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CHEMICAL KINETICS AND CATALYSIS

Studying the Kinetics of the Alkaline Processing of Boron Production Wastes under Different Conditions

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Abstract—The kinetics are studied of topochemical reactions of the formation of calcium hydrosilicate in a multicomponent aqueous system consisting of waste products of boric acid production. The waste products include silicon dioxide and calcium sulfate in equal molar fractions, an alkali metal hydroxide in a stoichiometric ratio to the molar content of calcium sulfate and silicon oxide for obtaining hydrosilicate calcium, and the volume of water calculated to obtain a solution of alkali metal sulfate with a concentration below saturation. Data are obtained on the kinetics of the formation of calcium hydrosilicates in different modes of processing (normal conditions with constant stirring; ultrasonic action at a temperature of 20°C; microwave exposure with constant stirring at a temperature of 95°C; and autoclaving at a temperature of 220°C). It is found that the fastest reaction rate is characteristic of microwave treatment, and the largest proportion of reacted alkali metal hydroxide is obtained during autoclave treatment.

Keywords: kinetics, topochemical reaction, waste of boric acid production, alkaline treatment, potassium hydroxide, ultrasonic action, microwave action, autoclave treatment

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INTRODUCTION

When studying the kinetics of chemical reactions in heterogeneous systems, one of the main parameters characterizing the process is the characteristic kinetic constants determined from the empirical equations that describe the experimental data. The time parameters of different chemical processes are important for obtaining the optimum parameters of industrial technologies.

To analyze the time dependences of changes in the concentrations of the initial components in a given system or the products of a reaction, researchers use a number of equations of formal kinetics. Such equations use time dependence α_t corresponding to, e.g., the fraction of the reacted substance (in the equations of Erofeev and Kolmogorov–Erofeev). In the kinetic equation of N.S. Akulov, α_t corresponds to the relative value referred to by the author as the degree of conversion of the substance. This is the analytical dependence of the fraction of the reacted component in the system on time, or the fraction of the final substance obtained in relation to its maximum values at the time of the reaction as $t \to \infty$. The above authors obtained a kinetic equation by considering the probabilistic mechanism of the interaction between the molecules that participate in the reaction, and did not consider the specific mechanism of the processes under study.

It was shown in [1] that the sorption of ions by a sorbent should be considered a topochemical reaction between an aqueous solution of sorbate with concentration C_{from} and a solid sorbent with a relative content of active centers in the sorbent ready to participate in an exchange reaction equal to $C_s = (1 - A_t/A_m)$, where A_t and A_m are respectively the current and maximum possible values of the sorption capacity of the sorbent, which are directly related to the concentration of active centers that participate in exchange reactions. Applying the law of mass action to similar chemical processes (which is considered in textbooks of physical chemistry) and equating the rates of sorption and desorption under equilibrium conditions, analytical expressions were obtained for sorption isotherms (similar equations were obtained by I. Langmuir in 1918), but if we consider the time factor as in [1] and the dependence of relative value

A_t/A_m on the concentration of sorbate in the solution, we obtain

$$C_c t\left(1-\frac{A_t}{A_m}\right)k_1=\frac{A_t}{A_m}C_c k_2 \qquad (1)$$

(with sorption α_t and α_m correspond to values A_t and A_m), from which it follows that the dependence of relative value α_t on time is

$$\alpha_t=\alpha_m Kt\left[\frac{1}{(1+Kt)}\right], \qquad (2)$$

where K is a constant (time^{-1}); α_t is rate of the reaction at time t; α_m is the maximum value of the rate of the reaction; and t is the length of the reaction.

Equation (2) shows that constant K can be determined from the experimental dependences of the values of α_t on t via calculation using the equation

$$K=\Sigma\left[\frac{\alpha_t}{t}\left(\frac{1}{\alpha_m-\alpha_t}\right)\Big/N\right], \qquad (3)$$

where N Is the number of values α_t at the corresponding reaction rate, and graphically when presenting experimental data on kinetics in the form of linear dependence $1/\alpha_t$ on $1/t$:

$$\frac{1}{\alpha_t}=\frac{1}{\alpha_m}+\frac{1}{Kt\alpha_m}, \qquad (4)$$

where $1/\alpha_m$ is the value of the ordinate at $t \to \infty$; K is determined from the slope of a straight line or with an equation obtained via least squares processing of experimental results:

$$y=a+bx, \qquad (5)$$

where $a = 1/\alpha_m$, $b = (1/\alpha_m)(1/K)$, and $K = a/b$...

The proposed equation for the kinetics of topochemical reactions with minimal deviations describes the sorption of metal ions by sorbents, the mechanism for which is associated with ion exchange; the kinetics of the reaction for obtaining calcium hydrosilicates; and the kinetics of sorption of heavy metal ions on ion-exchange resins [1–4]. In this work, the proposed equation was used to analyze the kinetics of the topochemical reaction of the formation of calcium hydrosilicates from waste products of boric acid (borohypsum) production in an alkaline medium in different modes: mechanical stirring under normal conditions, along with ultrasonic, microwave, and autoclave processing. It is known that calcium silicates are widely used in the production of building materials, paper, paints, plastics, composite polymer and ceramic metal materials, and sorbents for water purification [5–9]. Large-tonnage wastes from boric acid production are of certain practical interest in obtaining these compounds, since they contain both calcium and silicon components in the optimum ratio, and no raw materials from additional sources are required for blending the initial mixture [10].

EXPERIMENTAL

Characteristics of Boric Acid Production Waste (Borogypsum)

Borogypsum is a solid waste resulting from the decomposition of datolite concentrate with sulfuric acid, the main components of which are calcium sulfate dihydrate and amorphous silica. It is characterized by the following content of the main components, wt %: SiO_2, 26–28; CaO, 26–28; SO_4^{2-}, 38–40; Fe_2O_3, 1.8–2; Al_2O_3, 0.6–0.8; B_2O_3, 0.7–1.2; MnO, 0.2; and MgO, 0.1–0.2.

Alkaline Treatment of Borogypsum to Obtain Calcium Hydrosilicates

Initial components borogypsum and potassium hydroxide (or sodium hydroxide) were mixed for different periods of time in a stoichiometric ratio that ensured complete interaction between calcium sulfate with a potassium hydroxide solution to obtain hydrated calcium silicate and potassium sulfate [3, 10, 11]. Water was added in a volume calculated to obtain an unsaturated solution of potassium sulfate with complete interaction between borogypsum and potassium hydroxide, (according to the stoichiometric coefficients in Eq. (I)).

The temperatures of waste treatment were (°C) 20 and 95 for stirring and sonication, respectively; 95 for microwave processing; and 220 in an autoclave. Depending on the mode of processing, synthesis was conducted by stirring the reaction mixture on a laboratory shaker, in an ultrasonic unit, in a microwave treatment apparatus, or in the autoclave. After a specified time interval, the resulting mixture was removed from the reaction vessel. The precipitate was separated from the solution by filtering it through a blue ribbon paper filter. It was then washed with distilled water, heated to 60–70°C, and dried for 3–5 h at 85°C. The rate of the reaction was monitored according to the residual concentration of potassium hydroxide in the solution. The concentration of potassium hydroxide was determined via acid–base titration using 0.1 N sodium hydroxide as a titrant. HCl solution was prepared using fixanal.

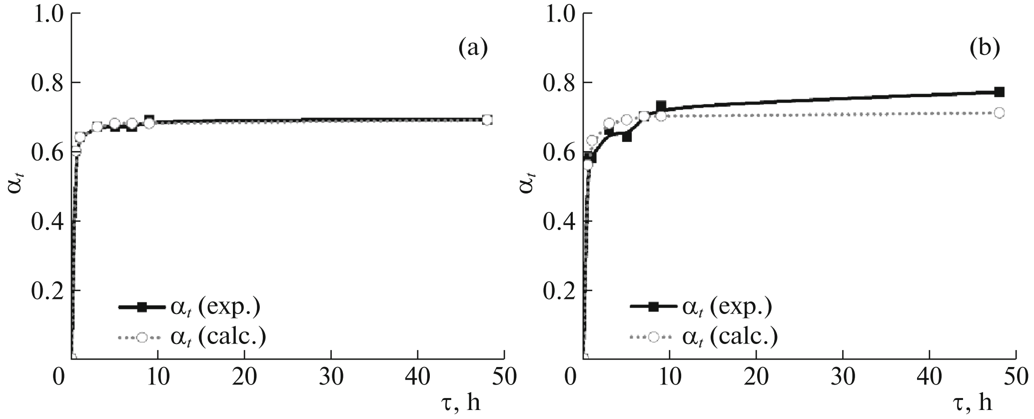

Fig. 1. Dependences of the reaction rate on time at 20°C: (a) normal conditions, (b) ultrasonic treatment of the reacting mixture.

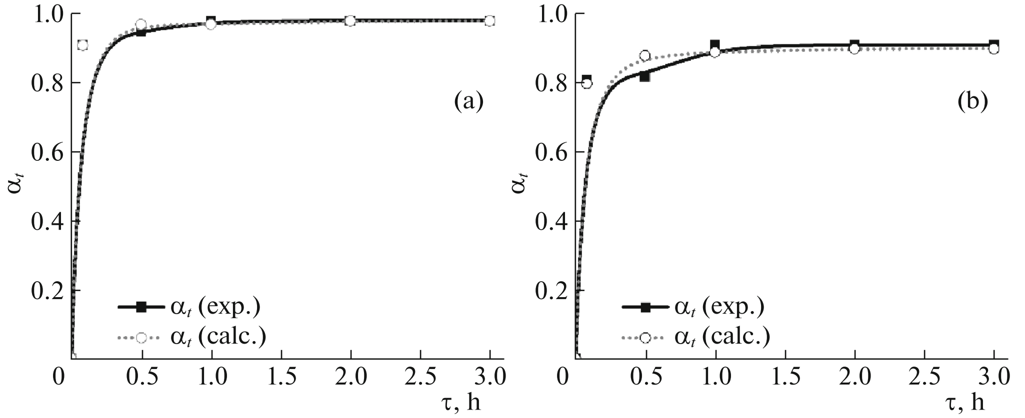

Fig. 2. Dependences of the reaction rate on time at 95°C: (a) microwave treatment, (b) normal stirring of the reacting mixture.

The following reactions are possible in the investigated multicomponent borohypsum–alkali–water ($CaSO_4–SiO_2–KOH–H_2O$) system:

$$CaSO_4 \cdot 2H_2O + 2KOH \rightarrow K_2SO_4 + Ca(OH)_2 + 2H_2O, \quad (I)$$

$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3 + H_2O \quad (II)$$

or

$$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O, \quad (III)$$

$$K_2SiO_3 + CaSO_4 \rightarrow CaSiO_3 + K_2SO_4. \quad (IV)$$

According to calculations, Gibbs free energy $\Delta G°$ is −118, −35.4, −123, and −38.4 kJ, respectively, for reactions (I)–(IV). The total (absolute) value of free energy for reactions (I) and (II) is higher than for reactions (III) and (IV); i.e., reactions (III) and (IV) are more thermodynamically likely.

RESULTS AND DISCUSSION

Using the obtained values of α_m and constant k, we constructed theoretical (calculated) curves of the time

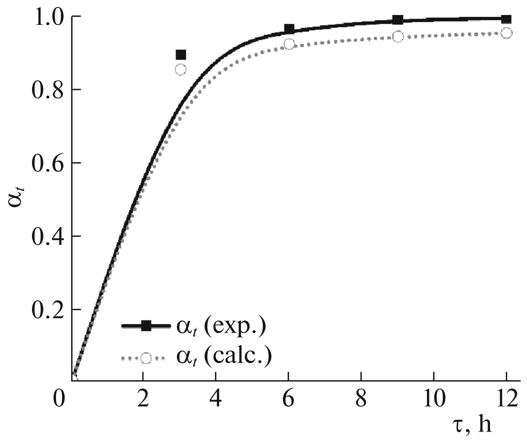

Fig. 3. Dependences of the reaction rate on time during autoclave treatment (temperature 220°C).

Table 1. Calculated and experimental values of rate α_t of the formation of calcium hydrosilicates from borohypsum in an alkaline medium (potassium hydroxide) under normal conditions (20°C), and difference Δ in % between the experimental and calculated values of α_t (where *t* is time)

t, h	α_t, exp.	α_t, calc.	Δ, %
0.5	0.6	0.60	0.0
1	0.64	0.64	0.0
3	0.67	0.67	0.0
5	0.67	0.68	1.5
7	0.67	0.68	1.5
9	0.69	0.68	1.5
48	0.69	0.69	0.0

dependences of the investigated topochemical process according to (2), calculated the difference Δ in % between the calculated values of α_t and those obtained experimentally at a given time.

Figures 1–3 show the kinetics calculated according to the proposed Eq. (2) and the experimentally obtained dependences of the rate of the formation of calcium hydrosilicates from borohypsum in an alkaline medium (potassium hydroxide) on time.

As can be seen from our calculated and experimental dependences, the maximum difference between the reaction rates is no more than several percent (Table 1). This applies only to some points, which can be attributed to incorrect measurements during an experiment. Most of the compared values differ by tenths of a percent, confirming the suitability of Eq. (2) for describing the kinetics of such processes.

Table 2 shows the parameters obtained graphically in presenting the experimental data on kinetics in the form of the dependence of the reciprocal of the rate of the formation of calcium hydrosilicate on the reciprocal of the length of the process (Eq. (4), Fig. 4).

As can be seen from the data in Table 2, the proposed equation can be used to describe the kinetics of the studied processes, according to the corresponding correlation coefficients.

CONCLUSIONS

We analyzed the kinetics of the topochemical reaction of the formation of calcium hydrosilicates from the waste of boric acid production (borogypsum) in an aqueous alkaline medium in different modes of processing modes. Time constants (K h^{-1}) of the formation of calcium hydrosilicate, the reciprocal values of which correspond to the time of reaching 1/2 the maximum value of the fraction of calcium hydrosilicate formation, were determined from the residual value of potassium hydroxide in the system. It was found that in the investigated "borohypsum–alkali–water" ($CaSO_4$–SiO_2–KOH–H_2O) system, $1/K = 0.073$ h in the mode of processing with constant mixing of the components under normal conditions. With ultrasonic treatment, $1/K = 0.135$ h; with microwave treatment, $1/K = 0.007$ h; with constant stirring at a temperature of 95°C, $1/K = 0.01$ h; and with autoclaving at 220°C, $1/K = 0.476$ h. The fastest rate of the formation of calcium hydrosilicate is characteristic of the mode of microwave processing, while the most complete process of formation using 99% potassium hydroxide is typical of autoclave processing.

Table 2. Parameters of the kinetic equation for the formation of calcium hydrosilicate from wastes of boron production in different modes of synthesis

No.	Mode of processing	Equation parameters		
		α_{max}	*K*, h^{-1}	R^2
1	Stirring under normal conditions, 20°C, KOH (NaOH)	0.69 (0.64)	13.7 (62.0)	0.9695 (0.8356)
2	Ultrasonic treatment, 20°C, KOH (NaOH)	0.71 (0.69)	7.4 (19.4)	0.6911 (0.6441)
3	Microwave processing, 95°C	0.97	153.8	0.9315
4	Stirring under normal conditions, 95°C	0.89	98.2	0.7535
5	Autoclave, 220°C	0.99	2.1	0.9939

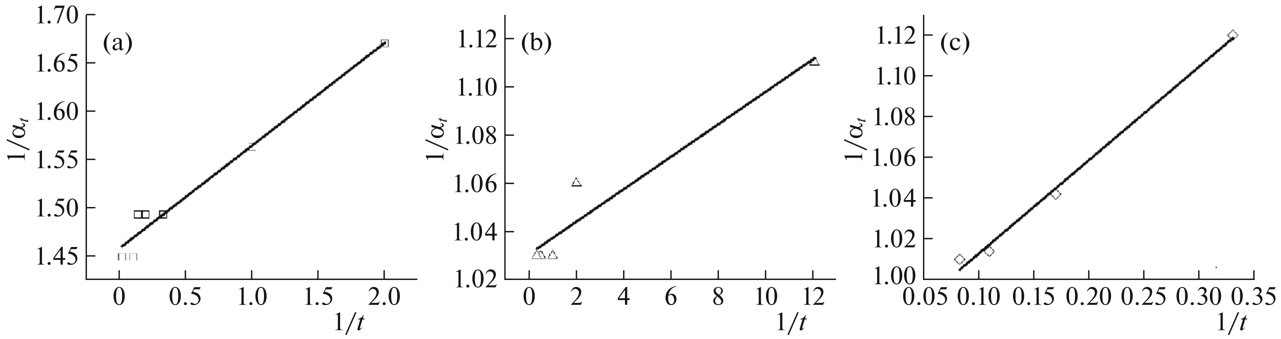

Fig. 4. Reverse quantity dependences of reaction rate α_t on $1/t$: (a) mixing under normal conditions, 20°C(KOH); (b) microwave processing, 95°C; and (c) autoclaving, 220°C.

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