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KINETICS OF LANGBEINITE CONVERSION INTO SCHENITE IN THE PRESENCE OF MIRABILITE, SYLVINE AND WATER

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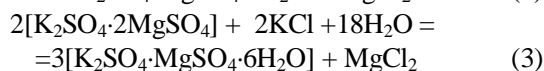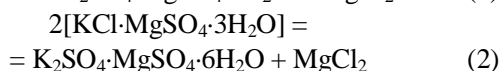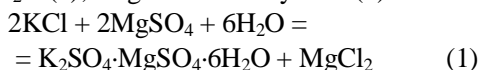*[2]State Enterprise "Scientific-Research Gallurgi Institute"*
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Abstract. The conversion of langbeinite into schenite has been investigated under isothermal conditions within 273–333 K in the presence of mirabilite, sylvine and water. The reaction rate has been determined at various temperatures and "apparent" activation energy has been examined within 293–303 K. The reaction order by langbeinite has been determined as well.

Keywords: langbeinite, conversion, schenite, sodium sulfate, reaction rate, activation energy.
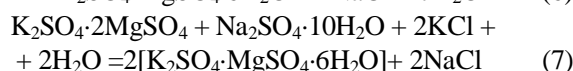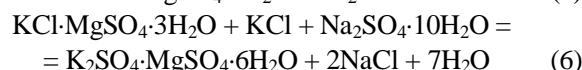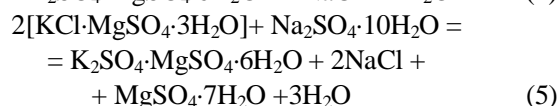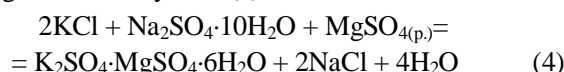
1. Introduction

The polymineral potassium-magnesium ores processing is accompanied by dilution of chloride, chloride-sulfate potassium and potassium-magnesium minerals, as well as by schenite crystallization ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$). As a result, the following reactions proceed with the participation of sylvine KCl (1); kainite $KCl \cdot MgSO_4 \cdot 3H_2O$ (2); langbeinite and sylvine (3):

$$2KCl + 2MgSO_4 + 6H_2O =$$
$$= K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + MgCl_2 \qquad (1)$$
$$2[KCl \cdot MgSO_4 \cdot 3H_2O] =$$
$$= K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + MgCl_2 \qquad (2)$$
$$2[K_2SO_4 \cdot 2MgSO_4] + 2KCl + 18H_2O =$$
$$= 3[K_2SO_4 \cdot MgSO_4 \cdot 6H_2O] + MgCl_2 \qquad (3)$$

Magnesium chloride is formed and directed for step evaporation in the form of excess schenite solution to reduce the losses of valuable components [1]. Thus the capital outlays and energy consumption increase and cost efficiency decreases.

To avoid the formation of magnesium chloride is possible by contacting the initial feedstock with chloride potassium (sylvine) and potassium-magnesium (kainite, carnalite $KCl \cdot MgCl_2 \cdot 6H_2O$) minerals with sodium sulfate or it's minerals (mirabilite $Na_2SO_4 \cdot 10H_2O$, tenardite Na_2SO_4 or vanthoffite $3Na_2SO_4 \cdot MgSO_4$). As a result potassium-magnesium sulfates and sodium chlorides are formed according to the reactions (4-7) with the participation of sylvine (4); kainite (5); kainite and sylvine (6); langbeinite and sylvine (7):

$$2KCl + Na_2SO_4 \cdot 10H_2O + MgSO_{4(p.)} =$$
$$= K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + 2NaCl + 4H_2O \qquad (4)$$
$$2[KCl \cdot MgSO_4 \cdot 3H_2O] + Na_2SO_4 \cdot 10H_2O =$$
$$= K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + 2NaCl +$$
$$+ MgSO_4 \cdot 7H_2O + 3H_2O \qquad (5)$$
$$KCl \cdot MgSO_4 \cdot 3H_2O + KCl + Na_2SO_4 \cdot 10H_2O =$$
$$= K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + 2NaCl + 7H_2O \qquad (6)$$
$$K_2SO_4 \cdot 2MgSO_4 + Na_2SO_4 \cdot 10H_2O + 2KCl +$$
$$+ 2H_2O = 2[K_2SO_4 \cdot MgSO_4 \cdot 6H_2O] + 2NaCl \qquad (7)$$

Schenite is formed in the presence of sodium sulfate without magnesium chloride formation.

It is known [2] that in the presence of water or salt solutions sparingly soluble langbeinite is hydrated into easily soluble schenite. One can see from above-mentioned reactions that crystal water of sodium sulfate minerals participates in the langbeinite hydration into schenite. Converted polymineral potassium-magnesium ore contains only schenite and halite if the sylvine content is sufficient. Impurities of other minerals with sodium sulfate are absent in it [3].

All above-mentioned facts were the main principles underlying the development of technological process. The initial raw material after conversion is directed for dilution in a heated recycle schenite solution, where schenite is dissolved. The saturated solution is separated from non-soluble halite and clay impurities. Then it is cooled for schenite crystallization. The latter one is filtered, dried and the potassium-magnesium is obtained or schenite is decomposed for potassium sulfate. The solution is

recycled for dilution of the initial raw material converted with sodium sulfate. The magnesium chloride concentration in the solution is sustained constant by addition of sodium sulfate. As a result, there is no necessity to evaporate schenite solution and the processing technology becomes simpler. Insoluble halite and clay sludge are directed to fill waste excavations. Easily soluble potassium and potassium-magnesium minerals quickly and completely react with sodium sulfate. Langbeinite, the amount of which in the ore achieves 30 %, slowly converts due to its low dilution rate. Therefore we studied the conversion of pure natural langbeinite mixed with sodium sulfate, potassium chloride and water.

2. Experimental

The samples of natural langbeinite from Dombrovsk open-pit (Kalush-Golyn mineral deposit) were taken for the investigations. The samples were grinded to the size of 5 mm, then the fraction of 3–5 mm was sifted and washed by cold water to remove impurities. The residual moisture was removed by 50 % and then by 98 % alcohol followed by drying at 323 K. The chemical composition of the washed and dried mineral is (wt %): K^+ – 18.31, Mg^{2+} – 11.35, Ca^{2+} – 0.11, Na^+ – 0.49, Cl^- – 0.66, SO_4^{2-} – 67.74 and H_2O – 1.35. To recalculate for the mineral composition (wt %): langbeinite is 97.79, halite is 1.17 and polyhalite is 1.13.

The experiments were carried out at the temperatures of 273, 293, 303, 313, 323 and 333 K.

The initial langbeinite and laboratory glassware before the experiments were stored hermetically packed in the air bath at the experimental temperature. For the investigations we mixed 1020.4 g of langbeinite, 352.2 g of decahydrate sodium sulfate and 267.8 ml of distilled water. The mix in a polyethylene pack was placed in a desiccator and in the air bath at the definite temperature. The samples were withdrawn after 1, 2, 3, 5, 7, 10, 15 and 20 days. For this purpose the contents of polyethylene pack was thoroughly mixed and 100g was withdrawn. Then the sample was placed into a double-walled temperature-controlled reactor equipped with a stirrer and filled by 400 ml of distilled water. The dilution was carried out at 293 ± 0.5 K. The samples were withdrawn every 10 and 15 min and filtered using a Buchner funnel fixed on the Bunsen flask into the test tube which was previously weighted. The contents of the test tube were analyzed using well-known methods: methodtetraphenyl-borate weight method (for K^+ ions), flame photometric method (for Na^+ ions), complexometric method (for Mg^{2+} and Ca^{2+} ions), mercurimetry (for Cl^- ions) and weight method (for SO_4^{2-} ions). The blank experiment was also carried out with the initial mixture before the reaction.

3. Results and Discussion

The conversion degree of langbeinite was calculated using the results of liquid phases chemical analysis and Eq. (8):

$$a = \frac{(m_l \cdot C_{Mg^{2+}}) - (m_{l(b)} \cdot C_{Mg^{2+}(b)})}{m_{La} \cdot C_{Mg^{2+}La}} \cdot 100\% \qquad (8)$$

where m_l – weight of liquid phase after dilution, g; $m_{l(b)}$ – weight of liquid phase after dilution in the blank experiment, g; $C_{Mg^{2+}}$ – concentration of Mg^{2+} ions in the sample, %; $C_{Mg^{2+}(b)}$ – concentration of Mg^{2+} ions in the sample of the blank experiment, %; m_{La} – weight of langbeinite in 100 g of the mixture withdrawn for the experiment, g; $C_{Mg^{2+}La}$ – content of Mg^{2+} ions ion the natural langbeinite, %.

The weight of liquid phase after dilution was calculated according to the formula:

$$m_l = \frac{400 + m_{H_2O_{mix}}}{C_{H_2O_l}} \qquad (9)$$

where $m_{H_2O_{mix}}$ – weight of water in 100 g of the mixture withdrawn for dilution, g; $C_{H_2O_l}$ – concentration of water in the sample after dilution, %.

The experimental results are represented in Fig. 1.

The degree of langbeinite conversion with sodium sulfate and potassium chloride into schenite increases all the time but the most intensive increase is observed during first 5 days. The maximum conversion is achieved within the range of 303–323 K. The lowest conversion is obvious at 333 K that is explained by langbeinite stabilization with the temperature growth. The conversion slight increase is observed at 273 K but it is smaller compared with that at 293–323 K. The reason is the low reaction rate with the decrease in temperature. Thus, one can see that that conversion is practically completed after 10 days for the langbeinite particles of 3–5 mm. If we decrease the particles size, we may decrease the process time.

The surface area of investigated samples was determined using a kinetic dilution method of monofractional particles mixture [4] on the assumption of availability of long straight section observed on the dependence of langbeinite dilution degree on the process time. To determine the sample surface area we mixed 6000 cm^3 of distilled water and 50 g of langbeinite in temperature-controlled round-bottom flask equipped with a stirrer at 293 ± 0.5 K. The samples were periodically withdrawn and analyzed by above-mentioned methods.

Recalculating the change of concentration for the change of dissolved langbeinite weight we obtain the dependence $m(t)$ (Fig. 2), similar to $C(t)$.
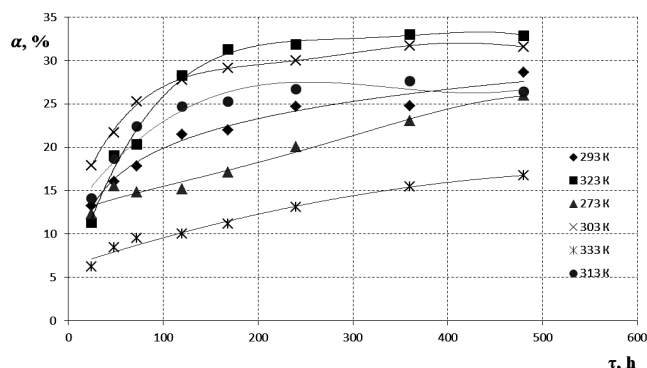
Fig. 1. Degree of langbeinite conversion with sodium sulfate into schenite *vs.* process time at different temperatures
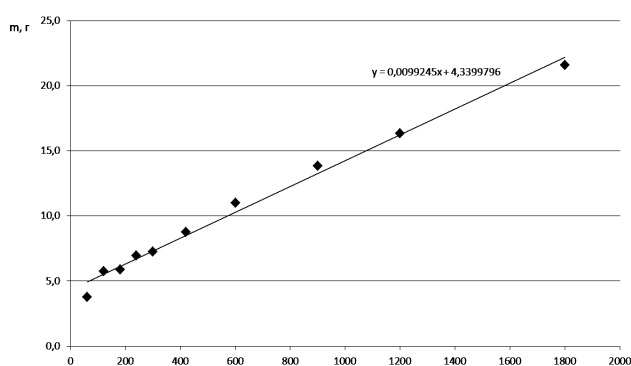

Fig. 2. Weight of dissolved langbeinite *vs.* time

For the section of linear dependence $m(t)$ we obtain:

$$\Delta m = m_1 - m_2 \qquad (10)$$

$$\Delta t = t_1 - t_2 \qquad (11)$$

$$tgb = \frac{\Delta m}{\Delta t} \qquad (12)$$

Taking into account the known rate of langbeinite dilution at 293 K [4] we determine the surface area of the sample (S) according to Eqs. (13-14):

$$n = \frac{\Delta m}{S \cdot \Delta t} \qquad (13)$$

$$F = \frac{\Delta m}{u \cdot \Delta t} = \frac{tgb}{u} \qquad (14)$$

where u– rate of langbeinite dilution calculated by the method of rotating disk [4].

The calculated surface area of langbeinite with the particles size of 3–5 mm is 15.75 cm^2/g or 1.575 m^2/kg.

The conversion rate is calculated according to Eq. (15):

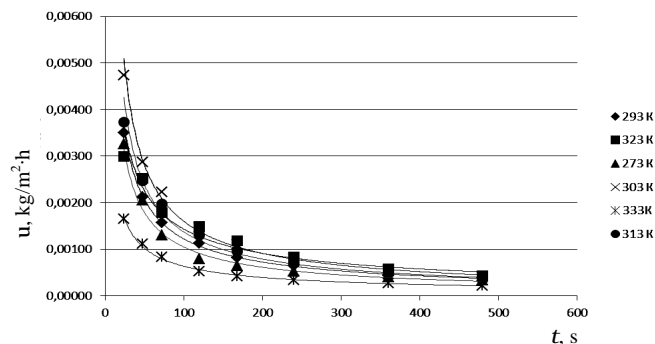$$u = \frac{a \cdot m_{La}}{S \cdot t} \qquad (15)$$

Fig. 3. Langbeinite conversion rate *vs.* process time

where a – langbeinite conversion degree, %; m_{La} – langbeinite weight in 100 g of the mixture for dilution, kg; t – conversion time, h; S – surface area of langbeinite in 100 g of the mixture for dilution, m^2.

The results of calculations are given in Fig. 3.

"Apparent" activation energy is determined according to the Arrhenius equation (16):

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad (16)$$

It is known [5] that ratio (17) is valid for the chemical processes:

$$\frac{k_2}{k_1} \approx \frac{C_2}{C_1} \qquad (17)$$

where C_2 and C_1 – concentrations of the compound at T_2 and T_1, respectively.

The concentration of reacted compound in the liquid phase is changed proportionally to its decomposition degree and conversion rate. Therefore the "apparent" activation energy is calculated according to (18):

$$\ln(u_2 / u_1) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad (18)$$

Then

$$E_a = \frac{R T_1 T_2}{T_2 - T_1} \ln \left(\frac{u_2}{u_1} \right) \qquad (19)$$

where R – gas constant; T_2 and T_1 – process temperature, K; υ_2 and υ_1 –conversion rates at T_2 and T_1, respectively.

"Apparent" activation energy is determined according to Eq. (19) using values of the rate for the first 24 h ($E_{a(in)}$) and average rates for all conversion period ($E_{a(av)}$). The results are represented in Table 1.

"Apparent" activation energy at the temperatures above 303 K has negative values caused by langbeinite stabilization and decrease in its solubility under mentioned conditions.

Table 1

"Apparent" activation energy of langbeinite conversion in the presence of mirabilite, sylvite and water

T, K	$E_{a(in)}$, kJ/mol	$E_{a(av)}$, kJ/mol
273–293	2.362	4.259
293–303	22.229	21.085

The initial value of "apparent" activation energy is 2.36 kJ/mol within the range of 273–293 K and 22.23 kJ/mol – within 293–303 K. The average value for the whole period is 4.26 and 21.08 kJ/mol, respectively. It means the diffusive character of the conversion process and constancy of its character with the increase of the amount of formed products. The reaction products have not essential effect on "apparent" activation energy and process rate. The lowest processes proceeded in the moist mixture are ions moving to the langbeinite surface and

removing the reaction products from it. Hence, we may increase the conversion rate by the extension of reacted particles surface, *i.e.* by the increase of their reduction ratio.

To determine the reaction order [6] by the definite compound it is necessary to create conditions under which the concentration of only this compound would be changed. For this aim the concentrations of other compounds would be so great that the changes in their concentrations may be neglected. Hence, we may introduce these concentrations into the rate constant expression and for Eq. (20) we obtain (21):
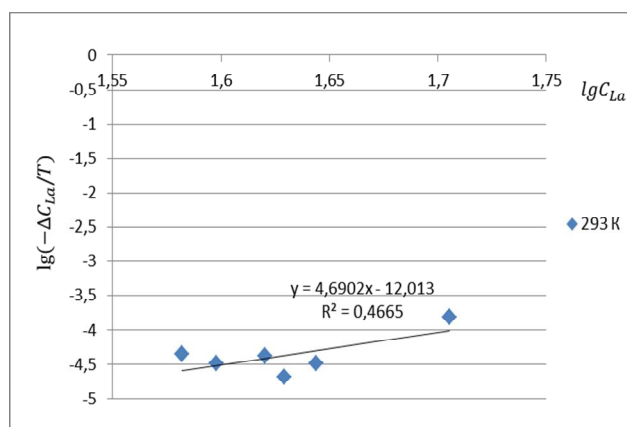
$$aA + bB + cC = dD + eE \qquad (20)$$

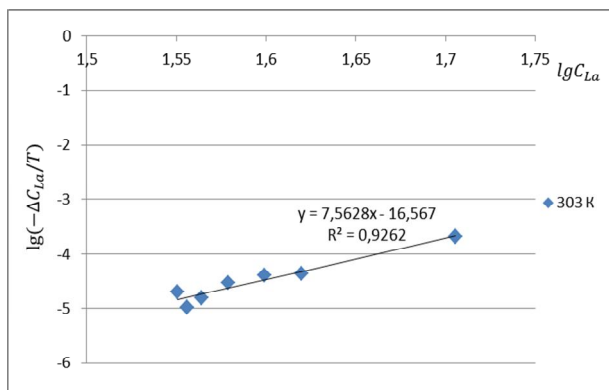$$-\frac{\partial C_A}{\partial t} = k_1 \cdot \Delta C_A^n \qquad (21)$$

where n – the degree of the compound A concentration in the reaction equation determining its order by a given reagent.
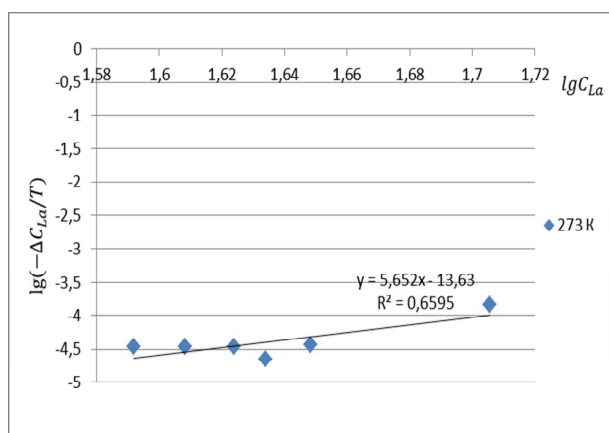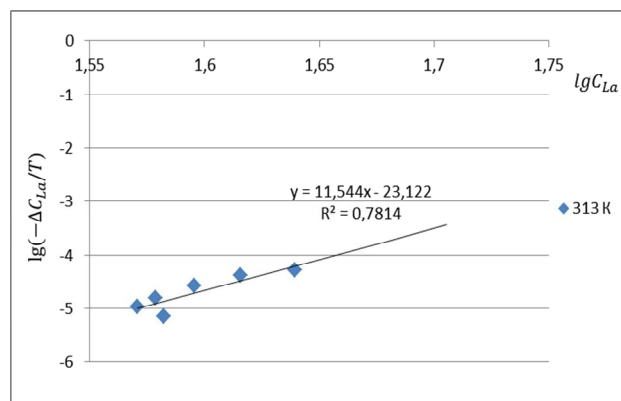

a)

b)

c)

d)

Fig. 4. Dependence of lg ($-\Delta C_{La}/T$) on lgC_{La} at different temperatures (K): 273 (a); 293 (b); 303 (c) and 313 (d)

To establish the reaction order by langbeinite it is necessary to determine the concentration change for time t taking into account that we have two initial values of its concentration and the concentrations of other compounds are very large (to neglect their change for time t). We select stoichiometric amounts of langbeinite, sodium sulfate, and potassium chloride and 50 % of stoichiometric amount of water. But langbeinite is a solid phase and the reaction proceeds in the intercrystalline solution where the amount of dissolved langbeinite is only a small part of its initial weight. Moreover, sodium sulfate and potassium chloride are easy soluble and their consumption for the reaction is quickly replenished due to the crystals dilution. Thus, we actually have constant excess of all reagents except langbeinite which passes slowly into the liquid phase. In other words, during the conversion in the intercrystalline liquid phase there is a great deficiency in a dissolved langbeinite compared with other reagents due to its slow replenishment from the solid phase.

The reaction order may be determined from Fig. 4. If we put $\lg(-\Delta C_{La}/T)$ on the ordinate axis and $\lg C_{La}$ on the abscissa, we get the straight line, slope ratio of which is equal to the reaction order by the given compound.

The reaction order values determined at 273–313 K by means of Fig. 4 are represented in Table 2.

Table 2

Dependence of the conversion reaction order on temperature

T, K	n	Correlation coefficient, r
273	0.21	0.6595
293	0.16	0.4665
303	0.18	0.9262
313	0.22	0.7814

The reaction order of langbeinite conversion in the presence of mirabilite, sylvine and water is within the range of 0.18–0.22 that approaches it to the reaction of zero order. In such a case the reaction rate is determined only by the surface of langbeinite particles and does not depend on the concentration of reagents and reaction products in the bulk of reaction mass.

4. Conclusions

For langbeinite particles with the size of 3–5 mm the conversion is completed during 10 days. "Apparent" activation energy is 2.36 kJ/mol within the range of 273–293 K and 22.23 kJ/mol – within 293–303 K. The average value for all period is 4.26 and 21.08 kJ/mol, respectively. It means the diffusive character of the conversion process and constancy of its character with the increase of the amount of formed products. The reaction products have not essential effect on "apparent" activation energy and process rate. The lowest processes proceeded in the moist mixture are ions moving to the langbeinite surface and removing the reaction products from it. The reaction order of langbeinite conversion in the presence of mirabilite, sylvine and water is within the range of 0.18–0.22 that approaches it to the reaction of zero order. In such a case the reaction rate is determined only by the surface of langbeinite particles and does not depend on the concentration of reagents and reaction products in the bulk of reaction mass.

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КІНЕТИКА КОНВЕРСІЇ ЛАНГБЕЙНІТУ В ШЕНІТ В ПРИСУТНОСТІ МІРАБІЛІТУ, СИЛЬВІНУ ТА ВОДИ

Анотація. *Досліджено конверсію лангбейніту в присутності мірабіліту, сильвіну та води в ізотермічних умовах за температури 273–333 K в шеніт. Визначено швидкість процесу за різної температури, «уявну» енергію активації за температури 293–303 K, а також порядок реакції за лангбейнітом.*

Ключові слова: *лангбейніт, конверсія, шеніт, натрію сульфат, швидкість, енергія активації.*