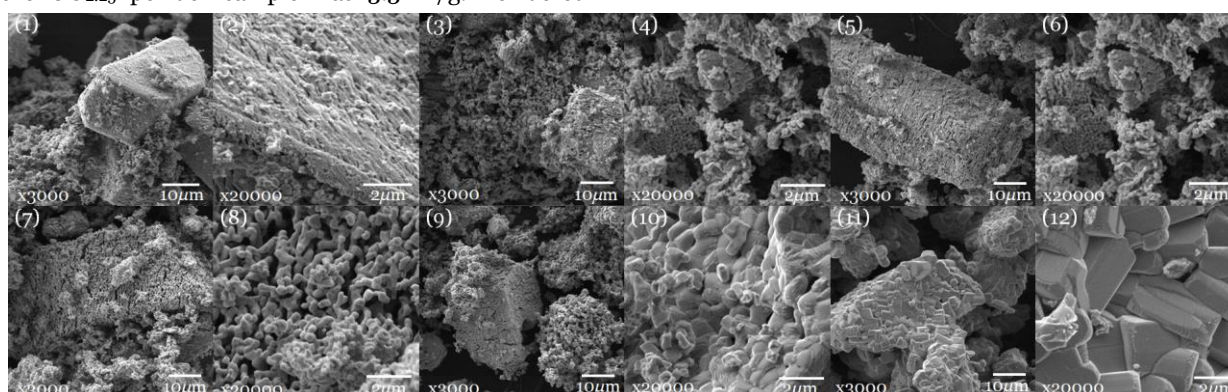


Figure 1. SEM micrographs of the initial UO_2 powder sample (1,2) and U_3O_8 powder samples, were obtained at 480°C (3,4), 600°C (5,6), 800°C (7,8), 1000°C (9,10), and 1200°C (11,12)

Table 2. Particle-size distribution of $UO_{2.25}$ and U_3O_8 powder samples.

Size range, μm	Fraction (% by mass)					
	$UO_{2.25}$	$U_3O_8(480^\circ\text{C})$	$U_3O_8(600^\circ\text{C})$	$U_3O_8(800^\circ\text{C})$	$U_3O_8(1000^\circ\text{C})$	$U_3O_8(1200^\circ\text{C})$
1–2	35.31	22.78	24.93	19.68	14.27	8.91
2–3	20.67	10.59	10.40	9.15	9.04	5.79
3–4	11.22	6.53	5.78	5.19	6.16	4.83
4–5	6.77	5.38	4.25	3.89	4.80	3.93
5–6	6.76	5.62	5.28	4.54	3.63	2.14
6–7	2.90	4.06	4.17	3.28	3.04	2.41
7–8	1.87	3.55	3.02	2.53	3.57	4.24
8–9	4.48	4.17	3.12	3.04	3.85	4.27
9–10	5.63	4.56	3.83	3.42	3.35	4.27
10–20	4.40	25.83	27.21	18.04	19.09	21.20
20–30	0.00	6.92	8.02	27.19	29.03	32.90
30–40	0.00	0.00	0.00	0.05	0.16	5.11
Total	100.00	100.00	100.00	100.00	100.00	100.00

An increase in the calcination temperature of the $\text{UO}_{2.25}$ initial powder leads to increasing the quantity of particle size fraction 10–40 μm and reducing the quantity of particle size fraction 1–6 μm for the U_3O_8 samples (see Table 2). Particle size distribution (D_{50}) for $\text{UO}_{2.25}$ and U_3O_8 samples, obtained at 480, 600, 800, 1000, 1200°C was 2.6, 5.8, 5.9, 8.6, 9.5, and 11.3 μm , respectively.

The process of U_3O_8 oxidative dissolution was carried out in a 100 mL jacketed stirred stainless steel cell. The temperature was maintained with an accuracy of $\pm 0.1^\circ\text{C}$. The mixing of the suspension was carried out with a magnetic stirrer. All experiments were performed at the solid-to-liquid ratio (S/L) equal 1/50.

The content of U(VI) in the aqueous solutions with concentration over 1.0 g/L was established by titration, using 8.4 mmol/L solution of ammonium vanadate as the titrant and diphenylamine-4-sulfonic acid sodium salt as the indicator [27]. The content of U(VI) in the solutions with a concentration lower than 1.0 g/L was established by the spectrophotometric method with Arsenazo III, per the absorbance spectra of the green-blue complex compound arsenazo-uranyl ($\lambda_{\text{max}} = 651 \text{ nm}$, detection limit $\sim 0.025\text{--}0.05 \mu\text{gU/L}$) [28]. Before analysis, all liquid samples were centrifuged for 10 min at 1500 rpm.

The value of U_3O_8 dissolution yield ($\alpha(\text{U}_3\text{O}_8)$) was calculated by the following equation: $\alpha(\text{U}_3\text{O}_8) = (M_t/M_i) \cdot 100$ where M_i is the initial quantity of the U_3O_8 . The M_t value was calculated based on the experimentally determined concentration of U(VI) in the aqueous phase. The relative error in the determination of U(VI) concentration in alkaline solutions was 0.5–5.0 %. When the U_3O_8 powder sample was completely dissolved in NaOH solution (S/L = 1/50), the U(VI) concentration was equal to 17 g/L.

Concentrations of H_2O_2 from were measured spectrophotometrically using UV-vis HP Diode Array Spectrophotometer 8452A with a one to 10 mm quartz cuvette at 350 nm [29] or titrimetrically [30].

The phase composition of $\text{UO}_{2.25}$ and U_3O_8 powders was determined by XRD. Diffraction patterns were recorded by D2 PHASER (Bruker, Germany).

Microscopic study of samples was performed with the Vega3 scanning (raster) electron microscope (Tescan, Czech Republic).

The specific surface area was calculated by the BET method using QuadraWin software (version 5.02) based on an argon gas adsorption isotherm on test powder samples, obtained on a Quadrasorb Kr/SI device (Quantachrome Instruments, USA).

3. RESULTS AND DISCUSSION

To remove volatile and gaseous fission products (FPs) before the SNF oxidative dissolution step, it is proposed to carry out volume oxidation (voloxidation) [31]. The voloxidation temperature, depending on the task, can vary from 480 to 1200°C. As a result, UO_2 , the main component of the spent fuel composition, transforms into U_3O_8 .

To maintain the required redox potential value in the alkaline solutions and concentration of complexing peroxide ligand, is necessary, excessive and/or fractional feeding of H_2O_2 shall be used [32]. At fractional feeding, a fresh portion of the initial 30% H_2O_2 aqueous solution should be added every 10 min in 1.0 mol/L NaOH solution.

It was found, that in the case of a single addition of the stoichiometric amount of H_2O_2 (in terms of U(IV) oxidation and the formation of mixed peroxide-hydroxide complex anion $[\text{UO}_2(\text{OH})_2(\text{O}_2)_2]^{4-}$ [19]), the completeness of oxidation of U(IV) to U(VI) and, accordingly, the completeness of dissolution of the U_3O_8 powder samples is not achieved. This is due to decomposition and a decrease in the concentration of the oxidizer/ligand in an alkaline solution. As is known [33], H_2O_2 is an unstable compound whose decomposition is promoted by increasing pH, temperature and by the presence of catalytic metal ions (Mn, Fe, Cu, Pb, Ag, Pt, and others). The rate of H_2O_2 decomposition in aqueous solutions of NaOH is one order of magnitude lower compared to solutions of NaHCO_3 and Na_2CO_3 [33,34]. Increasing the concentration of NaOH, pH and temperature accelerates the decomposition of H_2O_2 in alkaline solutions. Maintaining the required concentration of H_2O_2 in an alkaline solution during oxidative dissolution of uranium oxides is a key condition for achieving high process rate, completeness of dissolution of the oxide and stabilization of U(VI) in an alkaline solution.

In the case of oxidative dissolution of powdered U_3O_8 samples, obtained at different temperatures (480, 600, 800, 1000, and 1200°C) in aqueous solutions of 1.0 mol/L NaOH – 0.1 mol/L H_2O_2 in the temperature range of 25–75°C and fractional supply of H_2O_2 , the completeness of dissolution was achieved at 75°C only for $\text{U}_3\text{O}_8(480^\circ\text{C})$ powder sample (Fig. 2). When the dissolution of $\text{U}_3\text{O}_8(1200^\circ\text{C})$ powder sample under comparable conditions, the $\alpha(\text{U}_3\text{O}_8)$ value did not exceed $75 \pm 3 \%$, and in the case of $\text{U}_3\text{O}_8(800^\circ\text{C})$ or $\text{U}_3\text{O}_8(1000^\circ\text{C})$ powder samples about $85\text{--}85 \pm 2\text{--}3 \%$. For $\text{U}_3\text{O}_8(480^\circ\text{C})$ and $\text{U}_3\text{O}_8(600^\circ\text{C})$ samples, the constancy of U(VI) concentration in alkaline-peroxide solutions after 30–60 min of agitation (Fig. 2) was observed. At the same time, for $\text{U}_3\text{O}_8(1200^\circ\text{C})$ sample, the maximum concentration and dissolution yield was achieved after 60 min of agitation (Fig. 2), when the last portion (aliquot) of 30 % H_2O_2 was added into the 1.0 mol/L NaOH solution. In this system, the constancy of U(VI) concentration in the mixture NaOH- H_2O_2 after 60 min of agitation was not achieved. For the $\text{U}_3\text{O}_8(600^\circ\text{C})$ powder sample, the maximum value $\alpha(\text{U}_3\text{O}_8)$ at 50°C after 60 min of agitation was $97 \pm 2 \%$ (Fig. 2). Based on the obtained results (Fig. 2–4), it was found that the temperature of the alkaline solution and the conditions of high-temperature treatment of U_3O_8 are important factors affecting on the rate of U_3O_8 powdered samples oxidative dissolution process. An increase in the temperature of alkaline solution from 25 to 50°C leads to a significant increase of the powdered $\text{U}_3\text{O}_8(480^\circ\text{C})$ and $\text{U}_3\text{O}_8(600^\circ\text{C})$ sample dissolution rate in 1.0 mol/L NaOH – 0.1 mol/L H_2O_2 solution (Fig. 3,4).

An increase in the temperature of the alkaline solution to 75°C slightly affects on the increase of the $U_3O_8(480^\circ C)$ oxidative dissolution process rate (Fig. 3). In the case of $U_3O_8(600^\circ C)$ sample dissolution, an increase in the temperature of the alkaline solution from 50 to 75°C led to a decrease in the $\alpha(U_3O_8)$ achieved in 60 min of agitation from 97 ± 3 to 88 ± 3 % (Fig. 4). This may be caused by an increase in the rate of H_2O_2 decomposition in alkaline solution at elevated temperature, which makes it necessary to increase the consumption of H_2O_2 under these conditions.

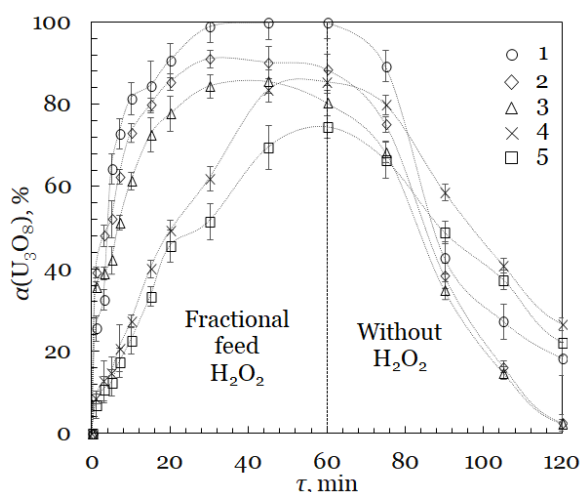


Figure 2. Kinetic curves of powdered U_3O_8 samples dissolution in aqueous 1.0 mol/L NaOH – 0.1 mol/L H_2O_2 solutions at 75°C. Fractional feed H_2O_2 (every 10 min within 60 min). 1, (○) – $U_3O_8(480^\circ C)$; 2, (◇) – $U_3O_8(600^\circ C)$; 3, (△) – $U_3O_8(800^\circ C)$; 4, (×) – $U_3O_8(1000^\circ C)$; 5, (□) – $U_3O_8(1200^\circ C)$.

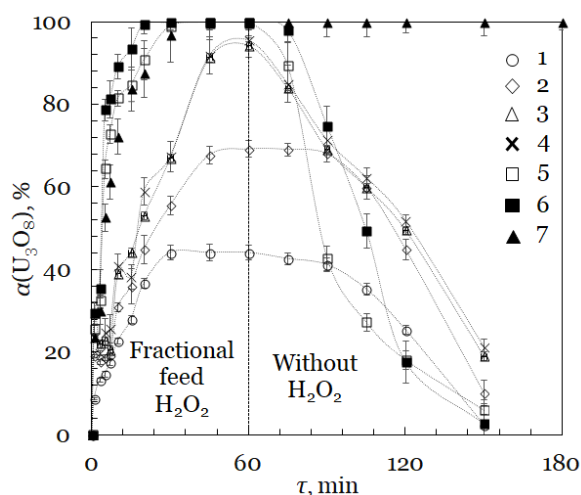


Figure 3. Kinetic curves of powdered $U_3O_8(480^\circ C)$ dissolution in aqueous 1.0 mol/L NaOH – 0.1 mol/L H_2O_2 solution. Fractional feed H_2O_2 (every 10 min within 60 min). 1, (○) – 25°C; 2, (◇) – 40°C; 3, (△) – 50°C; 4, (×) – 60°C; 5, (□) – 75°C; 6, (■) – 0.2 mol/L H_2O_2 (fractional feed H_2O_2 every 10 min within 60 min, 75°C); 7, (▲) – fractional feed H_2O_2 every 10 min within 150 min, 75°C.

When the concentration of H_2O_2 in 1.0 mol/L NaOH solution, it was increased by two times (from 0.1 to 0.2 mol/L), the $U_3O_8(480^\circ C)$ powder oxidative

dissolution rate increased (Fig. 3, curve 6). Complete dissolution of the powder oxide sample in such conditions was achieved in 15 min (in contrast to 20–30 min in the case of 0.1 mol/L H_2O_2). A similar effect is observed when the time interval of 30 % H_2O_2 feeding into the solution has been reduced from 10 to 5 min.

It is also obvious that the U_3O_8 dissolution rate in NaOH solutions significantly decreases with a decrease in the SSA of the well crystallized U_3O_8 powder, which was obtained at high temperatures.

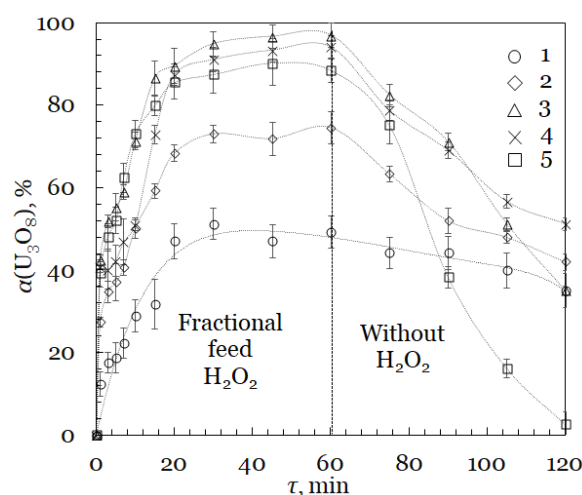


Figure 4. Kinetic curves of powdered $U_3O_8(600^\circ C)$ dissolution in aqueous 1.0 mol/L NaOH – 0.1 mol/L H_2O_2 solution. Fractional feed H_2O_2 (every 10 min within 60 min). 1, (○) – 25°C; 2, (◇) – 40°C; 3, (△) – 50°C; 4, (×) – 60°C; 5, (□) – 75°C.

After stopping the feed of H_2O_2 into the liquid phase, there is a significant decrease in the U(VI) concentration associated with the decomposition of mixed uranyl(VI) peroxy-hydroxide species, $[UO_2(OH)(O_2)]^-$, $[(UO_2)_2(OH)(O_2)_2]^-$, $[UO_2(OH)_2(O_2)]^{2-}$, $[UO_2(OH)_2(O_2)_2]^{4-}$ [17]–[19], which are preliminarily formed during U_3O_8 dissolution. These species are stable in alkaline solution only in the presence of excess amount of H_2O_2 . Without an additional supply of H_2O_2 in alkaline U(VI)-containing solution, excess of free H_2O_2 rapidly decomposes as a result of alkaline and temperature exposure. This leads to a shift in the chemical equilibrium in the alkaline system and the decomposition of soluble uranyl(VI) peroxy-hydroxide species with the formation of poorly soluble amorphous deposits (secondary precipitates) presumably polyuranates with a complex structure. The rate of secondary precipitate formation and completeness of U(VI) deposition rise up with increasing alkaline solution temperature. This explains the presence of the right (descending) branch of the kinetic curve, the slope of which depends on the temperature of the alkaline solution (Fig. 2–4).

The pH value of the initial 1.0 mol/L NaOH solution was 13.5. No change in the pH of the liquid phase when the U_3O_8 samples were dissolved in the presence of 0.1–0.2 mol/L H_2O_2 was observed. After the formation of uranyl(VI) secondary precipitates, the pH of the alkaline solution decreased to 13.2–13.4.

One of the possible products of U(VI) soluble species decomposition in alkaline solutions according to the literature [35] can be polyuranate with clarkeite structure $\text{Na}_2\text{U}_2\text{O}_x(\text{OH})_{14-2x}(\text{H}_2\text{O})_q$ or U(VI) peroxides.

Alkaline-peroxide U(VI)-containing solutions after oxidative dissolution were colored in a bright orange color. The absorption spectrum of these solutions is characterized by a continuous absorption region in the wavelength range from 300–450 nm. Characteristic bands of uranyl(VI) (424, 436, 448, 464 nm) are not observed in this region, as in the case of carbonate solutions containing uranyl(VI) tricarboxylate complex $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ (Fig. 5). The structure of the absorption spectrum is similar to the spectra of carbonate solutions containing mixed anionic complexes U(VI) formed by dissolving UO_2 or U_3O_8 in $\text{Na}_2\text{CO}_3 - \text{H}_2\text{O}_2$ mixtures [36]–[38].

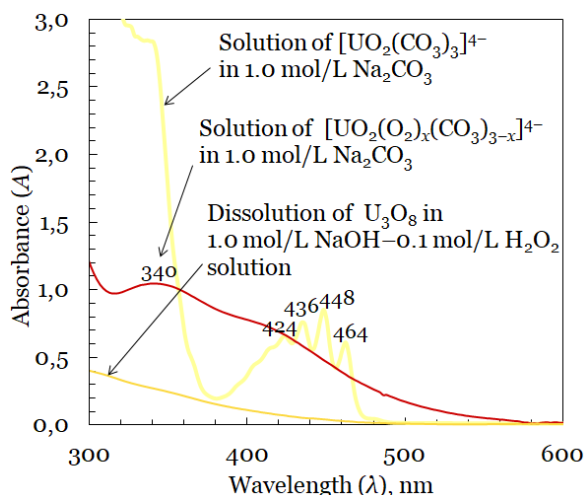


Figure 5. Absorption spectra of carbonate, peroxy-carbonate, and peroxy-hydroxide uranyl(VI) species.

To determine the dissolution rate constants and the rate-limiting stage of process, mathematical modeling of the experimental dependences $\alpha(\text{U}_3\text{O}_8) = f(\tau)$ with applying of 14 kinetic models (Kolmogorov-Erofeev

$-\ln(1-\alpha)^{1/3} = k(\tau - \tau_0)$; Prout-Tompkins $\ln(\alpha/(1-\alpha)) = k\tau$; first order $\ln(1/1-\alpha) = k\tau$; Yander $(1-(1-\alpha)^{1/3})^2 = k\tau$; Ginstling-Brownstein $1-(2/3)\alpha - (1-\alpha)^{2/3} = k\tau$; anti-Yander $((1+\alpha)^{1/3} - 1)^2 = k\tau$; anti-Ginstling $1-(2/3)\alpha - (1+\alpha)^{2/3} = k\tau$; shrinking core model $1-(1-\alpha)^{1/3} = k\tau$; exponential law model $\ln(\alpha) = k\tau$; Kroger-Ziegler $(1-(1-\alpha)^{-1/3})^2 = k\tau$; Zhuravlev $((1-\alpha)^{-1/3} - 1)^2 = k\tau$; shrinking cylinder model $1-(1-\alpha)^{1/2} = k\tau$; shrinking cube model $1-(1-\alpha)^{1/3} = k\tau$; and Valenci $(1-\alpha)\ln(1-\alpha) + \alpha = k\tau$ was carried out [32].

The results of the mathematical modeling showed that the Yander equation satisfactorily describes experimental kinetic curves and can be used for calculation of the oxidative dissolution rate constants (k) for studying hydroxide-peroxide system under various conditions. The calculated k values determined the initial (ascending) branch (0–30 min of agitation) of the kinetic curve (Fig. 2–4) on the slope values of the anamorphoses in the Yander equation coordinates are shown in Table 3.

It was found that the k value increases from $9 \cdot 10^{-4}$ to $1.8 \cdot 10^{-2} \text{ min}^{-1}$ (for $\text{U}_3\text{O}_8(480^\circ\text{C})$) and from $1.5 \cdot 10^{-3}$ to $9.8 \cdot 10^{-3} \text{ min}^{-1}$ (for $\text{U}_3\text{O}_8(600^\circ\text{C})$) by increasing the medium temperature from 25 to 75°C . The k value decreased by an order of magnitude when compared dissolution of $\text{U}_3\text{O}_8(480^\circ\text{C})$ ($\text{SSA} = 3.8 \text{ m}^2/\text{g}$) and $\text{U}_3\text{O}_8(1200^\circ\text{C})$ ($\text{SSA} = 0.1 \text{ m}^2/\text{g}$) powder samples. With an increase in the H_2O_2 concentration from 0.1 to 0.2 mol/L (for $\text{U}_3\text{O}_8(480^\circ\text{C})$ powder dissolution), the k value increases from $1.8 \cdot 10^{-2}$ to $2.8 \cdot 10^{-2} \text{ min}^{-1}$.

Based on the slope value of the line dependence in the coordinates $\ln k - 1/T$, the value of the apparent activation energy (E_{app}) of the U_3O_8 powder samples oxidative dissolution process in 1.0 mol/L NaOH – 0.1 mol/L H_2O_2 solutions with fractional feeding of H_2O_2 was calculated. The E_{app} value at $\text{U}_3\text{O}_8(480^\circ\text{C})$ powder dissolution was 47 kJ/mol and 33.8 kJ/mol in the case of $\text{U}_3\text{O}_8(600^\circ\text{C})$ powder dissolution. Estimated E_{app} values indicate that the process occurs in the outer kinetic region.

Table 3. The k values for the oxidative dissolution of powdered U_3O_8 samples in 1.0 mol/L NaOH – 0.1 mol/L H_2O_2 solutions, calculated in the coordinates of the Yander equation. R – correlation coefficient, $t(\text{U}_3\text{O}_8)$ – calcination temperature

Medium temperature – 75°C					
$t(\text{U}_3\text{O}_8), ^\circ\text{C}$	480	600	800	1000	1200
k_i, min^{-1}	0.0179	0.0108	0.0074	0.0021	0.0014
R	0.9809	0.9939	0.9940	0.9515	0.9544
$\text{U}_3\text{O}_8(480^\circ\text{C})$ powder sample					
$t, ^\circ\text{C}$	25	40	50	60	75
k, min^{-1}	0.0009	0.0017	0.0027	0.0029	0.0179
R	0.9770	0.9705	0.9558	0.9509	0.9787
$\text{U}_3\text{O}_8(600^\circ\text{C})$ powder sample					
k, min^{-1}	0.0015	0.0044	0.0136	0.0100	0.0098
R	0.9646	0.9897	0.9895	0.9895	0.9647

In the case of dissolution of the $U_3O_8(480^\circ C)$ sample with a high SSA value, the process rate depends on the temperature of the medium. A gradual decrease of SSA, an increase in the average particle size and crystallinity of the U_3O_8 powder contribute to the transition of the dissolution process to the external kinetic region, when on the process rate, in addition to temperature, is influenced by the external surface of the solid phase.

It should be noted that the oxidative dissolution rate is significantly affected by the H_2O_2 excess concentration in the NaOH solution. The participation of H_2O_2 in the processes of oxidation and complexation determines the chemistry of U_3O_8 oxidative dissolution in alkali solutions. At the same time, the formation, composition, and stability of soluble uranyl(VI) species in alkaline solutions depends on the concentration of H_2O_2 and alkali (alkali/peroxide molar ratio), nature(type) of the alkali metal (countercation), and temperature of the medium [17]–[21].

4. CONCLUSION

The kinetic study of the oxidative dissolution of U_3O_8 powder samples in aqueous 1.0 mol/L NaOH solutions at the fractional feeding mode of the hydrogen peroxide at various temperatures was carried out. The influence of the U_3O_8 calcination temperature on the oxidative dissolution rate is established. Reducing the specific surface area from 3.8 m^2/g ($U_3O_8(480^\circ C)$ powder sample) to 0.1–0.2 m^2/g ($U_3O_8(1200^\circ C)$ powder sample) results in a decrease of the oxidative dissolution rate by one order. For $U_3O_8(480^\circ C)$ sample, the complete dissolution in 1.0 mol/L NaOH – 0.1 mol/L H_2O_2 solution at 75°C is achieved for 45 min. At the same time U(VI) concentration in NaOH solution (S/L = 1/50) was 17 g/L.

The formation of soluble uranyl(VI) species, including highly soluble U(VI) peroxide clusters [15,16,21] cannot proceed without an excess of H_2O_2 . The fundamental importance for the development of processes of oxidative dissolution of uranium oxides in hydroxide systems is redox reactions, complexation, and polymerization processes (formation of highly soluble clusters) involving peroxide ion. In the absence of excess not associated H_2O_2 , the hydroxide solutions of U(VI) are unstable due to the decomposition of soluble uranyl(VI) species with the formation of poorly soluble amorphous products.

Determination of kinetic parameters of U_3O_8 powders oxidative dissolution in NaOH – H_2O_2 solution allowed establishing that the process takes place in the kinetic region (limiting rate stage – chemical reaction). This is confirmed by the influence of temperature on the dissolution rate.

Due to the possibility of achieving high U(VI) concentrations in alkaline solutions, hydroxide-peroxide systems, as well as carbonate-peroxide systems (CARBEX process [4,31,36]), can be considered as basic systems for developing approaches to the SNF dissolution, which, in the future, can be an alternative to existing processing schemes using hot

nitric acid. In particular obtained data makes it possible to develop approaches to the processes of selective leaching of uranium from voloxidized SNF and its hydrolytic reagent-free precipitation from alkaline solutions in the form of a preliminary concentrate purified from the bulk of highly radioactive FPs. Such an approach may be one alternative to replacing the first exhaustive solvent extraction cycle of U(VI) from carbonate solutions after the oxidative dissolution of SNF in the CARBEX process.

Further development of this approach requires optimization of conditions and modes of U_3O_8 oxidative dissolution to achieve complete dissolution of highly calcined U_3O_8 samples and obtain more concentrated U(VI)-containing solutions. It is also necessary to study in more detail the chemistry of peroxide-hydroxide solutions and secondary precipitates, as well as determine the structure and properties of uranyl(VI) peroxide and mixed peroxide-hydroxide species.

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