



OXIDATIVE DISSOLUTION OF TRIURANIUM OCTOXIDE IN CARBONATE SOLUTIONS

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Abstract. Oxidative dissolution is the key stage of uranium oxide spent nuclear fuel (SNF) reprocessing technology in carbonate media. The ability to quickly and completely dissolve the main component of the SNF matrix - UO_2 in sodium or ammonium carbonate solutions in the presence of hydrogen peroxide at room temperature made it possible to substantiate carbonate media as an alternative to nitric acid media in the SNF reprocessing technology. Before the SNF oxidative dissolution stage, in the CARBEX (CARBONATE EXtraction) process, voloxidation (volume oxidation) is carried out. As a result, UO_2 completely turns into U_3O_8 . In this work, the dissolution of U_3O_8 in sodium carbonate solutions, in the presence of hydrogen peroxide, and sodium percarbonate was studied. The optimal dissolution conditions were determined. With the help of mathematical experimental data processing, the dissolution rates and the apparent activation energy values were calculated.

Key words: Hydrogen peroxide, oxidative dissolution, sodium carbonate, sodium percarbonate, triuranium octoxide, uranium dioxide.

1. INTRODUCTION

New hydrochemical approaches of the spent nuclear fuel (SNF) reprocessing in carbonate (pH < 11–12) or carbonate-alkaline (pH > 11–12) solutions is regarded as an alternative direction in relation to different options of the PUREX technology [1]–[7]. Formulated concepts of radiochemical methods of SNF management, as well as currently developed full technological schemes and certain stages of alternative approaches, were aimed at the solution of the problems of increasing fire and explosion safety, decreasing the corrosive activity of the media in which SNF processed, lowering of the volume of all types of radioactive waste (first of all, liquid high-level waste), increase of selectivity of fissile materials purification from fission products (FPs).

Oxidative dissolution of uranium dioxide (UO_2) is the principal and fundamental stage of UO_2 -based SNF reprocessing in carbonate media. Possibility of quick and complete dissolution of UO_2 and triuranium octoxide (U_3O_8) in aqueous solutions of sodium or ammonium carbonates in the presence of hydrogen peroxide (H_2O_2) at room temperature allowed to justify carbonate media as an alternative to nitric acid media. Development and optimization of this key process was the object of efforts of all groups of researchers that were developing technological schemes for SNF reprocessing in carbonate media [1]–[7].

UO_2 and U_3O_8 have low solubility in carbonate solutions [8,9]. For efficient dissolution of these oxides in carbonate solution, it is required to oxidize U(IV) to U(VI), which has a significantly higher solubility. Oxidation is the main way to the solution of UO_2 , U_3O_8 , and UO_2 -based SNF in most carbonate processes.

For the oxidation of U(IV) to U(VI) in carbonate media, various oxidants can be used - oxygen, ozone, hydrogen peroxide, alkali metal or ammonium persulfates, sodium hypochlorite, etc. [2]–[15], as well as anodic oxidation [6]. Among the chemical oxidants proposed in the literature, hydrogen peroxide is the most suitable for use in the SNF oxidative dissolution processes. Hydrogen peroxide not only effectively oxidizes UO_2 and U_3O_8 but also participates in reactions of formation of the U(VI) mixed peroxo-carbonate species mainly with structure $[UO_2(O_2)_x(CO_3)_y]^{(2-2x-2y)}$, where $x = 1-3$, $y = 3-x$ [2,8,9]. With the increase of U(VI) concentration in carbonate solution polynuclear species $M_4[(UO_2)_2(O_2)_2(CO_3)_2]$ or $M_6[(UO_2)_3(O_2)_2(CO_3)_4]$, where M – Na^+ or NH_4^+ are formed [2,14].

The solubility of U(VI) peroxo-carbonate species is more than four times that of U(VI) carbonate species. This makes it possible to obtain solutions with U(VI) concentration up to 150–180 g/L [14]. A great advantage of H_2O_2 is that its addition does not complicate the chemical composition of carbonate solutions and does not lead to the accumulation of salts in them since the products of its decomposition are O_2 and H_2O . In addition, H_2O_2 is formed as a result of water radiolysis when exposed to α - and γ -radiation at the reprocessing of high-radioactive solutions.

Oxidative dissolution of U_3O_8 in carbonate media develops with increasing dissolution rate of UO_2 [9,10]. At the same time, it is impossible to fully dissolve U_3O_8 , for example in the system of 1.0 mol/L $(NH_4)_2CO_3$ - 0.1 mol/L H_2O_2 , which is related to the resistance of U_3O_8 against oxidation in carbonate-peroxide solutions [9]. It was established that U_3O_8 dissolves in 0.02–0.2 mol/L Na_2CO_3 solutions more rapidly than UO_2 in the absence of H_2O_2 , while in the

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presence of 0.5–3.0 mol/L H_2O_2 , the dissolution rate of UO_2 is higher than for U_3O_8 [11]. It was demonstrated that in carbonate solutions UO_3 dissolves more rapidly than U_3O_8 or UO_2 and that the dissolution rate values for U_3O_8 and UO_2 are approximately the same [10].

An increase in the UO_2 and U_3O_8 oxidative dissolution rate is significantly influenced by an increase of concentrations of CO_3^{2-} ions and oxidizer, as well as temperature [8,9], [11]–[15]. The influence of the temperature on the dissolution process strengthens with the increase of the carbonate concentration in solution [16]–[18].

The highest dissolution rate of UO_2 in 1.0 mol/L M_2CO_3 - 0.1 mol/L H_2O_2 solutions is achieved in case $(NH_4)_2CO_3$ [9]. In such a system, the dissolution rate for uranium oxides is increased in the row of $UO_3 > U_3O_8 > UO_2$ [9,13]. Thus, $(NH_4)_2CO_3$ and Na_2CO_3 are the most suitable carbonate reactants for UO_2 and U_3O_8 oxidative dissolution. These carbonate salts are also used for modeling scenarios for long-term storage of SNF in geological formations. Such processes often include the interaction of UO_2 with groundwater's (usually containing Na_2CO_3 and $NaHCO_3$), taking into account strong radiation fields and the formation of molecular and radical products of water radiolysis, including H_2O_2 [19]–[23].

In accordance with the CARBEX process, before the SNF oxidative dissolution step, the voloxidation (volume oxidation) is carried out, the task of which is to remove volatile and gaseous FPs. The voloxidation temperature, depending on the task, can vary from 480°C to 1200°C. As a result of this treatment, UO_2 (the main component of the fuel composition) is completely converted to U_3O_8 . After voloxidation and alkaline pretreatment stages to remove cesium and molybdenum, the fuel composition is dissolved in a carbonate solution in the presence of hydrogen peroxide. To optimize the key stage of SNF oxidative dissolution in the CARBEX process, it is necessary to further study the behavior of uranium oxides in solutions of sodium carbonate or sodium bicarbonate under oxidative conditions and search for the effective conditions and modes of this process.

As an alternative carbonate and oxidizing reagent for the dissolution of uranium oxides, sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) can be used. This is a widely available industrial product. Sodium percarbonate is a crystalline salt, which, unlike concentrated aqueous solutions H_2O_2 is more stable during storage, is a safer reagent, and does not require special storage conditions.

The purpose of this research was the optimization of oxidative dissolution of triuranium octaoxide in sodium carbonate solutions in the presence of hydrogen peroxide or sodium percarbonate.

2. MATERIALS AND METHODS

Solid salts Na_2CO_3 , $2Na_2CO_3 \cdot 3H_2O_2$, and 35% aqueous solution of hydrogen peroxide (H_2O_2) of the chemically pure grade were used.

As the initial uranium compound, the uranium(IV) oxide powder 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 Brunauer, Emmett, and Teller (BET) method for the $UO_{2.25}$ powder sample was 3.3 m^2/g . Triuranium octaoxide powders samples were obtained by heat treatment of the initial $UO_{2.25}$ powder in the air atmosphere for 120 min in the temperature range from 480°C to 1200°C. The heat treatment products were fine-crystalline powders, the color of which, depending on the treatment temperature, ranged from olive green to black. In all cases, the final product of $UO_{2.25}$ heat treatment in the range of 480–1200°C was U_3O_8 (PDF–2/2010 № 76–1850). In table 1, the SSA values for the powders samples of U_3O_8 are shown.

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

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

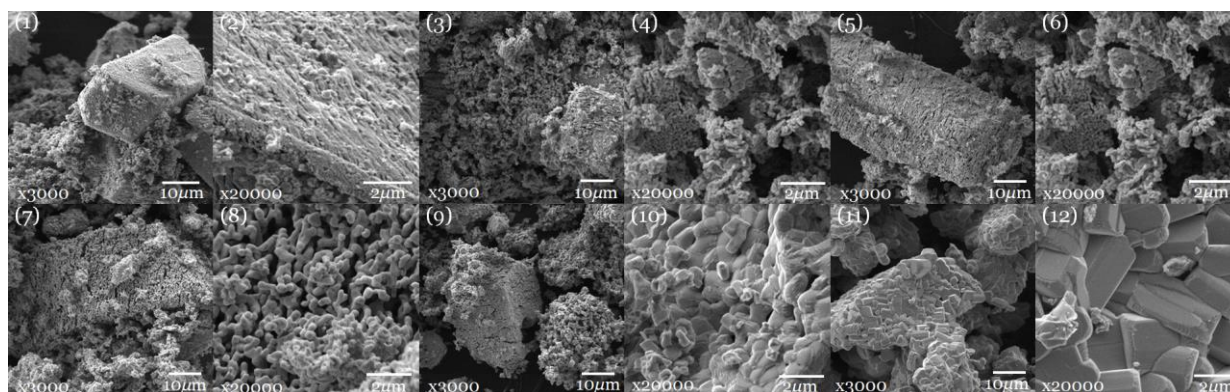


Figure 1. SEM micrographs of the initial UO_2 powder sample (1,2) and U_3O_8 powder samples were obtained at 480°C (3,4), 600°C (5,6), 800°C (7,8), 1000°C (9,10), and 1200°C (11,12)

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

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

Figure 1 shows scanning electron microscope (SEM) micrographs of UO_2 (1,2) and U_3O_8 (3–12) samples

An increase in the calcination temperature of the $UO_{2.25}$ 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).

The process of U_3O_8 oxidative dissolution was carried out in 100 mL jacketed stirred glass cell. The temperature was maintained with an accuracy of $\pm 0.1^\circ\text{C}$. Mixing of suspension was carried out by using of magnetic stirrer.

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 [24]. The content of U(VI) in the solutions with 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 $\sim 0.025\text{--}0.05 \mu\text{gU/L}$) [25]. Before analysis, all liquid samples were centrifuged for 10 min at 1500 rpm.

The value of U_3O_8 dissolution yield ($\alpha(U_3O_8)$) was calculated by the following equation: $\alpha(U_3O_8) = (M_r/M_i) \cdot 100$ where M_i is the initial quantity of the U_3O_8 . The M_r value was calculated based on the experimentally determined concentration of U(VI) in the aqueous phase. The relative error for the determination of the U(VI) concentration in carbonate solutions was not more than 0.5%.

The phase composition of $UO_{2.25}$ 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

An important characteristic of the typical chemical oxidation system is the magnitude of the redox potential (ROP). The rate of ROP decrease in aqueous sodium carbonate solution containing hydrogen peroxide increases with temperature and carbonate concentration. This is due to an increase in the decomposition (thermal/alkaline) rate of the peroxide oxidant. To maintain the required ROP value in the carbonate or carbonate-alkaline systems is necessary excess and/or fractional feeding of peroxide oxidant shall be used. At fractional feeding a fresh portion of the initial H_2O_2 aqueous solution should be added every 10–20 min, depending on the dissolution process conditions (mainly temperature, concentration of carbonate or alkaline reagents).

Fractional feeding mode is the most optimal way to add an oxidant to the carbonate system. With a single stoichiometric supply of H_2O_2 , the effect of ROP increasing and U(IV) oxidation process will occur only during the initial period of dissolution time, until the moment of complete decomposition of H_2O_2 . During this time U_3O_8 powder (especially for samples obtained at temperatures greater than 600°C) doesn't get completely oxidize and can't be completely dissolved in aqueous Na_2CO_3 solutions.

In the case of oxidative dissolution of U_3O_8 powders obtained at various temperatures, it was established that increasing the temperature of formation of U_3O_8 from 480°C to 1200°C leads to decreasing of the dissolution rate in the aqueous 1.0 mol/L Na_2CO_3 - 0.1 mol/L H_2O_2 solutions with fractional feeding of H_2O_2 every 10 min (see Figure 2). This is caused by a decrease in a specific surface area and an increase in the particle size of U_3O_8 powders. Complete dissolution at 75°C, solid-to-liquid (S/L) ratio = 1/50 for 90 min was achieved only for the U_3O_8 sample obtained at 480°C ($U_3O_8(480^\circ C)$). The equilibrium state of a carbonate system with a U_3O_8 sample obtained at 1200°C ($U_3O_8(1200^\circ C)$) was not observed even after dissolution time (τ) equal 180 min, while for the remaining U_3O_8 samples equilibrium state was reached after 30–60 min of the dissolution process. The value of $\alpha(U_3O_8)$ reached for 90 min was 77.7% for $U_3O_8(600^\circ C)$, 62.1% for $U_3O_8(800^\circ C)$, 51% for $U_3O_8(1000^\circ C)$, and 41.3% for $U_3O_8(1200^\circ C)$ (see Figure 2).

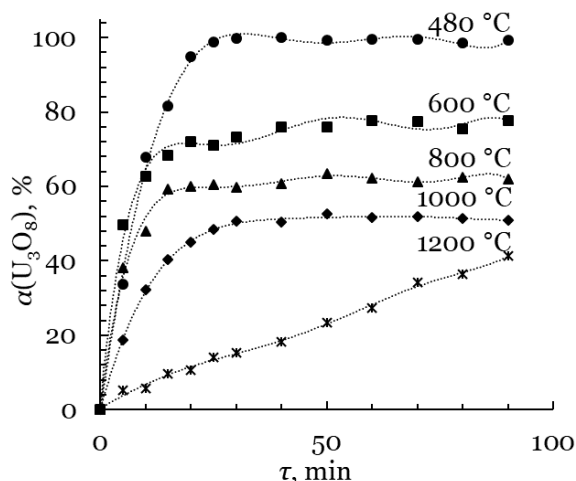


Figure 2. Kinetic curves of U_3O_8 powders dissolution in aqueous 1.0 mol/L Na_2CO_3 - 0.1 mol/L H_2O_2 solutions at 75°C and S/L = 1/50.

To determine the dissolution rate constants and the rate-limiting stage, mathematical modeling of the experimentally obtained dependences $\alpha(U_3O_8) = f(\tau)$ was carried out according to kinetic equations: 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 $(1-\alpha)\ln(1-\alpha) + \alpha = k\tau$ which are widely used to describe the kinetics of heterogeneous processes in the solid-gas systems. The applicability of these equations to solid-liquid systems can be confirmed by the adequacy of the description of the experimental data, which depends on the degree of linearization of the kinetic curves in the coordinates of the corresponding equation (anamorphoses).

The results of the mathematical modeling showed that the Yander equation satisfactorily describes experimental kinetic curves and can be used to calculation of the oxidative dissolution rate constants (k) for studied carbonate systems under various conditions. The calculated k values determined on the slope values of the anamorphoses in the Yander equation coordinates are shown in Table 3.

When deriving the Yander equation, the following assumptions were used: (1) spherical particles of the same size react; (2) the process is stationary (a homogeneous layer of the solid product has already formed); (3) diffusion proceeds only towards the center of the particles; (4) the formation of solid solutions does not occur; (5) the diffusion coefficient is constant; (6) the film's thickness of the reaction products on the surface of the solid body changes according to the parabolic law. The Yander equation implies that the process proceeds in diffusion mode. At the initial stages of the process, a layer (film) of reaction products is formed. Thus, the process of oxidative dissolution of U_3O_8 in aqueous solutions can be described from the diffusion model.

Oxidative dissolution of U_3O_8 in Na_2CO_3 - H_2O_2 solutions is the heterogeneous process that proceeds in a solid-liquid two-phase system. This process involves several steps: (i) transport of reagents (oxidant and carbonate) through the carbonate solution layer to the surface of the oxide particles; (ii) adsorption of reactants on the surface of the oxide particles; (iii) oxidizing U(IV) to U(VI) on the oxide surface and interaction the oxidation products with carbonate; (iv) desorption of reaction products (mixed peroxo-carbonate complexes of U(VI)); and (v) transport of reaction products from the surface of the oxide particles to the carbonate solution.

Generally, the formation of a layer of oxidation products on the oxide surface is not formed in carbonate solutions, since they are easily dissolved in the presence of HCO_3^- and CO_3^{2-} ions and are removed from the surface of the oxide particles. However, in carbonate systems, two main factors can cause a decrease in the process of the oxidative dissolution rate: (i) increasing of diffusion resistance (diffusion of the oxidant and carbonate to the surface of the particles and in the pores of U_3O_8 , and transport of reaction products to the carbonate solution); (ii) hydrolysis of carbonate and mixed peroxo-carbonate complexes of U(VI) (for example, as a result of an increase in the concentration of OH^- ions during the dissolution process), the formation of low soluble compounds that can form secondary precipitates in carbonate solution and films on the surface of the oxide particles.

In the case of secondary precipitates formation, a decrease in the process rate occurs and a second fragment appears on the anamorphoses, which may have a negative trend.

Sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) and sodium peroxide (Na_2O_2) also belong to peroxide-containing compounds that can be used as an alternative oxidation reagent for U_3O_8 oxidative dissolution in carbonate media. However, at Na_2O_2 use as an oxidizer the $U_3O_8(1200^\circ C)$ dissolution yield value doesn't exceed 15–20% (1.0 mol/L Na_2CO_3 solution).

The low solubility of U_3O_8 in the presence of Na_2O_2 is associated with an increase in the pH of the carbonate solution (<12) as a result of Na_2O_2 decomposition with the formation and accumulation (at fractional feeding

mode) of sodium hydroxide. Under such conditions, alkaline hydrolysis of good soluble carbonate and mixed peroxy-carbonate species of U(VI) occurs to form poorly soluble sodium polyuranates.

Table 3. The k values for the oxidative dissolution of U_3O_8 powder in 1.0 mol/L Na_2CO_3 - 0.1 mol/L H_2O_2 solutions at 75°C and S/L = 1/50, calculated in the coordinates of the Yander equation. R – correlation coefficient, $t(U_3O_8)$ – calcination temperature

$t(U_3O_8)$, °C	480	600	800	1000	1200
k , min ⁻¹	0.0230	0.0070	0.0040	0.0020	<0.0001
R	0.9644	0.9783	0.9794	0.9895	0.9599

Table 4. The k values for the oxidative dissolution of $U_3O_8(480^\circ C)$ and $U_3O_8(1200^\circ C)$ powders in aqueous Na_2CO_3 - H_2O_2 solutions with fractional feeding of $2Na_2CO_3 \cdot 3H_2O_2$ at the different temperatures and S/L = 1/50, calculated in the coordinates of the Yander equation.

t , °C	Sample - powder of $U_3O_8(480^\circ C)$			Sample - powder of $U_3O_8(1200^\circ C)$				
	25	50	75	25	40	50	60	75
k , min ⁻¹	0.0073	0.0141	0.0167	0.0014	0.1850	0.2513	0.3226	0.7099
R	0.7825	0.8245	0.8022	0.996	0.9793	0.9977	0.9798	0.9952

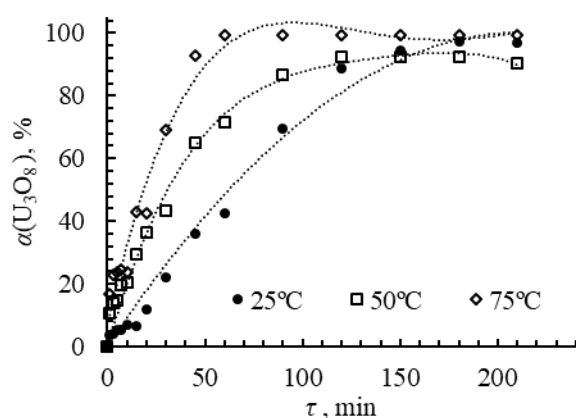


Figure 3. Kinetic curves of $U_3O_8(480^\circ C)$ powder dissolution in aqueous Na_2CO_3 - H_2O_2 solutions with fractional feeding of $2Na_2CO_3 \cdot 3H_2O_2$ at different temperatures and S/L = 1/50.

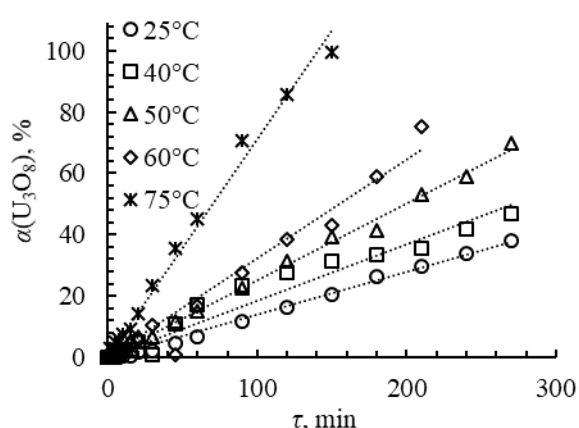
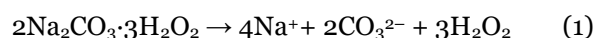


Figure 4. Kinetic curves of $U_3O_8(1200^\circ C)$ powder dissolution in aqueous Na_2CO_3 - H_2O_2 solutions with fractional feeding of $2Na_2CO_3 \cdot 3H_2O_2$ at different temperatures and S/L = 1/50.

In the case of oxidative dissolution of $U_3O_8(480^\circ C)$ powder (see Figure 3) and $U_3O_8(1200^\circ C)$ powder (see Figure 4) in aqueous $2Na_2CO_3 \cdot 3H_2O_2$ solution at

reagent fractional feeding mode it was found that dissolution rate of $U_3O_8(1200^\circ C)$ sample is lower.

The feeding mode of crystalline $2Na_2CO_3 \cdot 3H_2O_2$ into the aqueous solution was such that, with the addition of the full amount of peroxosolvate, the concentration of carbonate ions in the final aqueous solution was 1.0 mol/L. Sodium percarbonate rapidly dissolves in water (solubility 140 g/L at 20°C [26]) and dissociates into sodium ions, carbonate ions, and hydrogen peroxide:



When dissolving fresh portions of crystalline $2Na_2CO_3 \cdot 3H_2O_2$ in aqueous solution, an increase in the concentration of carbonate ions occurs, in contrast to hydrogen peroxide, the concentration of which is close to 0 mol/L after 10–15 min of dissolution.

Thus, the initial concentration of Na_2CO_3 in this carbonate system is lower in comparison with the system described above (see Figure 2), in which into initial 1.0 mol/L Na_2CO_3 solution added an aliquot of 35% aqueous H_2O_2 solution.

In the case of the $U_3O_8(480^\circ C)$ powder sample, the value of $\alpha(U_3O_8)$ equal to 97.3%, 92.4%, and more than 99.9% at 25°C, 50°C, and 75°C was reached for 180, 120, and 60 min respectively (Figure 3). For the $U_3O_8(1200^\circ C)$ powder sample, it took 150 min to reach complete dissolution at 75°C, at lower temperatures (25–60°C) complete dissolution was not achieved even in 270 min (Figure 4). At the same time, the value of $\alpha(U_3O_8)$ was 38% at 25°C, 46.8% at 40°C, 69.7% at 50°C, and 75.2% at 60°C.

The calculated k values for $U_3O_8(480^\circ C)$ and $U_3O_8(1200^\circ C)$ powder samples at the dissolution in the presence of $2Na_2CO_3 \cdot 3H_2O_2$ for different temperatures (t) are shown in Table 4.

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 Na_2CO_3 - H_2O_2 solutions with fractional feeding of $3Na_2CO_3 \cdot 3H_2O$ was calculated. The E_{app} value at

$U_3O_8(480^\circ C)$ powder dissolution was 14.2 kJ/mol and 27.2 kJ/mol in the case of $U_3O_8(1200^\circ C)$ powder dissolution. Estimated E_{app} values indicate, that the process occurs in the outer kinetic region in the case of $U_3O_8(480^\circ C)$ powder and the outer transition region or outer diffusional region in the case of $U_3O_8(1200^\circ C)$ powder. 4. CONCLUSION

In the work, it was found that when a stoichiometric amount of a peroxide oxidant (hydrogen peroxide or sodium percarbonate) is supplied once, the complete dissolution of U_3O_8 in aqueous Na_2CO_3 solutions cannot be achieved, unlike the fractional feeding mode.

The kinetic study of the oxidative dissolution of U_3O_8 powder samples in aqueous Na_2CO_3 solutions at the fractional feeding mode of the peroxide oxidants (H_2O_2 and $2Na_2CO_3 \cdot 3H_2O_2$) at various temperatures was carried out. The influence of the U_3O_8 calcination temperature on the oxidative dissolution rate in aqueous Na_2CO_3 solutions in the presence of $H_2O_2/2Na_2CO_3 \cdot 3H_2O_2$ is established. Reducing of the specific surface area from 3.8 m^2/g (for $U_3O_8(480^\circ C)$ powder sample obtained at $480^\circ C$) to 0.1–0.2 m^2/g (for $U_3O_8(1200^\circ C)$ powder sample obtained at $1200^\circ C$) results in a decrease of the oxidative dissolution rate by 2 orders. For $U_3O_8(480^\circ C)$ sample, the complete dissolution in 1.0 mol/L Na_2CO_3 - 0.1 mol/L H_2O_2 solution at $75^\circ C$ is achieved in 45–60 min. For U_3O_8 samples obtained at temperatures more than $600^\circ C$, the complete dissolution in the system 1.0 mol/L Na_2CO_3 - 0.1 mol/L H_2O_2 in one dissolution step at $75^\circ C$ is not achieved even for 270 min. In the case of the $2Na_2CO_3 \cdot 3H_2O_2$ - H_2O system, complete dissolution can be achieved in 60 minutes for $U_3O_8(480^\circ C)$ powder and 130 minutes for U_3O_8 ($1200^\circ C$) powder at a temperature of $75^\circ C$.

The $U_3O_8(1200^\circ C)$ was resistant against the oxidative dissolution process but the complete dissolution was achieved by using Na_2CO_3 - H_2O_2 solutions at elevated temperatures.

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