

# Crystallization of Kainite from Processing Solutions of Polymineral Saline Raw Material Marine Type

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## Abstract

This paper presents the results of laboratory researches evaporation processing solutions polymineral salt material that contain sulfates and chlorides of potassium, magnesium and halite. Determined degree of evaporation and temperature of the suspension in which achieved the highest level of separation ions of potassium and sulfate in the solid phase, and the solid phase-the highest content kainite and the lowest-sylvine and carnalite. The lowest content (2.6-5.7%) of carnalite in suspension achieved at temperature of 313-333 K and the degree of evaporation 19.2-26.5%. Cooling of the suspension with the degree of evaporation of 30.1% is not necessary, because it leads to increased degree of separation in the solid phase of carnalite. Regulate the depth of evaporation and cooling can be by concentrate on in the liquid phase of equivalents  $MgSO_4$  (0.016-0.032),  $MgCl_2$  (0.248-0.289), and the ratio between them (0.0579-0.125).

**Keywords:** Solution chloride-sulfates potassium-magnesium; Evaporation; Crystallization; Kainite; Carnalite; Sylvine

## Introduction

Processing of polymineral potassium-magnesium ore chloride-sulfate type accompanied by reactions conversion of chloride minerals of kainite ( $KCl \cdot MgSO_4 \cdot 3H_2O$ ), sylvine (KCl) in schoenite ( $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ ), during which crystallization in the liquid phase increases the concentration of  $MgCl_2$ . Therefore, for the purpose of regulation part of the solution after separation schoenite derive from the process. With this solution according to potash production thrown out 43.8% of potassium, 44.7%-magnesium and 17.1% of sulfate of their number of processed ore. It is obvious importance of extraction of salt from schoenite solution and returning them to the production of potassium fertilizers. Because these solutions are sent to the phasic evaporation to highlight potassium salt. During evaporation in the industrial conditions is achieved insufficient degree of solid phase extraction of valuable components, including 17.1% potassium, 9.3% magnesium and sulfate and 6.8% of their number in the ore, high dispersion of salts and as a consequence difficulty filtering sediment, and significant loss of liquid phase. Because of insufficient saturation of liquid phases by sulfate salts sulfate potassium-magnesium fertilizer getting low quality with content up to 25% chloride ions. Therefore, the degree of extraction in the solid phase of mineral components excess schoenite solution and their next conversion into schoenite determines the efficiency of processing technology of potash raw materials in general. During the evaporation is crystallized kainite in mixture with NaCl, KCl and other minerals. Kainite and chloride salts differ in their granulometric composition, structure and properties of crystals. The biggest size of crystals kainite is achieved at temperatures 363-368 K [1]. On the size of the crystals kainite significantly affects the depth of evaporation. What makes it more, the more substance for crystal growth is separate from the liquid phase [2]. But thus increases the density of the suspension and evaporation complicated. To decrease density of the suspension part of evaporated solution return to mixing with the initial. This increases the concentration of  $Mg^{2+}$  in the liquid phase and after achievement of 8.2% of its value crystallization of kainite stops, and in the liquid phase increases the concentration of  $SO_4^{2-}$  [3].

Evaporation of the solution after crystallization of kainite at

temperatures 388-403 K makes it possible to separate sulfate ions in the form of finely dispersed kieserite, suspension cooled to a temperature of 303 K in the solid phase crystallized bischofite. Separating of suspension leads to the formation of two layers of sediment: top-finely dispersed sulfate salts and bottom-bischofite. By decanting separate the top layer of sediment and together with liquid phase return to the stage crystallization of kainite. The bottom layer of sediment is filtered on a centrifuge, separating the crystalline bischofite as a commodity product, and the filtrate was returned to the stage crystallization of kainite [4]. Thus from excess solution of schoenite can be almost completely back of sulfate ions in the production of potash fertilizers.

During the cooling of evaporated suspension begins to crystallize carnalite, kainite dissolved in this case [3]. Therefore it was necessary to determine the limit depth of evaporation of solution and temperature of cooling of evaporated suspension for the achievement the greatest degree of extraction in the solid phase kainite and minimum of carnalite because crystallization of carnalite is accompanied by the dissolution of kainite, and the return to production of potassium fertilizers of solid phase which containing  $MgCl_2$ .

## Experimental Section

Research of processes of evaporation solution and crystallization kainite was carried out on a laboratory vacuum evaporating installation and in reactor with paddle mixer. The first included three throat round bottom flask with a capacity of 2500 cm<sup>3</sup>, mechanical paddle mixer with electric meter and electric heater, glass refrigerator of vapors, calibrated collection of condensate, vacuum pump and system manually adjust

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the depth of vacuum, by which the temperature of evaporation supported with precision of  $\pm 0.5$  K. Reactor includes a rubber cover closed double-walled glass vessel with a capacity of 1200 cm<sup>3</sup> elliptical bottom and glass paddle mixer with electric drive. For research use with cooled air compressor UK laboratory 25-1.6 M (SU), consumption of air meter measured the gas and air after the compressor was passed through heat exchanger with cooling water. Research suspension was poured into the reactor or a glass round bottom flask.

The initial solution was prepared in accordance with the composition of industrial hot saturated solution from the stage of evaporation and crystallization of kainite composition by wt.%: 5.50 K<sup>+</sup>; 4.39 Mg<sup>2+</sup>; 2.69 Na<sup>+</sup>; 16.74 Cl<sup>-</sup>; 7.03 SO<sub>4</sub><sup>2-</sup>; 63.65 H<sub>2</sub>O [5]. In this solution to avert crystallization of during long storage and added 30% water on its mass. Its before each experiment evaporated. Prepared also for mixing with the initial solution kainite solution by evaporation of industrial solution. Its composition (wt.%): 1.46 K<sup>+</sup>; 6.59 Mg<sup>2+</sup>; 0.56 Na<sup>+</sup>; 19.73 Cl<sup>-</sup>; 2.28 SO<sub>4</sub><sup>2-</sup>; 69.38 H<sub>2</sub>O. For one experiment in the flask to evaporate prepare 1917.5 grams of evaporated initial solution and added 822.4 g kainite solution. The composition of the mixed solution (wt.%): 4.28 K<sup>+</sup>; 5.05 Mg<sup>2+</sup>; 2.05 Na<sup>+</sup>; 17.64 Cl<sup>-</sup>; 5.60 SO<sub>4</sub><sup>2-</sup>; 65.38 H<sub>2</sub>O, or equivalent indices X=E SO<sub>4</sub><sup>2-</sup>: (E K<sup>+</sup>+E Mg<sup>2+</sup>); X=0.2221; Y=E Mg<sup>2+</sup>: (E K<sup>+</sup>+E Mg<sup>2+</sup>); Y=0.7915. The ratio of X:(Y-X)=E MgSO<sub>4</sub>:E MgCl<sub>2</sub> was 0.390. Evaporation was carried out under vacuum at a temperature of 353  $\pm$  0.5 K for obtaining kainite without impurities langbeinite. The degree of evaporation was determined as ratio of the mass evaporated water to the initial mass of the mixed solution.

From mixed solution was evaporated determined quantities of water to achieve a given degree within the limits 15.5-30.1% transferred evaporated suspension in a thermostatic reactor and through the bubbler turn on the flow air. 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<sup>+</sup> content; volumetric chelatometry to determine Mg<sup>2+</sup> and Ca<sup>2+</sup>; flame photometric analysis-for Na<sup>+</sup>; mercurrometry-for Cl<sup>-</sup> and gravimetry-for SO<sub>4</sub><sup>2-</sup>. Water content was determined by the difference. The material balance of the process, from which calculated degree extraction of components in the solid phase, and the contents of basic minerals by chemical composition of solid

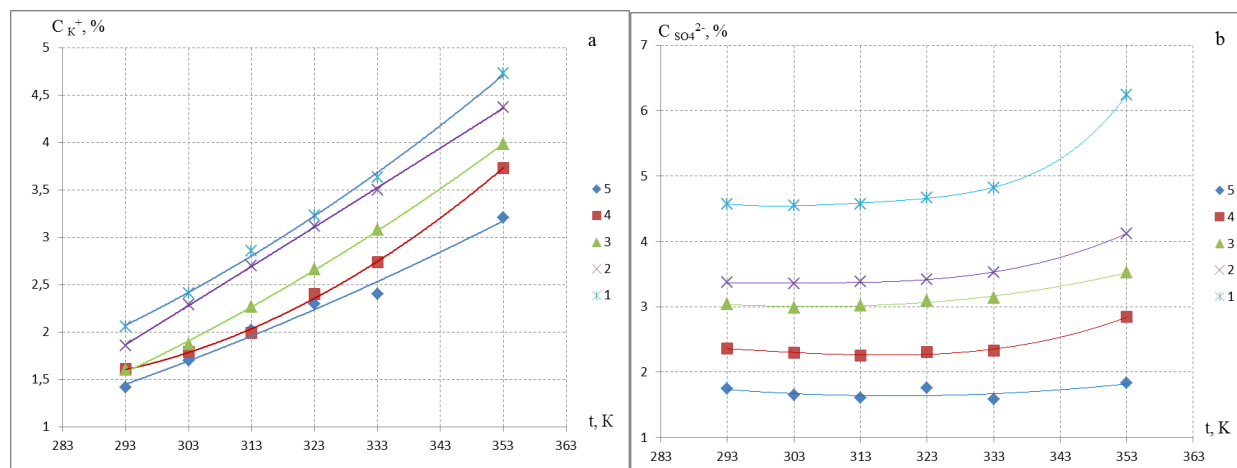
phases: sylvine, kainite, carnalite and halite whose presence determined by X-ray analysis, calculated on a PC with special software.

## Results and Discussion

Figure 1 shows the dependence of concentration of K<sup>+</sup> (a) and SO<sub>4</sub><sup>2-</sup>(b) in the liquid phase of the temperature during the cooling by air suspension of potassium-magnesium salts, evaporated to varying degrees. As can be seen from Figure 1a, the concentration of K<sup>+</sup> ions in the liquid phase of evaporated suspension at a temperature of 353 K decreases with increasing degree of evaporation. So for the degree of evaporation of 15.5%, it is 4.73% and decreased to 3.21% for the degree of evaporation of 30.1%. During the cooling by air K<sup>+</sup> concentration gradually decreases for all stages of evaporation and achieves the smallest values for temperature 293 K. The lowest concentration of K<sup>+</sup> is equal to 1.42% at 293 K and the degree of evaporation of a solution of 30.1%. For 19.2% degree of evaporation researched the process of cooling suspension evaporated through the wall of the reactor water. The obtained results are shown in Figure (red curve). As seen from obtained data that K<sup>+</sup> concentration in the liquid phase of suspension during the cooling by air slightly larger than on cooling water. It is explained by the partial drying by air of solution.

From Figure 1a shows that SO<sub>4</sub><sup>2-</sup> concentration in the liquid phase of evaporated suspension decreases with increasing degree of evaporation. So for his value to 15.5% is equal 6.24% and with an increase to 30.1% decreases to 1.83%. During the cooling suspension by air concentration of SO<sub>4</sub><sup>2-</sup> decreases, especially for the degree of evaporation 19.2 and 22.8%. At the temperature 293 K its decrease according to 3.37 and 3.04%. For the degree of evaporation 26.5 and 30.1% cooling of suspension has little effect on SO<sub>4</sub><sup>2-</sup> concentration in the liquid phase of evaporated suspension. So if the temperature of 353 K, it is respectively 2.84 and 1.83%, that the temperature at 293 K-2.36 and 1.74%.

Figure 2 shows the dependence of the ratio of equivalent concentration ( $\lambda$ ) MgSO<sub>4</sub> and MgCl<sub>2</sub> in liquid phase of the suspension potassium-magnesium salts, on the temperature cooling by air to different degree of evaporation. The minimum value of  $\lambda$  in liquid phase indicates to the extraction in the solid phase predominantly kainite. For the suspensions at a temperature of 353 K value  $\lambda$  is gradually decrease with increasing degree of evaporation from 0.3235 to 0.0659 for the



**Figure 1:** The dependence of concentration (C) K<sup>+</sup> (a) i SO<sub>4</sub><sup>2-</sup> (b) in the liquid phase vs temperature (T) during the cooling by air suspension of potassium-magnesium salts, evaporated to different degree, %: 1-15.5; 2-19.2; 3-22.8; 4-26.5; 5-30.1.

degrees of evaporation, respectively 15.5 and 30.1%. For the degree of evaporation 30.1% value  $\lambda$  almost unchanged. Therefore, according to the concentration in the liquid phase of ions  $\text{SO}_4^{2-}$  and value of  $\lambda$  can make a preliminary conclusion that the solutions is expedient evaporate to degree of evaporation 30.1% to achieve a value of  $\lambda$  equal to 0.0659, separate crystallized salts and return them to conversion and crystallization of schoenite. Figure 3 shows data on the degree extraction in solid phase of suspension  $\text{K}^+$  (a),  $\text{SO}_4^{2-}$  (b) i  $\text{Mg}^{2+}$  (c). As seen from the data (a), with increasing the degree of evaporation solution from 15.5% to 30.1% increases the degree of transition in the solid phase of  $\text{K}^+$ , respectively, from 26.0 to 65.2%. Cooling of suspension for all degree of evaporation contributes to an increase degree of extraction of  $\text{K}^+$  ions in solid phase. Most of the value is achieved for the degree of evaporation 30.1% at 293 K and is 91.7%.

The degree of transition in the solid phase ions  $\text{SO}_4^{2-}$  (b) also increases with the degree of evaporation the solution. For example, for the degree of evaporation 15.5%, it is 22.1%, and for the degree of evaporation 30.1% its 84.5%. Cooling by air of the suspension evaporated to the degree 15.5%, contributes to a significant increase to 42.0% degree of extraction  $\text{SO}_4^{2-}$  ions in the solid phase to a temperature 333 K. Continued cooling of suspension to the degree of extraction  $\text{SO}_4^{2-}$  ions in the solid phase affects little. For suspensions obtained with a higher degree of evaporation, cooling is even less effect on the extraction of  $\text{SO}_4^{2-}$  ions in solid phase. So to the degree of evaporation 30.1% degree of extraction  $\text{SO}_4^{2-}$  ions in the solid phase is 84.5% at temperature 353 K and 89.8% at temperature 293 K. For the degree of evaporation 22.8 and 26.5% respectively his the value is 61.7 and 71.3% at temperature 353 K and 70.3 and 80.4% at temperature 293 K. During the cooling of suspension by water degree of extraction in the solid phase ions  $\text{SO}_4^{2-}$  slightly smaller than by air. The degree of conversion ions  $\text{Mg}^{2+}$  (c) in the solid phase also increases with increasing the degree of evaporation, respectively, from 9.7% to 29.7% for the degree of evaporation 15.5 and 30.1%. Cooling by air of suspension to 293 K has little effect on the degree of separation in the solid phase  $\text{Mg}^{2+}$  ions for degree of evaporation 15.5, 19.2 and 22.8%. For the suspension evaporated to 30.1%, cooling causes a great increase of the degree extracted ions  $\text{Mg}^{2+}$  in solid phase. Figure 4 showing the results of calculation content in the solid phase sylvine (a) kainite (c) and carnalite (s). Separation of carnalite causes return of  $\text{MgCl}_2$  in the crystallization of schoenite and is not desirable. Extraction of sylvine is not desirable too because of its similarity his crystals to the crystals of sodium chloride and complicated of purification kainite from sodium chloride by hydroseparation.

As seen from the obtained results in the solid phase of the evaporated suspension content of sylvine during cooling from 353 to 273 K increases at the degree of evaporation 15.5; 19.2; 22.8%, 24.4% respectively to 19.5 and 18.1%. At the degree of evaporation 26.5% content of sylvine increased from 5.4% at the temperature 353 K to 13.1% at the temperature 313 K. During continued cooling to 303 K and 273 sylvite content of decreases respectively to 7.7 and 5.8% due to its dissolution and crystallization of kainite. Cooling suspension evaporated to 30.1% causes conversion sylvine in kainite is complete at temperature 313 K. The content of kainite in the solid phase (c) of the suspension at a temperature of 353 K increases with the degree of evaporation from 15.5 to 19.2%, respectively, from 34.0 to 64.2%. The next increase the degree of evaporation to 22.8-30.1% decreases content of kainite to 57.3-61.2% at 353 K. Cooling the suspension evaporated to 15.5%, from 353 to 323 K causes increasing the contents of kainite from 34.0 to 53.5%, cooling to 313 K or less leads to decrease of the content kainite to 48.6-46.3%.

In the suspension with degree of evaporation of 22.8 and 26.5% during cooling to 333 K content of kainite increases by 1.5-2.2%, then decreases to 55.1-47.6%. With decreasing temperature of the suspension with the degree of evaporation 30.1% decreases content of kainite from 59.9% to 52.1; 47.2; 41.6; 42.9 and 39.3%, respectively, at a temperature of 353; 333; 323; 313; 303 and 293 K. Therefore, the highest content of kainite 64.2-63.4% the solid phase of the suspension achieved at the degree of evaporation 19.2-26.5% and temperature 333-353 K. The lowest content (2.6-5.7%) of carnalite in suspension is achieved at temperatures 313-333 K and the degree of evaporation 19.2-26.5%. Cooling of the suspension with the degree of evaporation of 30.1% results to a significant increase of carnalite in the solid phase of the suspension (wt.%): 28.6; 35.0; 44.5; 47.1 respectively in temperatures 333; 323; 313 i 293 K.

The degree of evaporation of mixed solution changes in dependence on the quantity returned to the mixing of evaporated solution. Therefore, to obtain of the suspension with a high content in solid phase of kainite and lowest content of sylvine and carnalite the

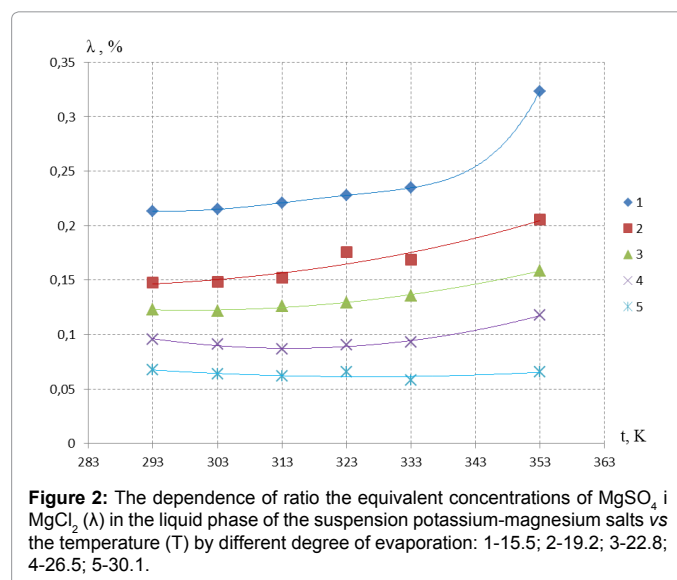


Figure 2: The dependence of ratio the equivalent concentrations of  $\text{MgSO}_4$  i  $\text{MgCl}_2$  ( $\lambda$ ) in the liquid phase of the suspension potassium-magnesium salts vs the temperature (T) by different degree of evaporation: 1-15.5; 2-19.2; 3-22.8; 4-26.5; 5-30.1.

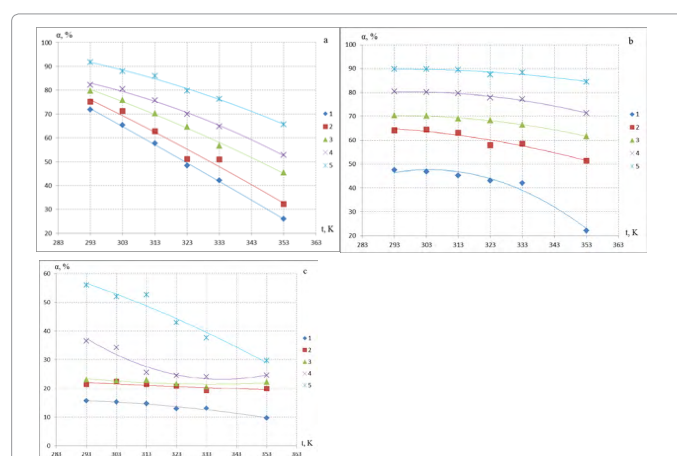
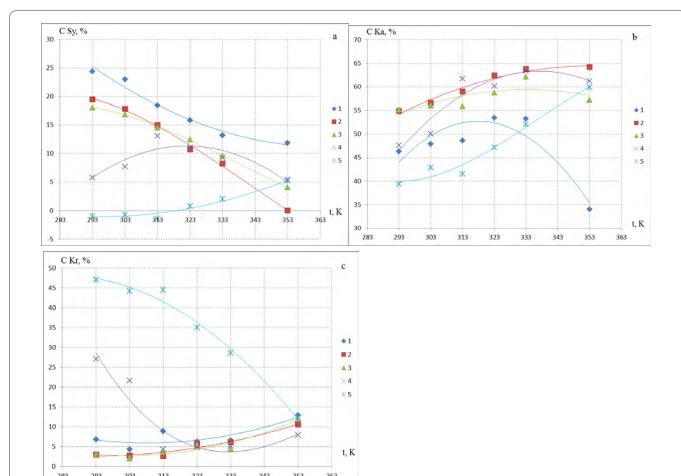


Figure 3: Dependence the degree of transition (a)  $\text{K}^+$  (a),  $\text{SO}_4^{2-}$  (b) i  $\text{Mg}^{2+}$  (c) in the solid phase vs temperature (T) during the cooling by air of suspension potassium-magnesium salts, evaporated to different concentrations of  $\text{Mg}^{2+}$  in liquid phase %: 1-24.64; 2-24.48; 3-25.77; 4-26.75; 5-29.34.



**Figure 4:** The dependence of content (C) sylvine (a), kainite (b), and carnalite (d) in the solid phase of the suspension vs the temperature (T) during the cooling by air of the suspension potassium-magnesium salts, evaporated to different degree, %: 1-24.64; 2-24.48; 3-25.77; 4-26.75; 5-29.34.

degree of evaporation at a temperature of 353 K should be 22.8-26.5%. Regulate the depth of evaporation and cooling can be by concentration in the liquid phase equivalents  $MgSO_4$  (0.016-0.032),  $MgCl_2$  (0.248-0.289), and the ratio between them (0.0579-0.125).

## Conclusion

The results of research showed that the concentration and degree of extraction of compounds potassium and sulfates in the solid phase increases with increasing degree of evaporation of the solution and decreasing temperature of the suspension. The highest content of kainite and smallest of carnalite in the solid phase is achieved at a temperature of 333-353 K. Without cooling of the suspension can be separated with a high degree of extraction kainite at the degree of evaporation of 30%, equivalent to the concentration of  $MgSO_4$  0.016-0.020,  $MgCl_2$  0.301 i ratio between them 0.035-0.058.

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