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KINETIC STUDY OF THE OXIDATIVE DISSOLUTION OF URANIUM DIOXIDE AND TRIURANIUM OCTAOXIDE IN CARBONATE MEDIA

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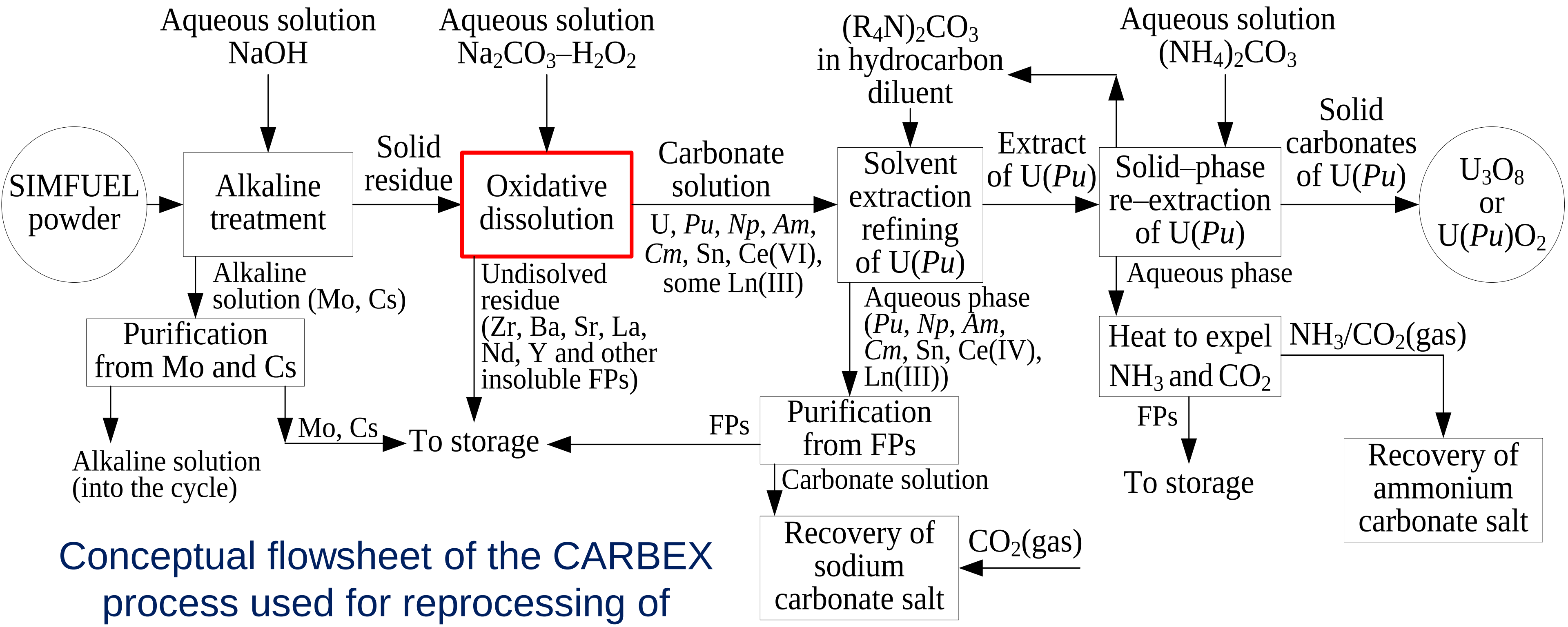
BACKGROUND



Conceptual flowsheet of the CARBEX process used for reprocessing of voloxidized uranium oxide SIMFUEL

Kinetic study of the oxidative dissolution of uranium oxides in carbonate media under oxidative conditions is critical for the development and improvement of a key stage in new alternative approaches for reprocessing spent nuclear fuel.

Aim:

KINETIC STUDY OF UO_2 AND U_3O_8 DISSOLUTION IN AQUEOUS SOLUTIONS OF Na_2CO_3, $NaHCO_3$ AND $(NH_4)_2CO_3$ IN THE PRESENCE OF H_2O_2.

Tasks:

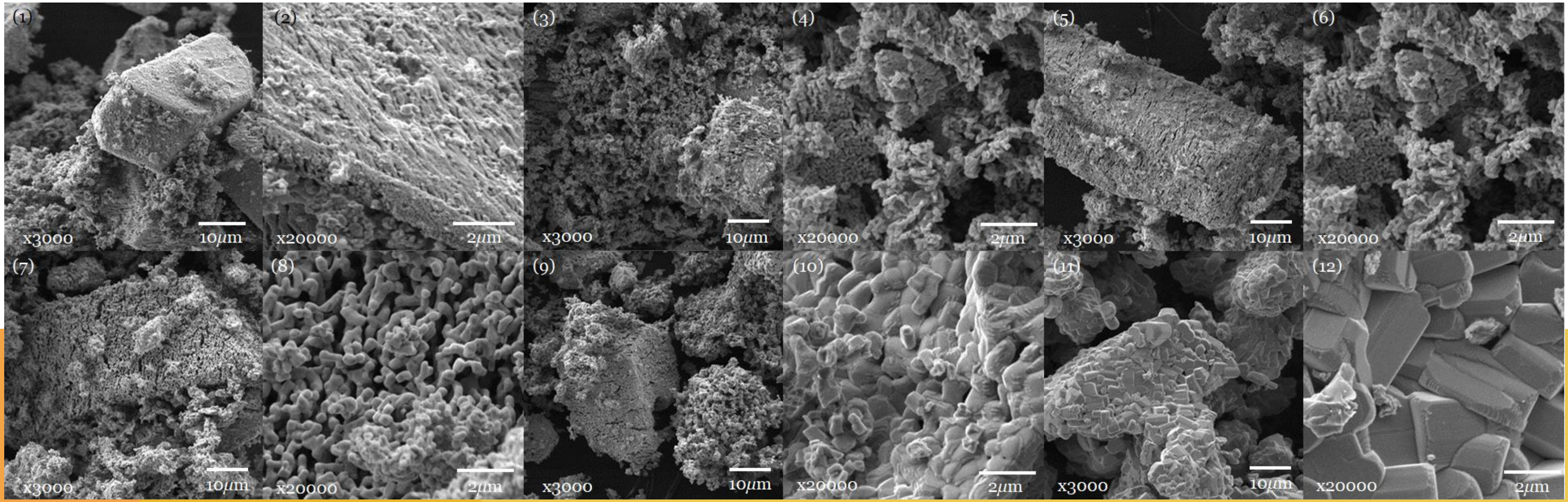
- *kinetic study of UO_2 and U_3O_8 powders dissolution in aqueous carbonate solutions in the presence of hydrogen peroxide;*
- *mathematical processing and analysis of obtained experimental data.*

MATERIALS AND METHODS

Calcination temperature, °C	*SSA*, m²/g
480	3,8
600	3,7
800	1,8
1000	0,8
1200	0,1

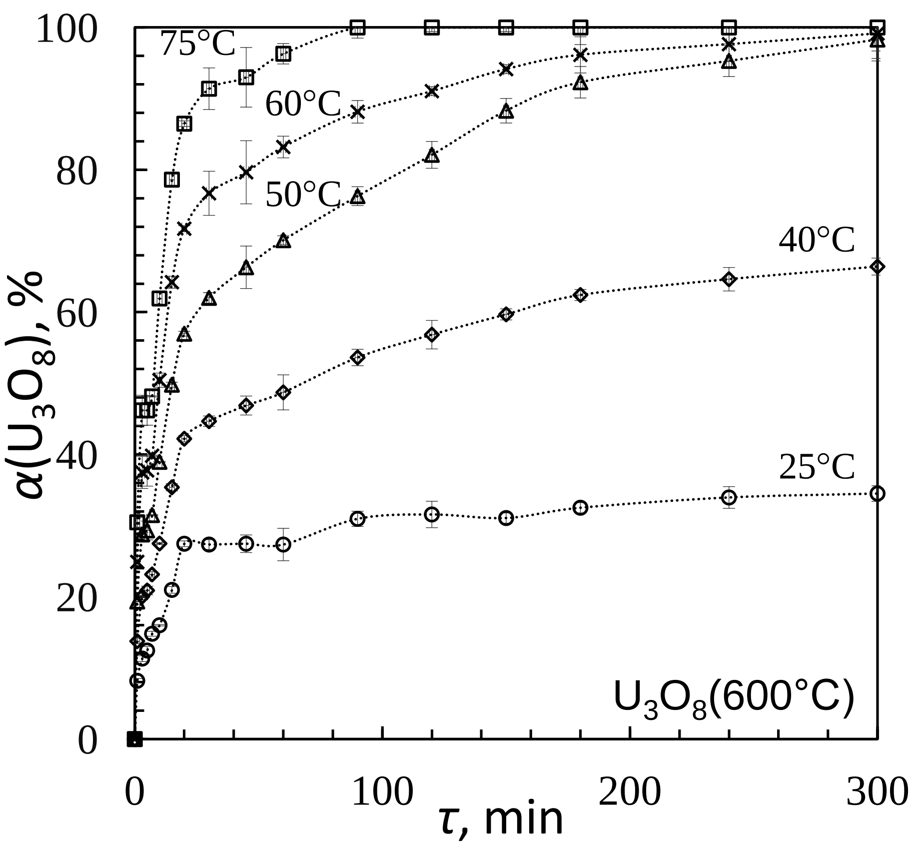
Specific surface area (SSA) value of the U_3O_8 samples

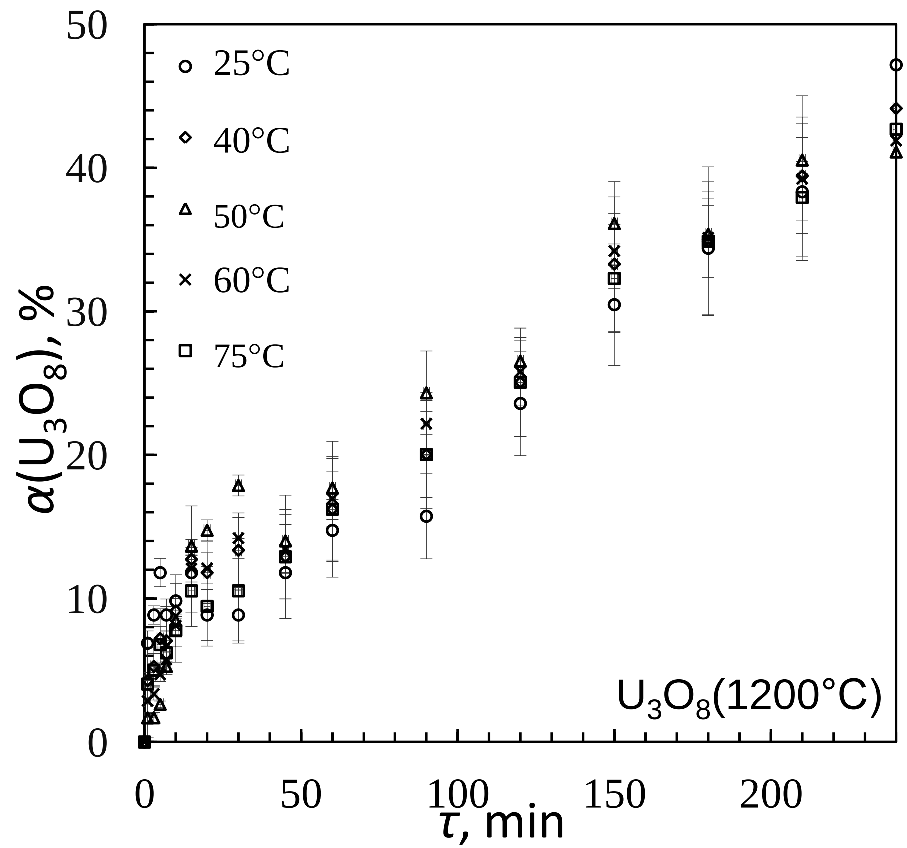
The initial UO_2 powder was heat treated in a muffle furnace in an air atmosphere. Heat treatment mode: 60 min heating, 240 min holding at a set temperature, passive cooling to ambient temperature.



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

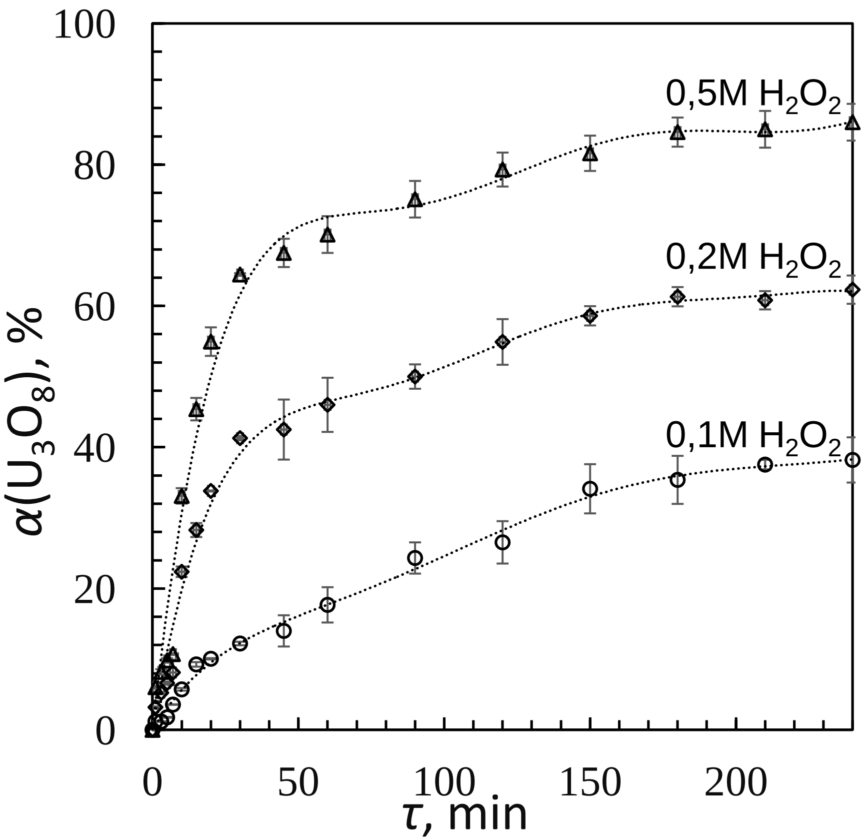
RESULTS AND DISCUSSION





Kinetic curves of U_3O_8(600°C) and U_3O_8(1200°C) dissolution in 1,0 mol L^{-1} Na_2CO_3 - 0,1 mol L^{-1} H_2O_2 at different temperatures and solid-to-liquid (S/L) ratio - 1:50.

RESULTS AND DISCUSSION



Oxidative dissolution U_3O_8 in aqueous solution Na_2CO_3 in the presence of H_2O_2, proceeds in accordance with the following reactions:

$$U_3O_8 + H_2O_2 \rightarrow 3UO_3 + H_2O$$

$$UO_3 + xCO_3^{2-} + H_2O \rightarrow [UO_2(CO_3)_x]^{2-2x} + 2OH^-$$

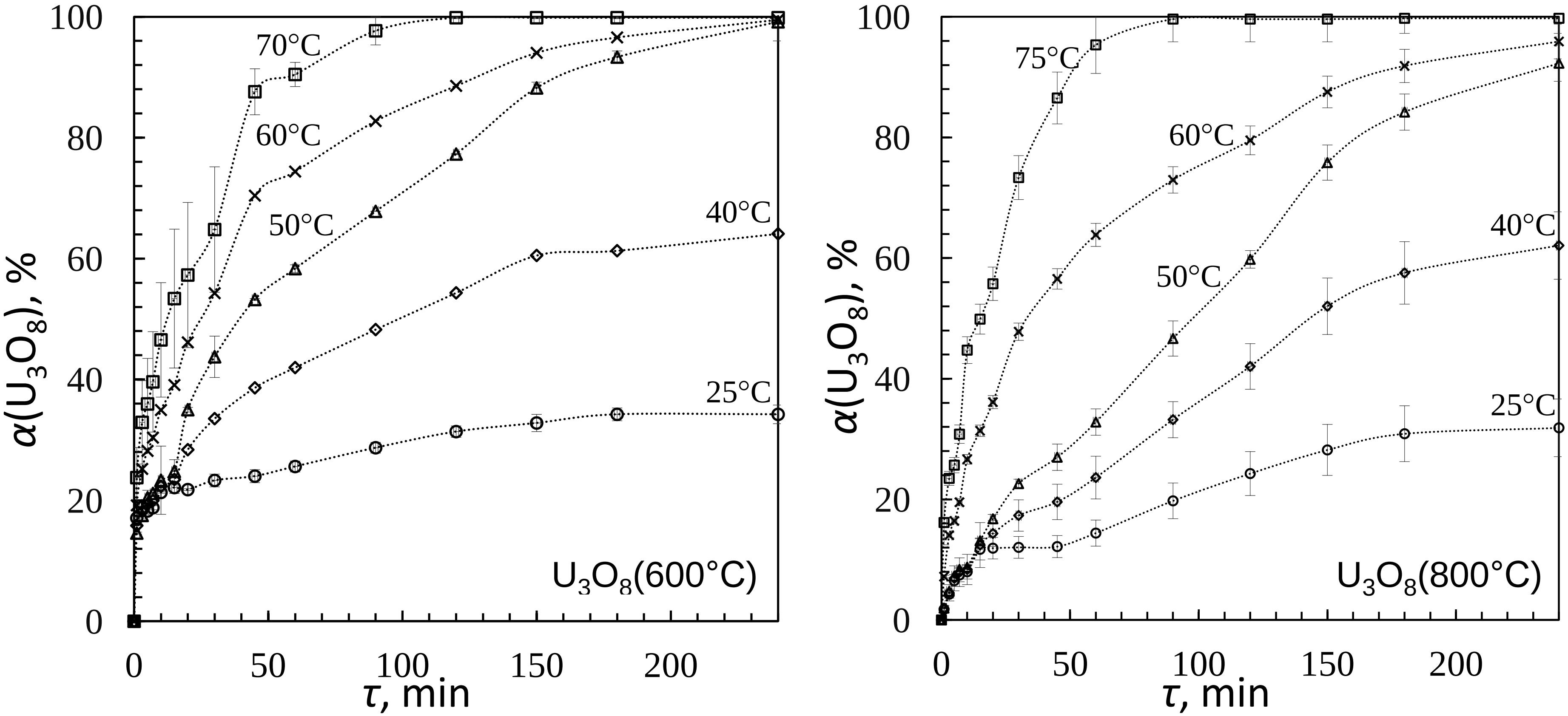
$$UO_2^{2+} xCO_3^{2-} \rightarrow [UO_2(CO_3)_x]^{2-2x}$$

$$[UO_2(CO_3)_3]^{4-} + xH_2O_2 \rightarrow [UO_2(O_2)_x(CO_3)_{3-x}]^{4-} + 2xH^+ + (3-x)CO_3^{2-}$$

where x – 0, 1 or 2.

Kinetic curves of U_3O_8(1200°C) dissolution in
1,0 mol L^{-1} Na_2CO_3 - 0,1 mol L^{-1} H_2O_2
at 75°C and S/L - 1:50.

RESULTS AND DISCUSSION



Kinetic curves of U_3O_8(600°C) and U_3O_8(800°C) dissolution in
1,0 mol L^{-1} $NaHCO_3$ - 0,1 mol L^{-1} H_2O_2 at different temperatures and S/L=1:50.

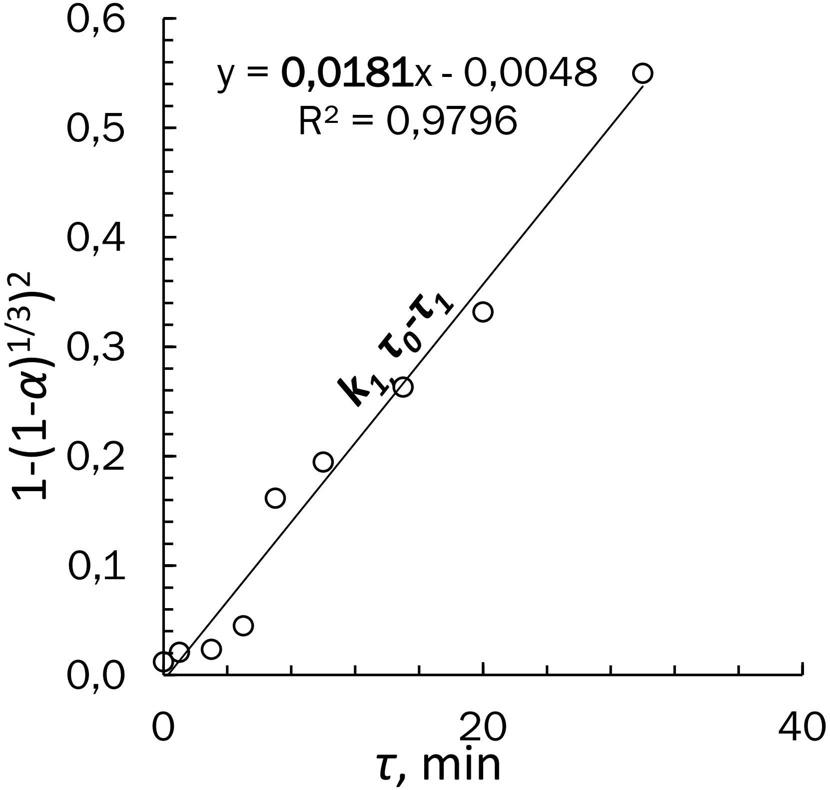
RESULTS AND DISCUSSION

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:

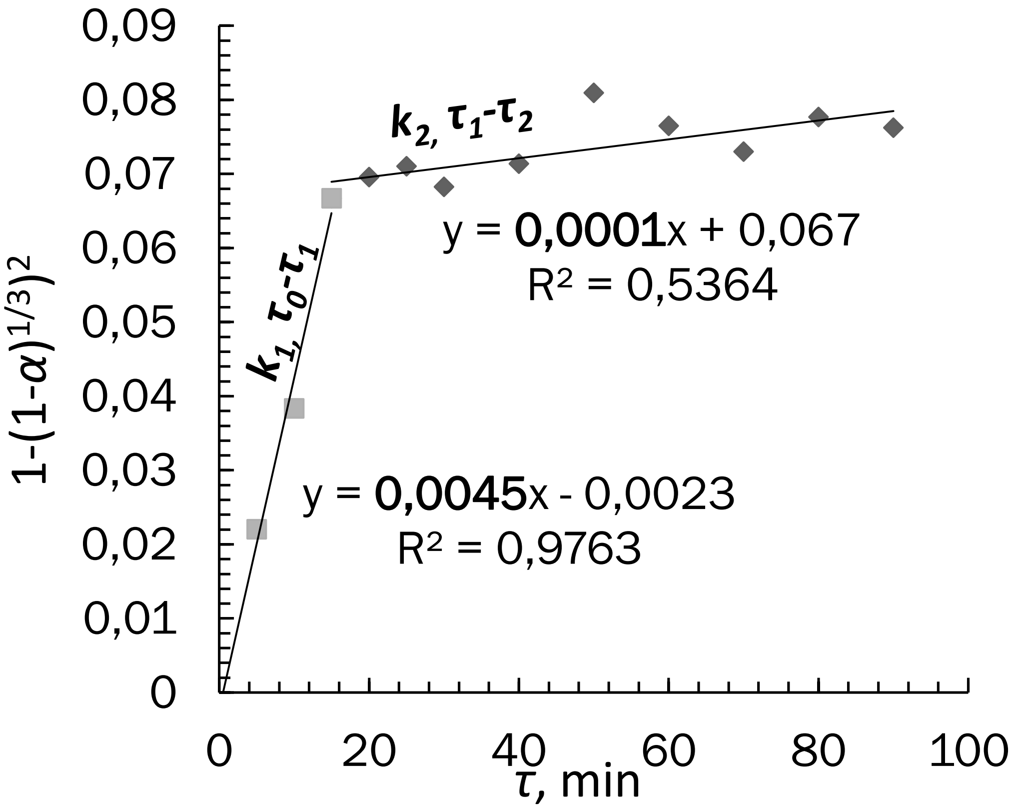
1. Kolmogorov-Erofeev $(-\ln(1-\alpha))^{1/3}=k(\tau-\tau_0)$;
2. Prout-Tompkins $\ln(\alpha/(1-\alpha))=k\tau$;
3. first order $\ln(1/1-\alpha)=k\tau$;
4. Yander $(1-(1-\alpha)^{1/3})^2=k\tau$;
5. Ginstling-Brownstein $1-(2/3)\alpha-(1-\alpha)^{2/3}=k\tau$;
6. anti-Yander $((1+\alpha)^{1/3}-1)^2=k\tau$;
7. anti-Ginstling $1-(2/3)\alpha-(1+\alpha)^{2/3}=k\tau$;
8. Shrinking core model $1-(1-\alpha)^{1/3}=k\tau$;
9. Exponential law model $\ln(\alpha)=k\tau$;
10. Kroger-Ziegler $(1-(1-\alpha)^{-1/3})^2=k\tau$;
11. Zhuravlev $((1-\alpha)^{-1/3}-1)^2=k\tau$;
12. Shrinking cylinder model $1-(1-\alpha)^{1/2}=k\tau$;
13. Shrinking cube model $1-(1-\alpha)^{1/3}=k\tau$;
14. Valenci $(1-\alpha)\ln(1-\alpha)+\alpha=k\tau$.

The value of U_3O_8 dissolution yield ($\alpha(U_3O_8)$) was calculated by the following equation: $\alpha(U_3O_8) = (M_\tau/M_i)\cdot 100$ where M_i and M_τ are the initial quantity of the U_3O_8 and its quantity contained in the solution after dissolution.

RESULTS AND DISCUSSION



Linear anamorphosis in coordinates of the Yander equation for U_3O_8(480°C) powder oxidative dissolution in 1,0 mol L^{-1} Na_2CO_3 - 0,1 mol L^{-1} H_2O_2 at 75°C and S:L=1:50



Linear anamorphosis in coordinates of the Yander equation for U_3O_8(800°C) powder oxidative dissolution in 1,0 mol L^{-1} Na_2CO_3 - 0,1 mol L^{-1} H_2O_2 at 75°C and S:L=1:50

RESULTS AND DISCUSSION

Values of reaction rate constant (*k*) for oxidative dissolution of UO_2 and U_3O_8 in carbonate media

Oxide	Media	Oxidant	*t*, °C	k_1, min^{-1}	τ_0-τ_1, min	k_2, min^{-1}	τ_1-τ_2, min	k_3, min^{-1}	τ_2-τ_3, min
UO_2	$NaHCO_3$	H_2O_2	25	0,05449 R = 0,9066	0-15	0,000228 R = 0,7655	15-240	–	–
			50	2,0801 R = 0,8836		0,00009 R = 0,5503		–	-–
			75	0,02063 R = 0,8649		0,000189 R = 0,6891		–	–
	H_2O	Na_2CO_3•1,5H_2O_2	25	0,00706 R = 0,9784		0,00213 R = 0,9342	15-90	0,000115 R = 0,7681	90-300
			50	0,00929 R = 0,9263		0,001901 R = 0,9972		0,000151 R = 0,7251	
			75	0,01407 R = 0,9597		0,000706 R = 0,8158		0,000137 R = 0,7706	
U_3O_8 480°C			25	0,00739 R = 0,8846		0,002309 R = 0,9806		0,000297 R = 0,7796	90-240
			50	0,01412 R = 0,9080		0,001715 R = 0,9639		0,000031 R = 0,3813	
			75	0,01666 R = 0,8957		0,003045 R = 0,9725		0,000115 R = 0,6547	

RESULTS AND DISCUSSION

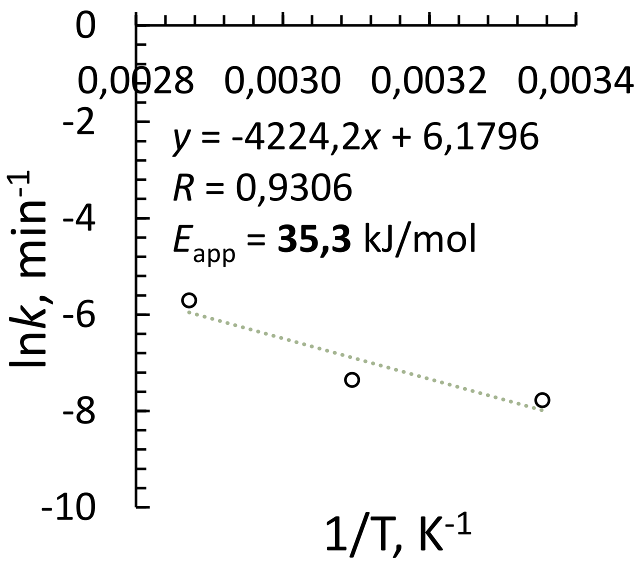
Values of rate constants oxidative dissolution of UO_2 and U_3O_8 in carbonate media

Oxide	Media	Oxidant	t, °C	k_1, min^{-1}	τ_0-τ_1, min	k_2, min^{-1}	τ_1-τ_2, min
U_3O_8 1200°C	H_2O	Na_2CO_3•1,5H_2O_2	40	0,185 R = 0,9896	0-270	–	–
			50	0,2513 R = 0,9989		–	–
			75	0,7099 R = 0,9976	0-150	–	–
U_3O_8 480°C	$NaHCO_3$	H_2O_2	25	1,274 R = 0,8991	0-15	0,0244 R = 0,8870	15-240
			50	1,7904 R = 0,8728		0,0386 R = 0,8936	
			75	2,2164 R = 0,8887		-0,006 R = 0,2581	
U_3O_8 1200°C			25	0,00042 R = 0,9931	0-210	–	–
			50	0,00064 R = 0,9886		–	–
			75	0,00333 R = 0,9959		–	–

RESULTS AND DISCUSSION

Values of apparent activation energy (E_{app}) for oxidative dissolution of UO_2 and U_3O_8 in carbonate media

Oxide	Media	Oxidant	E_{app}, kJ/mol
UO_2	$NaHCO_3$	H_2O_2	5,1
U_3O_8 (480°C)			9,6
U_3O_8(600°C)	Na_2CO_3		81,4
	$NaHCO_3$		93,9
U_3O_8 (1200°C)			**35,3**
UO_2	H_2O	Na_2CO_3•1,5H_2O_2	11,8
U_3O_8 (480°C)			14,2
U_3O_8 (1200°C)			27,2



Dissolution of U_3O_8(1200°C) in 1,0 mol L^{-1} $NaHCO_3$ - 0,1 mol L^{-1} H_2O_2 at S/L=1:50.

CONCLUSIONS

In this research, with applying of some kinetic models, in particular, Kolmogorov-Erofeev, Prout-Tompkins, first order, Yander, anti-Yander, Ginstling-Brownstein, anti-Ginstling, shrinking core model, exponential law model, Kroger-Ziegler, Zhuravlev, shrinking cylinder model, shrinking cube model and Valenci, the mathematical processing of experimental data on the oxidative dissolution of the UO_2 and U_3O_8 powders in aqueous carbonate and bicarbinate solutions in the presence of H_2O_2 at various temperatures and concentrations of reagents was carried out.

It was found that an adequate description of the experimental data occurs in the coordinates of the Yander equation: $1-(1-\alpha)^{1/3})^2=k\tau$. For all studied variants of oxidative dissolution UO_2 and U_3O_8, the reaction rate constants and apparent activation energy were calculated.

The obtained kinetic data can be useful in the development of a new process for dissolving spent nuclear fuel in carbonate media.

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