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KINETICS OF SCHOENITE CRYSTALLIZATION FROM THE SUSPENSION OF SATURATED SOLUTION AND ARTIFICIAL KAINITE

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Abstract. The conversion of kainite and solution saturated after ore dissolving into schoenite has been studied under laboratory conditions within 293–333 K for 1 h. The highest conversion was found to be at 333 K for 1 h. Using Arrhenius equation the "apparent" activation energy was calculated. Its value shows the transition area of the conversion. The cooling and conversion were studied under various values of air mixing intensity. The air consumption was determined to achieve the highest conversion. Kainite conversion into schoenite in the saturated solution at approximately 333 K is followed by cooling *via* air bubbling. This approach allows to produce schoenite by a simple way without special expensive equipment.

Keywords: magnesium chloride solution, schoenite, kainite, bischofite, crystallization, reaction rate.

1. Introduction

Schoenite ($K_2SO4 \cdot MgSO_4 \cdot 6H_2O$) crystallization from a saturated solution of processing polymineral potassium-magnesium ore of chloride-sulfate type is the main operation of the technological process. During its proceeding in the liquid phase the concentration of $MgCl_2$ increases due to the conversion of chloride minerals (KCl sylvite, $KCl \cdot MgSO_4 \cdot 3H_2O$ kainite) into sulfate ones. So, a part of the solution is removed from the process after schoenite extraction. According to the data of halurgy production 43.8 % of potassium, 44.7 % of magnesium and 17.1 % of sulfate (relative to their amount in a processed ore), or 72.1 % of potassium, 155.6 % of magnesium and 45.2 % of sulfates (relative to their amount in final schoenite) are removed together with the mentioned solution. It is obvious that salts regeneration from the excess schoenite solution and their reversion to potash fertilizers production are of great importance. It is the reason that these solutions are sent to be evaporated to extract potash salts. During evaporation under industrial conditions the extraction level into artificial kainite is insufficient. Kainite is a mixture of chloride and sulfate salts and other valuable components, including 17.1 % of potassium, 9.3 % of magnesium and 6.8 % of sulfates. Potassium-magnesium salts have high dispersion and therefore there are difficulties in sediment filtration and significant losses of liquid phase. Additional 11.0 % of potassium and 2.1 % of magnesium are released into artificial carnallite, which is a mixture of chloride salts with impurities of fine gypsum and calcium chloride in the intercrystalline solution, which cannot be used in the fertilizer production. Also, 7.9 % of potassium, 7.0 % of magnesium and 9.8 % of sulfates (relative to their amount in ore) are released into gypsum as a waste product, that has a negative influence on the efficiency of ore processing. Therefore, the transfer of potash salts extracted from the excess schoenite solution into schoenite determines the effectiveness of potash raw material processing technology.

In the current technology the artificial kainite extracted at the evaporation stage is directed to the stage of schoenite crystallization or ore dissolving [1]. Due to the high content of sodium chloride crystals the addition of artificial kainite at the crystallization stage causes additional pollution of final schoenite. Its addition at the stage of ore dissolving results in reduction of the potassium-magnesium minerals dissolution due to the high concentration of magnesium chloride in a liquid phase which is directed together with kainite. Kainite and chloride salts of artificial kainite are distinguished by their particles size, structure and properties of crystals [2]. Therefore, for partial separation of sodium chloride the artificial kainite is directed to hydrocyclone and the resulting thickened suspension of enriched fine kainite – to the crystallization stage of schoenite.

It was also proposed to dissolve the artificial kainite in the schoenite solution separately and to form a

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saturated solution, which would be mixed with a solution from the stage of ore dissolving. But for this purpose additional equipment is required and the total amount of saturated solution increases by 72 % that requires the increase in capacity of schoenite crystallization stage.

There is a known method according to which the natural kainite purified from sodium chloride under industrial conditions is converted into schoenite in the schoenite solution at ambient temperature [3]. Schoenite crystallization is also used for the conversion of langbeinite and kieserite with potassium chloride and natural mirabilite into schoenite [4].

Owing to the insufficient saturation of the solution by sulfate salts and possible insufficient conversion level of kainite into schoenite the resulting sulfate potassium-magnesium fertilizer was of poor quality and contained about 25 % of Cl^- ions [1]. Therefore, the search of effective way of schoenite crystallization using the components of recovered kainite is an urgent task.

2. Experimental

Kainite obtaining and investigations of Schoenite crystallization kinetics using crystalline kainite were carried out at laboratory vacuum evaporating installation and in a temperature-controlled glass reactor with a blade stirrer. The first one consists of three-necked round bottom flask of 2500 cm^3 by volume, mechanical blade stirrer with the electric drive, electroheater, glass coiled refrigerator for vapors, calibrated hotwell, vacuum pump and system of manual control of the vacuum depth, used to maintain the evaporation temperature of ±0.1 K. Temperature-controlled reactor consists of a double-walled glass vessel of 1200 cm^3 by volume with an elliptical bottom and rubber lid, a glass blade stirrer with the electric drive and a thermostat to maintain the temperature ±273.25 K. For the studies with air bubbling we used an air compressor. The air consumption was measured by the gas-meter. The air after gas-meter was passed through a schoenite suspension in a saturated solution for heating to the experimental temperature and saturation with water vapor at this temperature. The vessel with schoenite was installed in another thermostat at the experimental temperature. The investigated suspension was placed in the temperature-controlled reactor or thermos bottle of 2000 cm^3 by volume.

The initial solution was prepared in accordance with the composition of industrial hot saturated solution from the dissolution stage of polymineral potash ore (wt %): 5.16 K^+; 3.68 Mg^{2+}; 3.68 Na^+; 14.70 Cl^-; 8.64 SO_4^{2-}; 64.14 H_2O. For a long term storage 27 % of water (relative to a solution weight) was added. Kainite suspension was settled, decanted and then the fraction of 0.05–0.25 mm was separated using the sieves. The selected suspension was filtered under vacuum, washed at first by 50%, and then by 96% ethanol, and dried under periodic stirring in an air thermostat at 323 K. Kainite with the following composition was obtained (wt %): 14.74 K^+; 8.37 Mg^{2+}; 2.00 Na^+; 14.61 Cl^-; 35.73 SO_4^{2-}; 24.55 H_2O. Kainite mineral composition was calculated and further analyzed using D8 ADVANCE X-ray diffractometer and DRON-3 X-ray analyzer with a copper anode, nickel filter and radiation $Cu_{K\alpha}$-λ of 1.54 Å. Data interpretation was performed using diffraction standards (JCPDS). The content of kainite in the samples was found to be 92.0 %.

For the experiments we took 1 dm^3 of diluted solution, evaporated 286 cm^3 of water which was previously added for the dilution, transferred the evaporated solution (955 g) into the temperature-controlled reactor and added 95.5 g of artificial kainite at the experimental temperature under constant stirring. The samples were periodically taken and filtered under vacuum using heated Schott filter No. 16 fixed on Bunsen funnel. The filtrate trickled in pre-weighed test tube. The resulting liquid and solid phases were analyzed by tetraphenylborate gravimetric analysis to determine K^+ content; volumetric chelatometry – to determine Mg^{2+} and Ca^{2+}; flame photometric analysis – for Na^+; mercurrometry – for $Cl^-$and gravimetry – for SO_4^{2-}. Water content was determined by the difference. Material balances were calculated by PC using a special program.

3. Results and Discussion

The conversion level of kainite into schoenite was calculated by the relative change of chloride ions weight in the sediment, according to Eq. (1):

$$a_K = 1 - \frac{m_s \cdot C^{s}_{Cl^-} m^{0}_{Cl^-}}{m_{Ka} \cdot C^{Ka}_{Cl^-} - m_{Ka} \cdot C^{Ka}_{Na^+} \cdot 1.542} \qquad (1)$$

where m_{Ka} – weight of kainite added to the saturated solution, g; $C^{Ka}_{Cl^-}$ – content of Cl^-in kainite, wt %; m_s – sediment weight after conversion (from material balance), g; $C^{s}_{Cl^-}$ content of Cl^-in the sediment, wt %; $m^{0}_{Cl^-}$ – weight of Cl^- in the sediment of the blank test (schoenite crystallization from the saturated solution without kainite) at the corresponding temperature, g; $C^{Ka}_{Na^+}$ – content of Na^+ ions in kainite, wt %; 1.542 – coefficient for re-calculation of Na^+ content for Cl^-.

The experimental results are represented in Fig. 1.

The highest level of kainite conversion into schoenite in the saturated solution is observed at 333 K. This temperature corresponds to the temperature of industrial clarified saturated solution. Conversion achieves 57.4 % after 600 s and gradually increases to 76.1 % after 3600 s. The decrease in temperature gradually decreases the conversion level. The lowest value is observed at 293 K (14.0 % after 600 s and 42.3 % after 3600 s). Thus, for the technological process it is necessary to add purified from sodium chloride kainite to the clarified hot saturated solutions after ore dissolution, to stir for 3600 s and cool the suspension to crystallize schoenite from the liquid phase.

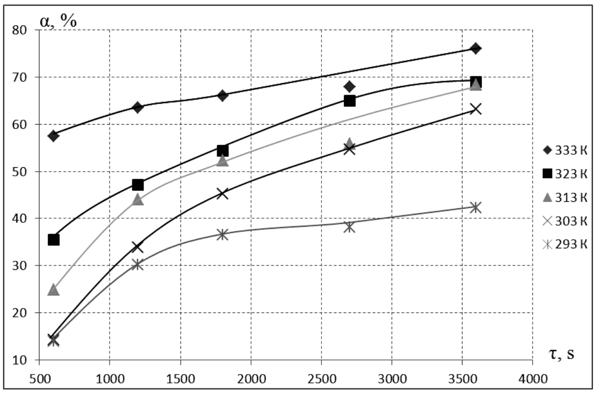

Fig. 1. Conversion level of kainite *vs*. time at different temperatures

The conversion rate was calculated according to Eq. (2):

$$u = \frac{a \cdot m_{Ka}}{S \cdot t} \tag{2}$$

where α – level of kainite conversion into schoenite, %; m_{Ka} – kainite weight in the sample, $m_{Ka} = 95.5 \cdot 0.92 = 87.86$ g; S – surface area of the sample of 87.86 g by weight, g/m^2; τ – conversion time, during which the accepted value of conversion level is achieved, h.

Kainite crystals have a lamellar and thick-pellet structure [2]. The size of kainite crystals is within 0.05–0.25 mm; we accept the mean value of 0.15 mm. To determine the surface and weight of the crystal with 17 different faces, it is difficult to divide the crystal into separate geometric figures. Therefore we prepared the 1000 increased model of the average crystal according to the known habitus of kainite thick-pellet crystal. Using the model we measured the surface area of the faces. The crystal volume was determined by immersing the sample in the measuring vessel filled by water. The crystal surface was found to be 1.741 mm^2, and weight – $62.416 \cdot 10^{-10}$ kg. So, the sample loaded in the reactor contained $1.40765 \cdot 10^7$ crystals of average size with a surface area of $2.45037 \cdot 10^7$ mm^2. The dependence of the conversion rate on temperature during the first 600 s is shown in Fig. 2. The conversion rate increases from 0.0415 kg/m^2·h at 293 K to 0.170 kg/m^2·h at 333 K.

"Apparent" activation energy was determined according to Arrhenius equation (Eq. (3)):

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3}$$

It is known that for the chemical processes Eq. (4) is valid:

$$\frac{k_2}{k_1} \approx \frac{C_2}{C_1} \tag{4}$$

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

The concentration of the reactive compound is proportional to the conversion rate. Therefore "apparent" activation energy is determined according to Eq. (5):

$$\ln(u_2 / u_1) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5}$$

Hence

$$E_a = \frac{RT_1T_2}{T_2 - T_1}\ln(u_2 / u_1) \tag{6}$$

where R – gas constant; T_2 and T_1 – final and initial conversion temperatures, respectively, K; υ_1 and υ_2 – conversion rate at the temperatures T_2 and T_1, respectively.

The value of "apparent" activation energy was determined according to Eq. (6), using the value of reaction rate during 600 s. The average value of activation energy within 303–333 K was found to be 38.8 kJ/mol indicating the transition area of the conversion. In the moist mixture the ions transition to the crystal surface and removal of the reaction products from it are the slowest processes. So, they are significantly affected by intensity of mixing.

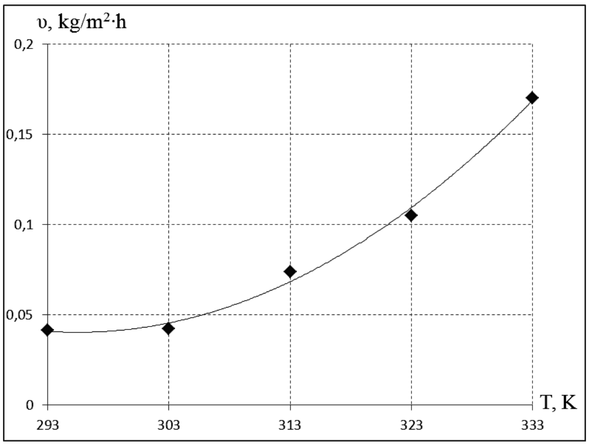

Fig. 2. Conversion rate *vs*. temperature for the first 600 s

In known technologies of schoenite crystallization with a saturated solution the multiple-effect vacuum crystallization units (WCU) are used. In summer they provide the temperature of 308 K; deeper cooling is achieved in surface water crystallizers or by condensation of water vapor in surface heat exchangers after WCU using cooled to 278–280 K water. To manufacture these apparatuses precious heavy plate metals are used. WCU and heat exchangers are often clogged up by salts and require periodic stops to be rinsed. Mechanical mixing and frequent pumping of the suspension lead to the crushing of schoenite crystals.

Therefore, the suspension mixing with air and its simultaneous cooling is of great interest. Owing to the air temperature and water vapor unsaturation the suspension is cooled and partially dried. It is accompanied by heat removal and additional cooling. Air bubbles do not break the salt crystals.

For the experiments we took 2.0 dm^3 of diluted solution, evaporated 572 cm^3 of previously added for the dilution water and transferred the evaporated solution to a thermos with bubbler. Then 191 g of kainite was added at 343 K under constant mixing by air. The intensity of air supply was 773 m^3/h·t per 1 ton of suspension. Experiments were carried out at different temperatures and air humidity. The results are shown in Fig. 3.

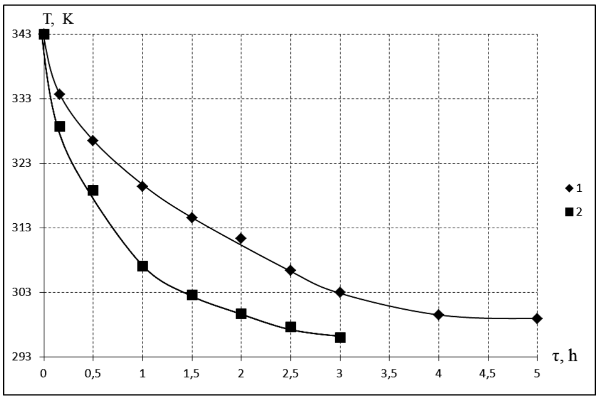

Fig. 3. Suspension temperature *vs.* bubbling time: air temperature 297 Kand humidity 65 % (1); air temperature 283 K and humidity 88 % (2)

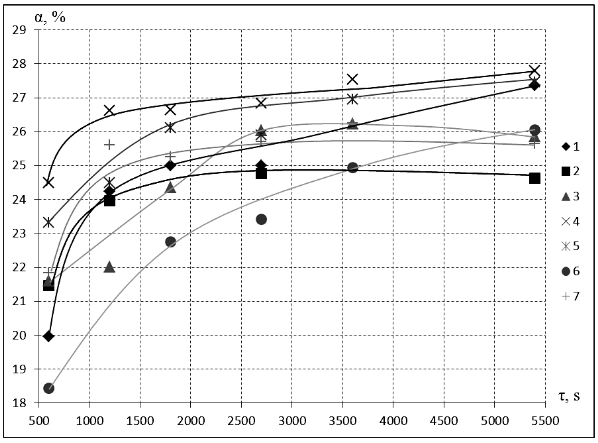

Fig. 4. Level of SO$_4^{2-}$ recovery from the solution and kainite into schoenite *vs.* process time under different intensity of air mixing (m^3/t·h): 111.4 (1); 188.5 (2); 317.0 (3); 451.2 (4); 542.6 (5) and 919.6 (6)

So, mixing with air at 297 K and relative humidity of 65 % allows to cool the suspension from 343 to 311 K for 2 h and to 298.85 K for 5 h. Air mixing at 283 K and relative humidity of 88 % reduces the suspension temperature from 343 to 307 K for 1 h, to 299.65 K – for 2 h and to 296 K – for 3 h. Thus, air mixing at the stage of schoenite conversion and crystallization allows to reach the final temperature of crystallization (especially quickly during the cold season) without expensive vacuum equipment and water for cooling and vapor condensation.

Since schoenite conversion and crystallization processes are in the transition area, we investigated the effect of air mixing intensity on them.

The suspension of saturated solution and kainite was prepared similarly to the previous experiments. The experimental temperature was 303 K. Air with the definite flow rate was passed through suspension layer at the experimental temperature. The suspension was thermostated in another thermostat. 955 g of saturated solution and 95.5 g of kainite were loaded into a reactor with bubbler at the experimental temperature and air supply was turned on. The samples were periodically withdrawn, filtered and liquid and solid phases were analyzed. The level of SO$_4^{2-}$ recovery from the solution and kainite to schoenite was calculated according to Eq. (7):

$$a_{SO_4^{2-}} = \frac{m_{Sh} \cdot C^{Sh}_{SO_4^{2-}}}{m_{Ka} \cdot C^{Ka}_{SO_4^{2-}} + m_{sol} \cdot C^{sol}_{SO_4^{2-}}} \qquad (7)$$

where m_{Sh} – schoenite weight after conversion (taken from a material balance), g; $C^{Sh}_{SO_4^{2-}}$ content in schoenite, wt %; m_{Ka} – weight of kainite added for conversion, g; $C^{Ka}_{SO_4^{2-}}$ – content in kainite, wt %; m_{sol} – weight of saturated solution for conversion, g; $C^{sol}_{SO_4^{2-}}$ – content in saturated solution, wt %.

The obtained results are represented in Figs. 4 and 5.

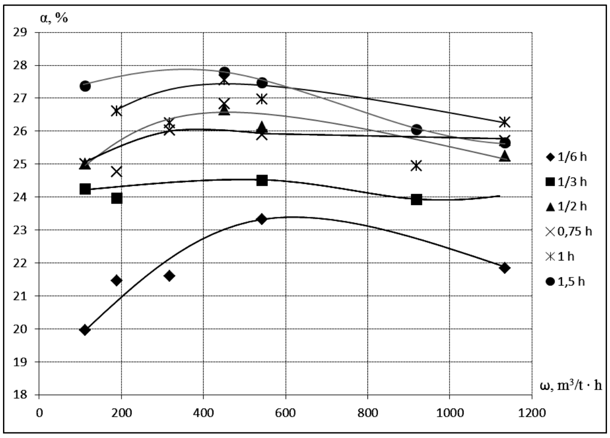

Fig. 5. Level of SO$_4^{2-}$ recovery from the solution and kainite into schoenite *vs.* intensity of air mixing

4. Conclusions

The highest degree of kainite conversion into schoenite in the saturated solution is achieved at 333 К and reaction time of 1 h. By using the Arrhenius equation the “apparent” activation energy was calculated. Its value of 38.8 kJ/mol indicates the transition area of the conversion process. Kainite conversion in the saturated solution into schoenite at approximately 333 К and cooling by bubbling air allow to realize schoenite conversion and crystallization in a simple industrial process without special equipment and expensive construction materials.

References

[1] Hrebenyuk D., YaremchukB.: Khim. Prom.Ukrainy, 1992, **2**, 41.
[2] Lazarenko E., Habinet M., Slyvko O.: Mineralogiya Osadochnykh Utvoren Prykarpattia. Lviv1962.
[3] Sokolov I. (Ed.): Pererabotka Prirodnykh Soleii Rastvorov. Khimiya, Leningrad 1986.
[4] Artus M., Kostiv I.: Chem. Chem. Technol., 2014, **8**, 455.
[5] Brdicka R.: Grundlagen der physikalischenChemie. 10 Auflage. VEB deutscherVerlag der Wissenschaften, Berlin 1971.

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КІНЕТИКА КРИСТАЛІЗАЦІЇ ШЕНІТУ ІЗ СУСПЕНЗІЇ НАСИЧЕНОГО РОЗЧИНУ І ШТУЧНОГО КАЇНІТУ

Анотація. *У лабораторних умовах досліджений процес конверсії каїніту і насиченого після розчинення руди розчину в шеніт за температури 293–333 К протягом 1 год. Встановлено, що найбільший ступінь конверсії досягається за температури 333 К і тривалості 1 год. За допомогою рівняння Арреніуса розрахована «уявна» енергія активації, яка дорівнює 38,8 кДж/моль і вказує на перехідну область перебігу процесу конверсії. Досліджено процес охолодження і конверсії за різної інтенсивності перемішування повітрям. Визначено витрату повітря для досягнення найбільшого ступеня конверсії. Показано, що конверсія каїніту у насиченому розчині в шеніт за температури близько 333 К і наступне охолодження барботуванням повітря дає змогу отримати шеніт у простому технологічному процесі без застосування спеціального обладнання із дорогих конструкційних матеріалів.*

Ключові слова: *магнійхлоридний розчин, шеніт, каїніт, бішофіт, кристалізація, швидкість реакції.*