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 octaoxide (U$_3$O$_8$) in aqueous solutions of sodium or ammonium carbonates in the presence of hydrogen peroxide (H$_2$O$_2$) 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$_3$O$_8$ 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$_3$O$_8$, 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$_3$O$_8$ but also participates in reactions of formation of the U(VI) mixed peroxo-carbonate species mainly with structure [UO$_2$(O$_2$)$_x$(CO$_3$)$_y$]$^{2-}$, where $x = 1$–$3$, $y = 3$–$x$ [2,8,9]. With the increase of U(VI) concentration in carbonate solution polymeric species $M_4[(UO_2)_2(O_2)x(CO_3)_y]$ or $M_3[(UO_2)_3(O_2)x(CO_3)_y]$, 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$_2$O$_2$ 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$_2$O. In addition, H$_2$O$_2$ 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 UO$_2$ in carbonate media develops with increasing dissolution rate of UO$_2$ [9,10]. At the same time, it is impossible to fully dissolve UO$_2$, for example in the system of 1.0 mol/L (NH$_4$)$_2$CO$_3$ – 0.1 mol/L H$_2$O$_2$, which is related to the resistance of UO$_2$ against oxidation in carbonate–peroxide solutions [9]. It was established that U$_3$O$_8$ dissolves in 0.02–0.2 mol/L Na$_2$CO$_3$ solutions more rapidly than UO$_2$ in the absence of H$_2$O$_2$, while in the
presence of 0.5–3.0 mol/L H₂O₂, the dissolution rate of UO₂ is higher than for U₃O₈ [11]. It was demonstrated that in carbonate solutions UO₂ dissolves more rapidly than U₃O₈ or UO₂ and that the dissolution rate values for U₃O₈ and UO₂ are approximately the same [10].

An increase in the UO₂ and U₃O₈ oxidative dissolution rate is significantly influenced by an increase of concentrations of CO₂⁻ 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 UO₂ in 1.0 mol/L M₂CO₃ - 0.1 mol/L H₂O₂ solutions is achieved in case (NH₄)₂CO₃ [9]. In such a system, the dissolution rate for uranium oxides is increased in the row of UO₂³⁺>U₃O₈>UO₂ [9,13]. Thus, (NH₄)₂CO₃ and Na₂CO₃ are the most suitable carbonate reactants for UO₂ and U₃O₈ 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 UO₂ with groundwater’s (usually containing Na₂CO₃ and NaHCO₃), taking into account strong radiation fields and the formation of molecular and radical products of water radiolysis, including H₂O₂ [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, UO₂ (the main component of the fuel composition) is completely converted to U₃O₈. 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 (2Na₂CO₃·3H₂O₂) can be used. This is a widely available industrial product. Sodium percarbonate is a crystalline salt, which, unlike concentrated aqueous solutions H₂O₂ 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 octoxide in sodium carbonate solutions in the presence of hydrogen peroxide or sodium percarbonate.

2. MATERIALS AND METHODS

Solid salts Na₂CO₃, 2Na₂CO₃·3H₂O₂, and 35% aqueous solution of hydrogen peroxide (H₂O₂) of the chemically pure grade were used.

As the initial uranium compound, the uranium(IV) oxide powder was used. The composition of the initial UO₂ powder, according to the x-ray diffraction (XRD) analysis corresponded to UO₂.5 (PDF–2/2010 № 20–1344). The specific surface area (SSA) value, calculated using Brunauer, Emmett, and Teller (BET) method for the UO₂.5 powder sample was 3.3 m²/g. Triuranium octoxide powders samples were obtained by heat treatment of the initial UO₂.5 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 UO₂.25 heat treatment in the range of 480–1200°C was U₃O₈ (PDF–2/2010 № 76–1850). In table 1, the SSA values for the powders samples of U₃O₈ are shown.

<table>
<thead>
<tr>
<th>t, °C</th>
<th>480</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSA/BET, m²/g</td>
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<td>3.7</td>
<td>1.8</td>
<td>0.8</td>
<td>0.1</td>
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</table>

Figure 1. SEM micrographs of the initial UO₂ powder sample (1,2) and U₃O₈ 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)
A. Boyarintsev et al., Oxidative dissolution of U3O8 in carbonate solutions, RAD Conf. Proc., vol. 5, 2021, 68–74

Table 2. Particle-size distribution of UO2.25 and U3O8 powders

<table>
<thead>
<tr>
<th>Size range, μm</th>
<th>Fraction (% by mass)</th>
<th>UO2.25</th>
<th>U3O8(480°C)</th>
<th>U3O8(600°C)</th>
<th>U3O8(800°C)</th>
<th>U3O8(1000°C)</th>
<th>U3O8(1200°C)</th>
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<tr>
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</tr>
</tbody>
</table>

Figure 1 shows scanning electron microscope (SEM) micrographs of UO2 (1,2) and U3O8 (3–12) samples.

An increase in the calcination temperature of the UO2.25 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 U3O8 samples (see Table 2).

The process of U3O8 oxidative dissolution was carried out in 100 mL jacketed stirred glass cell. The temperature was maintained with an accuracy of ±0.1°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 (λmax = 651 nm, detection limit ~0.025–0.05 μgU/L) [25]. Before analysis, all liquid samples were centrifuged for 10 min at 1500 rpm.

The value of U3O8 dissolution yield (α(U3O8)) was calculated by the following equation: α(U3O8) = (M/3)100 where M is the initial quantity of the U3O8. The M 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 UO2.25 and U3O8 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 H2O2 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 H2O2, 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 H2O2. During this time U3O8 powder (especially for samples obtained at temperatures greater than 600°C) doesn’t get completely oxidize and can’t be completely dissolved in aqueous Na2CO3 solutions.
In the case of oxidative dissolution of U₃O₈ powders obtained at various temperatures, it was established that increasing the temperature of formation of U₃O₈ from 480°C to 1200°C leads to decreasing of the dissolution rate in the aqueous 1.0 mol/L Na₂CO₃ - 0.1 mol/L H₂O₂ solutions with fractional feeding of H₂O₂ 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 U₃O₈ powders. Complete dissolution at 75°C, solid-to-liquid (S/L) ratio = 1/50 for 90 min was achieved only for the U₃O₈ sample obtained at 480°C (U₃O₈(480°C)). The equilibrium state of a carbonate system with a U₃O₈ sample obtained at 1200°C (U₃O₈(1200°C)) was not observed even after dissolution time (τ) equal 180 min, while for the remaining U₃O₈ samples equilibrium state was reached after 30–60 min of the dissolution process. The value of a(U₃O₈) reached for 90 min was 77.7% for U₃O₈(600°C), 62.1% for U₃O₈(800°C), 51% for U₃O₈(1000°C), and 41.3% for U₃O₈(1200°C) (see Figure 2).

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 U₃O₈ in aqueous solutions can be described from the diffusion model.

Oxidative dissolution of U₃O₈ in Na₂CO₃ - H₂O₂ 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 peroxy-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 HCO₃⁻ and CO₃²⁻ 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 U₃O₈, and transport of reaction products to the carbonate solution); (ii) hydrolysis of carbonate and mixed peroxy-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 (2Na₂CO₃·3H₂O₂) and sodium peroxide (Na₂O₂) also belong to peroxide-containing compounds that can be used as an alternative oxidation reagent for U₃O₈ oxidative dissolution in carbonate media. However, at Na₂O₂ use as an oxidizer the U₃O₈(1200°C) dissolution yield value doesn’t exceed 15–20% (1.0 mol/L Na₂CO₃ solution).
The low solubility of $\text{U}_3\text{O}_8$ in the presence of $\text{Na}_2\text{O}_2$ is associated with an increase in the pH of the carbonate solution (<12) as a result of $\text{Na}_2\text{O}_2$ decomposition with the formation and accumulation (at fractional feeding mode) of sodium hydroxide. Under such conditions, alkaline hydrolysis of good soluble carbonate and mixed peroxo-carbonate species of $\text{U}(\text{VI})$ occurs to form poorly soluble sodium polyuranates.

Table 3. The $k$ values for the oxidative dissolution of $\text{U}_3\text{O}_8$ powder in 1.0 mol/L $\text{Na}_2\text{CO}_3$ - 0.1 mol/L $\text{H}_2\text{O}_2$ solutions at 75°C and $\text{S/L} = 1/50$, calculated in the coordinates of the Yander equation. $R$ – correlation coefficient, $t(U_3O_8)$ – calculation temperature

<table>
<thead>
<tr>
<th>$t(U_3O_8)$, °C</th>
<th>480</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$, min$^{-1}$</td>
<td>0.0230</td>
<td>0.0070</td>
<td>0.0040</td>
<td>0.0020</td>
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</tr>
<tr>
<td>$R$</td>
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<td>0.9783</td>
<td>0.9794</td>
<td>0.9895</td>
<td>0.9599</td>
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</tbody>
</table>

Table 4. The $k$ values for the oxidative dissolution of $\text{U}_3\text{O}_8(480°C)$ and $\text{U}_3\text{O}_8(1200°C)$ powders in aqueous $\text{Na}_2\text{CO}_3$ - $\text{H}_2\text{O}_2$ solutions with fractional feeding of $2\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}_2$ at the different temperatures and $\text{S/L} = 1/50$, calculated in the coordinates of the Yander equation.

<table>
<thead>
<tr>
<th>$t$, °C</th>
<th>Sample - powder of $\text{U}_3\text{O}_8(480°C)$</th>
<th>Sample - powder of $\text{U}_3\text{O}_8(1200°C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample - powder of $\text{U}_3\text{O}_8(480°C)$</td>
<td>Sample - powder of $\text{U}_3\text{O}_8(1200°C)$</td>
</tr>
<tr>
<td>$k$, min$^{-1}$</td>
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<td>0.0141</td>
</tr>
<tr>
<td>$R$</td>
<td>0.7825</td>
<td>0.8245</td>
</tr>
</tbody>
</table>

Figure 3. Kinetic curves of $\text{U}_3\text{O}_8(480°C)$ powder dissolution in aqueous $\text{Na}_2\text{CO}_3$ - $\text{H}_2\text{O}_2$ solutions with fractional feeding of $2\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}_2$ at different temperatures and $\text{S/L} = 1/50$.

Figure 4. Kinetic curves of $\text{U}_3\text{O}_8(1200°C)$ powder dissolution in aqueous $\text{Na}_2\text{CO}_3$ - $\text{H}_2\text{O}_2$ solutions with fractional feeding of $2\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}_2$ at different temperatures and $\text{S/L} = 1/50$.

In the case of oxidative dissolution of $\text{U}_3\text{O}_8(480°C)$ powder (see Figure 3) and $\text{U}_3\text{O}_8(1200°C)$ powder (see Figure 4) in aqueous $2\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}_2$ solution at reagent fractional feeding mode it was found that dissolution rate of $\text{U}_3\text{O}_8(1200°C)$ sample is lower.

The feeding mode of crystalline $2\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}_2$ 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 1.40 g/L at 20°C [26]) and dissociates into sodium ions, carbonate ions, and hydrogen peroxide:

$$2\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}_2 \rightarrow 4\text{Na}^+ + 2\text{CO}_3^{2-} + 3\text{H}_2\text{O}_2$$

When dissolving fresh portions of crystalline $2\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}_2$ 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 $\text{Na}_2\text{CO}_3$ in this carbonate system is lower in comparison with the system described above (see Figure 2), in which into initial 1.0 mol/L $\text{Na}_2\text{CO}_3$ solution added an aliquot of 35% aqueous $\text{H}_2\text{O}_2$ solution.

In the case of the $\text{U}_3\text{O}_8(480°C)$ powder sample, the value of $\alpha(U_3O_8)$ equal to 97.3%, 92.4%, and more than 99.6% at 25°C, 50°C, and 75°C was reached for 180, 120, and 60 min respectively (Figure 3). For the $\text{U}_3\text{O}_8(1200°C)$ 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 $\text{U}_3\text{O}_8(480°C)$ and $\text{U}_3\text{O}_8(1200°C)$ powder samples at the dissolution in the presence of $2\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}_2$ 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 ($E_{\text{app}}$) of the $\text{U}_3\text{O}_8$ powder samples oxidative dissolution process in 1.0 mol/L $\text{Na}_2\text{CO}_3$ - $\text{H}_2\text{O}_2$ solutions with fractional feeding of $3\text{Na}_2\text{CO}_3$·3$\text{H}_2\text{O}$ was calculated. The $E_{\text{app}}$ value at
U₂O₈(480°C) powder dissolution was 14.2 kJ/mol and 27.2 kJ/mol in the case of U₂O₈(1200°C) powder dissolution. Estimated $E_{app}$ values indicate, that the process occurs in the outer kinetic region in the case of U₂O₈(480°C) powder and the outer transition region or outer diffusional region in the case of U₂O₈(1200°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 U₂O₈ in aqueous Na₂CO₃ solutions cannot be achieved, unlike the fractional feeding mode.

The kinetic study of the oxidative dissolution of U₂O₈ powder samples in aqueous Na₂CO₃ solutions at the fractional feeding mode of the peroxide oxidants (H₂O₂ and 2Na₂CO₃·3H₂O₂) at various temperatures was carried out. The influence of the U₂O₈ calcination temperature on the oxidative dissolution rate in aqueous Na₂CO₃ solutions in the presence of H₂O₂/2Na₂CO₃·3H₂O₂ is established. Reducing of the specific surface area from 3.8 m²/g (for U₂O₈(480°C) powder sample obtained at 480°C) to 0.1–0.2 m²/g (for U₂O₈(1200°C) powder sample obtained at 1200°C) results in a decrease of the oxidative dissolution rate by 2 orders. For U₂O₈(480°C) sample, the complete dissolution in 1.0 mol/L Na₂CO₃ - 0.1 mol/L H₂O₂ solution at 75°C is achieved by 35–60 min. For U₂O₈ samples obtained at temperatures more than 600°C, the complete dissolution in the system 1.0 mol/L Na₂CO₃ - 0.1 mol/L H₂O₂ in one dissolution step at 75°C is not achieved even for 270 min. In the case of the 2Na₂CO₃·3H₂O₂ system, complete dissolution can be achieved in 60 minutes for U₂O₈(480°C) powder and 130 minutes for U₂O₈ (1200°C) powder at a temperature of 75°C.

The U₂O₈(1200°C) was resistant against the oxidative dissolution process but the complete dissolution was achieved by using Na₂CO₃ - H₂O₂ solutions at elevated temperatures.

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References


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