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BRIEF COMMUNICATIONS

Kinetics of the Carnallite Synthesis

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Abstract— The kinetics of the carnallite synthesis from crystalline KCl and a $MgCl_2$ solution at temperatures from 20 up to 100°C was studied. The temperature dependence of the conversion degree was determined. The activation energy and the rate constant of the carnallite synthesis in the temperature range of 30–60°C were determined.

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Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) is used as a raw material for the electrolytic production of magnesium [1]. It is synthesized from natural and anthropogenic magnesium chloride raw material by the reaction

$$KCl_{solid} + MgCl_{2soln} + nH_2O = KCl \cdot MgCl_2 \cdot 6H_2O_{solid} + (n - 6)H_2O.$$

The limiting stage of the process is the KCl dissolution in a concentrated solution with the composition point located in the crystallization field of the system K^+, Mg^{2+} Q% Cl^- – H_2O.

It is known [2] that the duration of particles dissolution increases as their size increases, whereas the dissolution rate and KCl solubility decrease as the $MgCl_2$ concentration increases. In its 35.5% solution the solubility of KCl at 80°C is 1.8%.

Dissolved KCl reacts with excess $MgCl_2$ with a partial carnallite formation on a surface of KCl crystals, which hinders the further KCl dissolution. Intensive stirring results in the destruction of the carnallite layer, which has formed on the surface of KCl crystals [2].

EXPERIMENTAL

To study the kinetics of the carnallite synthesis, we used a solution of natural bischofite of the composition (wt %): K^+ 0.13, Mg^{2+} 6.76, Ca^{2+} 0.1, Na^+ 0.42, Cl^- 19.73, SO_4^{2-} 1.04, and H_2O 71.82 and also recrystallized potassium chloride. We prepared a saturated solution from pure-grade KCl, which was slowly dried in natural conditions to form large crystals. They were separated, crushed, and the fractions of size –0.5 and 0.2–0.315 mm were sifted out. A solution of natural bischofite was preliminarily desulfated by a 25% $CaCl_2$ solution, the precipitate of calcium sulfate was filtrated, and the resulting solution was evaporated and filtrated.

A solution of the composition (wt %): K^+ 0.16, Mg^{2+} 7.75 ($MgCl_2$ 30.35 %), Cl^- 22.82, and H_2O 69.27 was obtained. Its density was 1290 g dm^{-3}. The process of carnallite synthesis was studied under isothermal conditions at temperatures from 20 up to 100°C with permanent stirring in a laboratory two-wall glass temperature-controlled reactor with a stirrer. We filled 250 ml of the solution in the reactor, heated it up to a required temperature, and added 100 g of crystalline KCl at permanent stirring. Samples of the suspension were taken in 10, 20, 30, 45, 60, and 90 min, and filtered through a paper filter in vacuum on a Buchner funnel. The contents of K^+ and Na^+ in the resulting solid phases and solutions were determined by the flame-photometric method, those of Mg^{2+} and Ca^{2+}, by the chelatometric, and of Cl^-, by the mercurymetric methods. Material balances and mineral compositions of the obtained solid phases were calculated on a PC by the results of the analyses.

The degree of KCl conversion in carnallite α (%) was calculated by the formula

$$\alpha = \frac{m_{pr} c_{carn} M_{KCl}}{M_{carn} m_{KCl}}, \quad (1)$$

Here m_{pr} and m_{KCl} are weights of a precipitate and KCl added in the reactor, respectively, (c_{carn} is a calculated carnallite content in a precipitate (%); M_{KCl} and M_{carn}, molecular weights of KCl and carnallite, respectively.

The data obtained are given in Fig. 1, which shows that the highest conversion degree of 40.4% for the –0.5 mm KCl fraction and of 13.90% for the 0.2–0.315 mm KCl fraction is reached at 60°C. As temperature increases up to 80°C, the conversion degree is reduced and above 90°C it slightly increases. It can be explained by the facts that at temperatures higher than 90°C carnallite is coordinated with two molecules of water of crystallization ($KCl \cdot MgCl_2 \cdot 2H_2O$) [1] and that it has different thermodynamic properties being another reaction product. The obtained experimental data were treated by the known Shchukarev's rate equation of dissolution [3].

$$d_c/d\tau = kS(c_s - c), \quad (2)$$

Here k is a dissolution rate constant, c_s, saturation concentration, c, current concentration of a solute, τ, time of dissolution, and S, surface area of a dissolving crystal.

After integration under conditions of a constant volume of a solution and a known surface area S of dissolution equation (2) takes form (3).

$$\ln\frac{c_s}{c_s - c} = kS\tau. \quad (3)$$

To examine the experimental data, the information on the variation of the solid phase surface area during dissolution is necessary. In the calculations we accepted that the solid phase with the cubic shape of crystals [4] is monodispersed and has the edge size of 0.257 mm. A total initial dissolution surface area S_n was found by summing up surface areas of separate crystals, determining their quantity from an initial weight of a potassium chloride sample and a weight of one crystal. Furthermore we accepted that during the dissolution the solid phase surface area S decreases directly proportional to the conversion degree [3]

$$S = S_n(1 - \alpha). \quad (4)$$

Here S_n is the initial surface area of dissolution.

The surface areas calculated by equation (4) and the rate constants of dissolution calculated by equation (3) are given in the table. The variation of the value $\frac{\ln[c_s/(c_s - c)]}{S}$

Surface areas S calculated by equation (4) and dissolution rate constants k calculated by equation (3). Starting conditions: V_{soln} = 250 ml, KCl fraction 0.2–0.315 mm, S_n(KCl) =11.645 m^2 kg^{-1}

T, °C	τ, min	α, %	S, m^2 kg^{-1}	K, kg m^2 s^{-1}
20	45	0.2	11.62	0.486
	60	0.3	11.61	0.473
	90	0.4	11.60	0.478
Average				0.479
30	45	2.7	11.33	0.383
	60	3.2	11.27	0.385
	90	3.4	11.25	0.386
Average				0.384
40	45	3.6	11.23	0.617
	60	3.8	11.20	0.618
	90	4.0	11.18	0.662
Average				0.627
50	45	2.7	11.33	1.021
	60	3.8	11.20	0.744
	90	4.6	11.11	0.520
Average				0.710
60	45	12.4	10.20	2.435
	60	13.2	10.11	1.842
	90	13.9	10.03	1.238
Average				1.838
70	45	2.3	11.38	1.980
	60	2.6	11.34	1.418
	90	2.9	11.31	1.535
Average				1.644
80	45	0.9	11.54	1.315
	60	1.2	11.51	1.374
	90	1.3	11.49	1.216
Average				1.312
90	45	0.8	11.55	1.210
	60	1.1	11.52	1.213
	90	1.3	11.49	1.358
Average				1.462

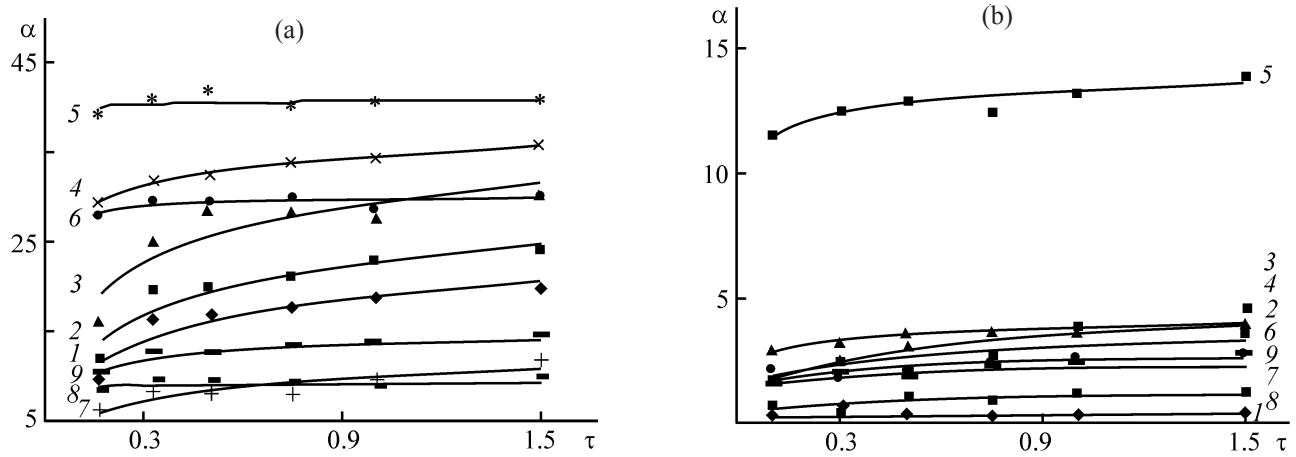

Fig. 1. Dependence of the degree of potassium chloride conversion α (%) on the process duration τ (h). Temperature (°C): (*1*) 20, (*2*) 30, (*3*) 40, (*4*) 50, (*5*) 60, (*6*) 70, (*7*) 80, (*8*) 90, (*9*) 100; the same for Fig. 2. Fraction (mm): (a) –0.5, (b) 0.2–0.315.

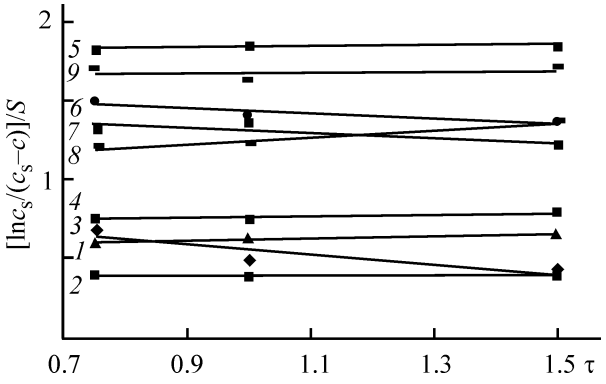

Fig. 2. Variation of the value $\frac{\ln[c_s/(c_s-c)]}{S}$ in a time τ (h).

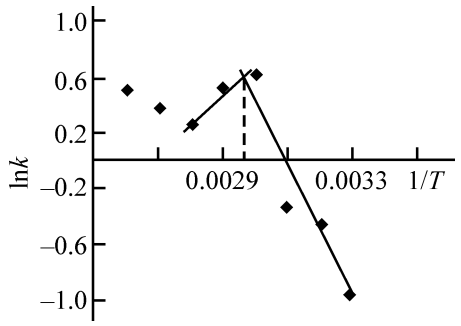

Fig. 3. Dependence of $\ln k - 1/T$ for the conversion of crystalline potassium chloride and $MgCl_2$ solution in carnallite on $1/T$.

in time is shown in Fig. 2. The linear character of this dependence, as it is known, points to the diffusion nature of the conversion process. The dissolution of KCl in water is also of the diffusion nature [5]. It is the slowest stage and thus defines the character of the conversion process as a whole.

The temperature dependence of the conversion rate constant is described by the Arrhenius equation [6], which has the logarithmic form (5)

$$\ln k = -E_a/RT + \ln A \quad (5)$$

or

$$E_x = 2.303R\,\frac{\log k_2 - \log k_1}{\frac{1}{T_1} - \frac{1}{T_2}}. \quad (6)$$

The temperature dependence of the conversion rate constant in the coordinates $\ln k - 1/T$ is presented in Fig. 3.

It is seen from Fig. 3 that the dependence of $\ln k$ on $1/T$ is described by a broken line with an inflection at 67°C.

Substitution of the calculated k values into equation (6) gives the activation energy of 43.29 kJ mol^{-1} for the temperatures range of 30–60°C that points to the diffusion field of passing the process [7]. The maximal value of the rate constant of the conversion process determined graphically (Fig. 3) is reached at 67°C.

CONCLUSIONS

1. The highest degree of conversion of crystalline potassium chloride and a magnesium chloride solution within the limits of temperatures 20–100°C is reached at 60°C.

2. The activation energy of process of the carnallite synthesis in the temperature range 30–60°C is 43.29 kJ mol^{-1} that points to the diffusion field of passing

the process. The optimal temperature of the process determined graphically is 67°C.

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