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THE RESEARCH OF URANIUM MONOXIDE-OXIDE DISSOLUTION PROCESS IN NITRIC ACID

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The kinetics of concentrates of uranium monoxide-oxide dissolution process by nitric acid solutions of 5...9 mole/l in the range of 11...90 °C has been studied. It is stated that initial nitric acid concentration increasing results in some uranium dissolution degree increasing only at the first process stage. Temperature increasing significantly raises uranium dissolution degree at the first stage as well. Uranium dissolution degree increases for all studied temperatures with increasing of the process period. The main feature of the studied process is that while dissolving uranium monoxide-oxide the behavior of iron, molybdenum, silicon additives is adequate to that of uranium. The equation of the reducing sphere describes the uranium leaching process from its nitric acid concentrates.

To obtain uranium hexafluoride used for enrichment according to the demands of International standard ASTM C 787-03 uranium refined from soluble and insoluble impurities to the certain limits is required. Concentrates which represent oxides of uranium and impurities after thermal treatment (U_3O_8 , MoO_3 , SiO_2 , Fe_3O_4 , CaO , MgO , Al_2O_3 etc.) may be used as a material for obtaining uranium of the required purity degree. Dissolution (leaching) of U_3O_8 from the concentrates is reasonable to be carried out with nitric acid as the extractant tributyl phosphate used for refining U(VI) from impurities works efficiently in nitrate medium. In the process of triuranium octaoxide dissolution in nitric acid U(IV) is oxidized to U(VI) without oxidizer. Nitric acid has low corrosive activity relative to constructive materials, for example, to steel 12X18H10T. The task of investigations included defining influence of temperature, nitric acid concentration, time of concentrate dissolution on the degree of extraction of uranium and impurities from it (iron, molybdenum, silicon) as well as investigation of kinetics of uranium and impurities dissolution, calculation of velocity constant and activation energy, choice of limiting process stage.

Experimental part

Triuranium octaoxide concentrate which represents a dark-grey powder of the following composition: U – 83,14 wt. %; U-234 – 53 mkg/g; impurities (% of U): Fe – 0,070, SiO_2 – 0,170, Mo – 0,031, Ca – 0,004, $As \leq 0,004$, $B \leq 0,00003$, $F \leq 0,0005$, halogens – 0,002, Mg – 0,001, P – 0,006, K – 0,01, Na – 0,010, $Th \leq 0,003$, $Ti \leq 0,001$, $V \leq 0,001$, $Zr \leq 0,001$, $W \leq 0,001$ was used as a subject of inquiry. Apparent and metric densities of the powder are 1, 65 and 6, 83 g/cm³, respectively. Powder particle size determined at sedimentometer BC-3 did not exceed 50 mkm. Grain-size composition: 3 % of fractions of 0...10 mkm, 18 % of fractions of 10...20 mkm, 35 % of fractions of 20...30 mkm, and 22 % of fractions of 30...40 mkm and of 40...50 mkm each.

Influence of nitric acid concentrations (5...9 mole/l), temperature (11...90 °C) and time on dissolution degree of uranium oxides and impurities was studied at laboratory setup (Fig. 1). Reactor (3) was filled up with nitric acid of specified concentration. The solution was stirred with mechanical mixer. Solution temperature in

the reactor was maintained by thermostat (2) with accuracy $\pm 1^\circ\text{C}$. Having obtained the specified temperature, batch of concentrate U_3O_8 (10 g) was introduced into acid solution and time reading was maintained.

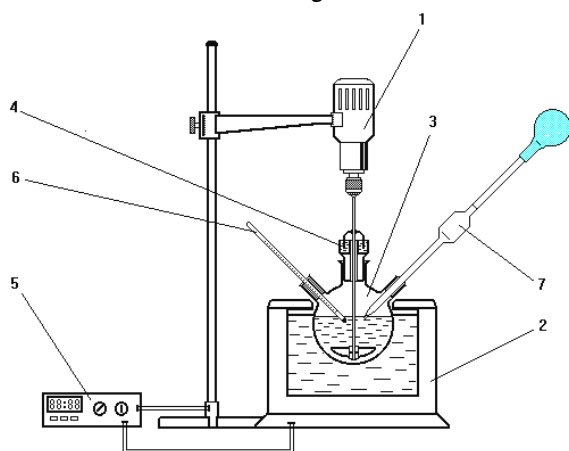


Fig. 1. Diagram of laboratory setup: 1) mechanical mixer motor; 2) electric thermostat; 3) dissolution reactor; 4) hydraulic lock; 5) controller of mixer number of revolutions; 6) thermometer; 7) sampler

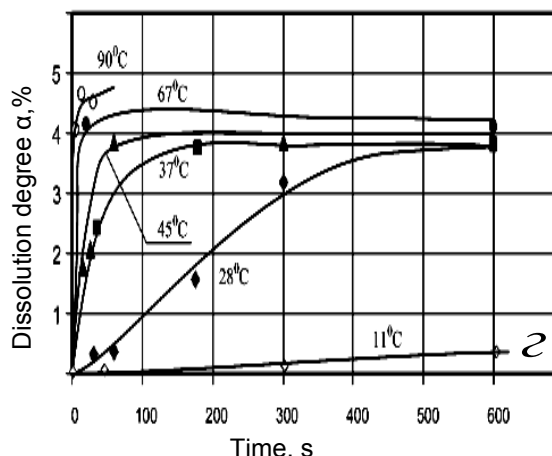
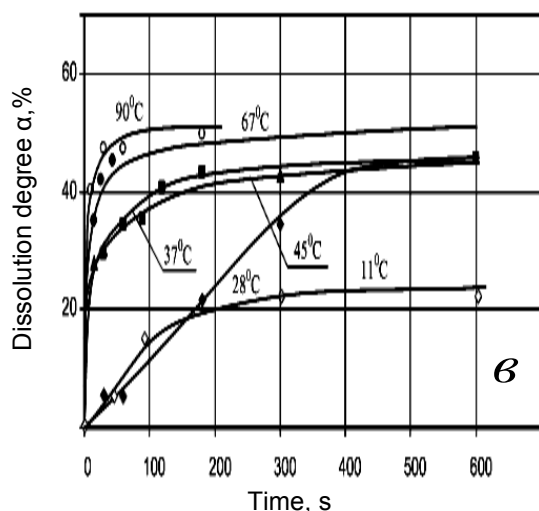
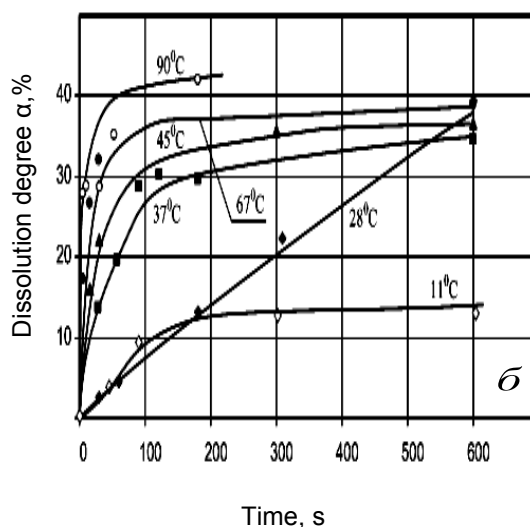
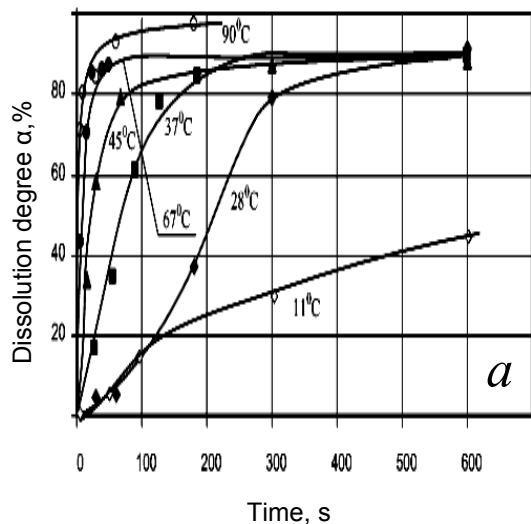


Fig. 2. Influence of temperature and time of reaction in the solution of 5 mole/l HNO_3 on dissolution degrees: a) U_3O_8 ; б) ferric oxide; в) molybdenum oxide; г) silicon oxide

Mass content of uranium and impurities in concentrate and solution samples was defined by the techniques of accredited laboratory of radiochemical plant at SGCE, Seversk.

Uranium content in the samples was defined by chelatometric method; relative definition error is 3, 0 %.

Impurity content in uranium solution was determined by chemical-spectral method [1]. Total error of definition is Mo 40...85 % depending on molybdenum content in the sample (at different dissolution conditions), Fe – 60...80 %, Si – 80...95 %.

Dissolution degree of uranium oxides and impurities was determined as a part of the element passed into solution by the moment of sampling relative to the initial amount of the element in the batch of concentrate U_3O_8 in %.

Results and discussion

It was stated that dissolution degree of U_3O_8 during the process changes nonmonotonically (Fig. 2, 3). For example, during the first 5...10 s 70...80 % of uranium (VI) passes into solution 5 mole/l HNO_3 at temperature 90°C and

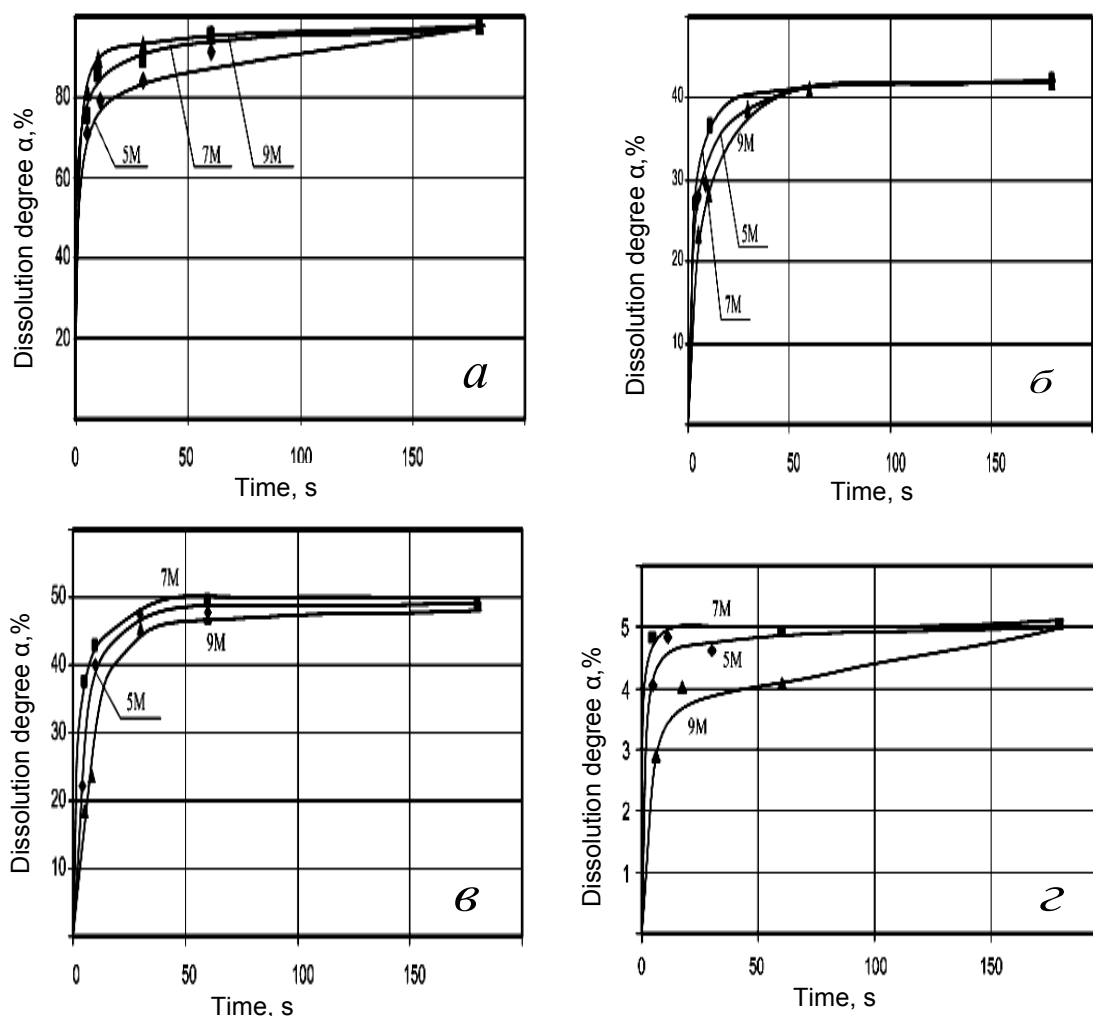


Fig. 3. Influence of HNO_3 concentration and reaction time at 90°C on dissolution degree: a) U_3O_8 ; б) ferric oxide; в) molybdenum oxide; г) silicon oxide

then during 180 s dissolution degree achieves 98,2 %. Increasing process duration the dissolution degree of U_3O_8 rises for all studied temperatures. Dissolution occurs slowly at 11°C . So during 30 s 4,4 % of uranium (VI) is extracted into solution, during 180 s it is 37,1 %, and during 1200 s it amounts to 96,8 %. Increasing the temperature uranium dissolution degree rises significantly at the same response time. Changing nitric acid concentration from 5 to 7...9 mole/l results in increasing dissolution degree of U_3O_8 at the initial stage of the process (in 10 s it increased by 5 % and 9,7 % respectively). But by the end of the process (in 180 s) dissolution degree of U_3O_8 becomes equal for all studied concentrations – 98,2 %.

Impurities behavior at dissolution of triuranium octoxide concentrate of nitric acid repeats the character of dependence of U_3O_8 dissolution degree on temperature and dissolution duration. Within two hours dissolution degree of molybdenum oxide amounted to 45...50 %, ferric oxide – 40...47 % and silicon oxide – 8...9 % (Fig. 4–9).

Dissolution process of uranium concentrates generally consisting of uranium oxides and attendant impurities refers to the heterogeneous one behaving by the

type $\text{S}+\text{L}>\text{S}+\text{L}+\text{G}$, where S is solid; L is liquid; G is gaseous state of reactants. Undissolved concentrate residue should be considered as a solid reaction product. Soluble nitrates of uranyl and impurities in various ionic forms [2, 3] pass into solution that subsequently may impede uranium extraction refining [4–6]. Nitric oxides NO , NO_2 are gaseous reaction products.

To describe the kinetics of heterogeneous processes various equations are applied in terms of reaction conditions [7–10]. For the process which rate depends both on agents diffusion to the response surface and on reaction velocity on the phase interface the equation of reducing surface was used:

$$1 - (1 - \alpha)^{1/3} = k \cdot \tau,$$

where α is the degree of conversion (reaction), parts; k is the velocity constant, c^{-1} ; τ is the time of reaction, s.

Processing the experimental data the dependence of dissolution degree on the time was made in coordinates $1 - (1 - \alpha)^{1/3}$; t and adequacy of applying chosen equation was estimated by correlation factor. The experimental data in these coordinates are well linearized, chosen equation describes the change of concentrate dissolu-

tion degree on time at different temperatures rather authentically and kinetic parameters of the process may be defined by this equation. Reaction velocity constant was calculated for each temperature by slope ratio of a line in coordinates $1-(1-\alpha)^{1/3}$; t and temperature dependence of reaction velocity constant was made in coordinates $\ln k$; $1/T$. On linear section of the $\ln k=f(1/T)$ the parameters $\ln k_0$ and E/R were found by the least square technique and activation energy E and pre-exponential factor k_0 were searched from them.

The results of calculation of kinetic parameters of U_3O_8 dissolution process are given in Tables 1, 2 and their mathematical treatment using the equation of reducing surface is represented by diagram in Fig. 4, *a* and 5, *a*.

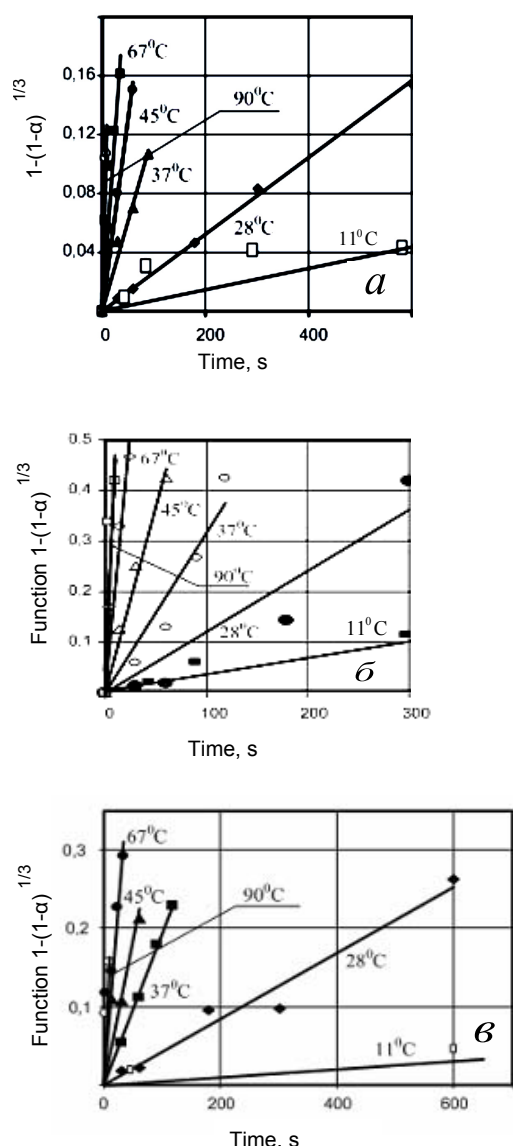


Fig. 4. Dependence $1-(1-\alpha)^{1/3}=k \cdot t$ for: a) U_3O_8 ; б) ferric oxide; в) molybdenum oxide

The analysis of the given data shows that the equation of reducing sphere describes rather authentically U_3O_8 dissolution process from its concentrates by nitric acid with initial concentration (5..9) mole/l in temperature range of 28...90 °C at S:L=1:2 (S is solid in mass,

L is liquid in volume). Reaction order determined by this model is close to a unit and apparent activation energy amounted to $E_a=52$ kJ/mole. Dissolution degree of U_3O_8 is determined to a large degree by process temperature. In the researched temperature range 37...90 °C U_3O_8 dissolution degree changes from 0 to 0,8 fractions. At temperature 11 °C within 60 s from the beginning of the process the breakdown time is noted. It might be supposed that in the range of relatively low temperatures there is more complicated response mechanism.

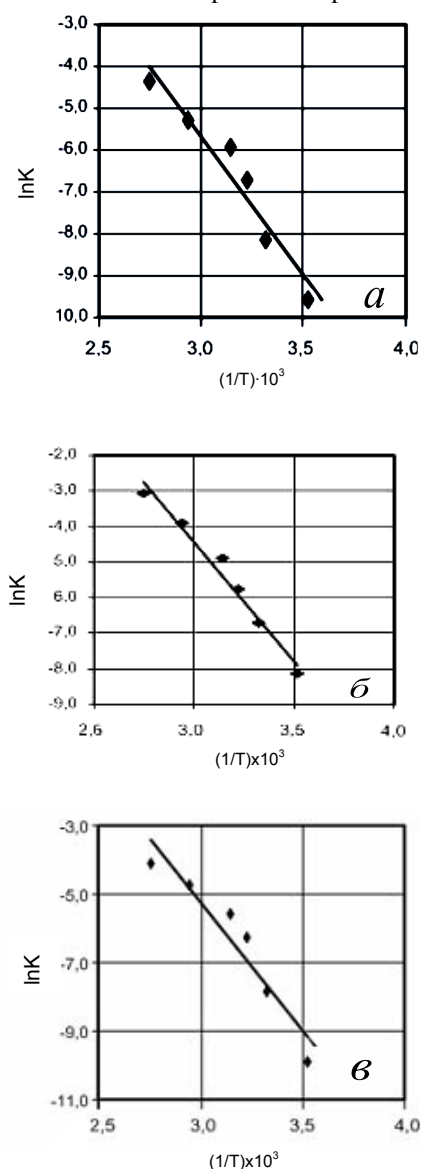


Fig. 5. Dependence of $\ln k$ on $1/T$ for: a) U_3O_8 ; б) ferric oxide; в) molybdenum oxide

The experimental data on dissolving the investigated impurities were similarly treated. The results showed that when solving uranium concentrate the behavior of ferric oxide impurities (Fig. 4, б and 5, б), molybdenum (Fig. 4, в and 5, в) and other impurities is adequate to U_3O_8 behavior.

Final results of processing experimental data in the form of parameters of kinetic equations for dissolution of triuranium octaoxide and impurities contained in concentrate are presented in Table 3.

Table 1. Calculation of rate constant of U_3O_8 dissolution process by solution HNO_3

Temperature, °C	Time, s	Dissolution degree of U_3O_8 , in fractions	Function $1-(1-\alpha)^{1/3}$	Reaction velocity constant, $k \cdot 10^4, c^{-1}$	Correlation factor
28	0	0	0	15	0,942
	30	0,044	0,0148		
	60	0,056	0,0191		
	180	0,371	0,1431		
	300	0,805	0,4201		
37	0	0	0	29	0,959
	30	0,1685	0,0148		
	60	0,344	0,0191		
	90	0,607	0,1431		
	120	0,81	–		
45	0	0	0	70	0,989
	15	0,337	0,1280		
	30	0,582	0,2524		
	60	0,81	0,4251		
	–	–	–		
67	0	0	0	179	0,966
	5	0,428	0,1699		
	15	0,700	0,3308		
	25	0,849	0,4678		
	35	0,859	–		
90	0	0	0	418	0,886
	5	0,711	0,3389		
	10	0,803	0,4181		

Table 2. Computation of apparent activation energy of U_3O_8 dissolution process by solution HNO_3

Temperature		$1/T \cdot 10^3$	Reaction velocity constant, $k \cdot 10^4, c^{-1}$	$\ln k$	Correlation factor	Apparent activation energy, kJ/mole
°C	K					
28	301	3,32	15	-6,502	0,964	52
37	310	3,23	29	-5,843		
45	318	3,14	70	-4,962		
67	340	2,94	179	-4,023		
90	363	2,75	418	-3,175		

To process the obtained experimental data the other equations were also checked [2, 3]. However, using the equation of reducing sphere turned out to be the most adequate.

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To decrease the volume of gases escaping the reactor-dissolver and nitric acid consumption for dissolution the following technique was developed. According to this technique uranium oxide powder is placed under water layer at the ratio of water layer height to height of uranium oxide layer is not less than 1,3 and nitric acid with consumption 0,30...0,36 t of HNO_3 per 1 t/h of uranium is introduced under the layer of uranium oxides.

Table 3. Results of calculation of kinetic parameters of U_3O_8 dissolution process and impurities contained in uranium concentrate in the range of temperatures of 20...90 °C Order of dissolution process of uranium oxides and impurities is the first

Element	Degree of element dissolution, in fractions	E_a , kJ/mole	k_0, c^{-1}
U	0...0,8	52	$(1,7 \pm 0,4) \cdot 10^5$
Mo	0...0,5	48	$(2,1 \pm 0,6) \cdot 10^5$
Fe	0...0,4	49,5	$(2,4 \pm 1,3) \cdot 10^5$
Si	0...0,1	51,3	$(3,6 \pm 0,7) \cdot 10^5$

For increasing the degree of separation of liquid and solid phases the method of uranium concentrate dissolution with obtaining uranium solutions (VI) with concentration 700...800 g/l at weight ratio of nitric acid to uranium 0,75...0,84 at temperature 85...100 °C was developed. The obtained pulp is diluted in uncooled state to the required uranium concentrations (VI) and nitric acid by weak nitrate solutions. After that aqueous phase is separated from insoluble residue.

Conclusion

- Kinetics of U_3O_8 concentrates dissolution by nitric acid solutions with concentration 5...9 mole/l at 11...90 °C was investigated and process kinetic equation is defined.
- The method of uranium oxide dissolution at 100 °C and nitric acid concentration 12...16 mole/l obtaining concentrated uranium solutions (VI) 700...800 g/l and further dilution to 400...500 g/l was developed.
- To decrease the volume of gases escaping the reactor-dissolver and reduction of nitric acid consumption the procedure of U_3O_8 concentrates dissolution supplying nitric acid under the layer of oxide powder was developed.

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