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Crystallization of Kainite from Solutions in System K^+, Mg^{2+}, Na^+ // Cl^-, SO_4^{2-} - H_2O

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Abstract

In isothermal conditions have been studied the influence of system solution sea salts during their evaporation and crystallization to composition of received liquid and solid phases. It is shown that evaporation of the solution leading to its supersaturation by sulfate salts. In the liquid phase before crystallization of kainite concentration of SO_4^{2-} ions increases to 10% and above. Through this probability of formation of crystals increases and the result of evaporation is the formation of finely dispersed kainite. During crystallization of kainite concentration of SO_4^{2-} in the liquid phase decreases rapidly. Decreasing its intensity increases with increasing value k=E SO_4^{2-} : E Mg^{2+} of initial solution. For the degree of evaporation of 20.0% and 31.0% concentration of SO_4^{2-} in evaporated solution on the value of k does not change. Most forms of potassium salts in the solid phase for the value k=0.7573 and reaches a maximum value at 82% evaporation rate of 31%. With the increasing degree of evaporation of the solution the degree of separate of SO_4^{2-} in solid phase also increases. Most of the value achieved the degree of evaporation of the solution is 31% and about 90% for all values of k. This is an increase of salting action of $MgCl_2$ of liquid phase at kainite.

Keywords: Kainite; Schenite; Crystallization; Evaporation; Magnesium chloride solution; Kieserite; Langbeinite; Potassium chloride; Sodium chloride

Introduction

Crystallization of kainite in technology of polymineral potassium processing raw of materials chloride sulfate type and natural salt solutions in nochloride potassium and potassium-magnesium fertilizers is a major operations of process. This is because during crystallization schenite of saturated solutions obtained by dissolving natural raw in the liquid phase as a result of reaction conversion chloride minerals (kainite $KCl \cdot MgSO_4 \cdot 3H_2O$, sylvine KCl) in sulfate (schenite $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) increases the concentration of $MgCl_2$. So part of the solution after crystallization of schenite separated from the sulfate process. With this solution according to the potash production separated to 40% of potassium and sulfate on their number of processed raw materials. Therefore, it is sent for multistage evaporation to separate of sulfate salts and return them to the production of sulfate potassium fertilizers. During evaporation in industrial conditions is not achieved a high degree of extraction of potassium and sulfate from excessive schenite solutions in kainite, high dispersion of the solid phase and therefore the difficulty of filtering and significant losses of liquid phase, which adversely affects to the work stages of dissolution of ore and crystallization schenite. This causes the low efficiency of polymineral potash ore processing in general. To increase the size of crystals kainite suggest reducing the intensity of evaporation from 450-600™ 50-250 kg/m³· hour [1], and mixing the initial solution with evaporated to reduce the correlation concentrations of $MgSO_4$ and $MgCl_2$ [2]. Previously [3], we have found that the change of composition of system solution sea salts for constant degree and intensity of evaporation has little effect on the size of the crystals kainite. Evaporation of the addition of solid phase kainite at constant composition of the liquid phase makes it possible to increase the average size of the crystals kainite only 11.9%. Increasing the depth of evaporation of the solution leads to a substantial increase in the average size of the crystals kainite, but it increases the content of solid phase and the density of the suspension, which hinders evaporation. So evaporated suspension should be diluted by concentrated on the final $MgCl_2$ solution. After separation of crystalline magnesium chloride

solution which containing sulfates [4] the past remain in the liquid phase and finely dispersed solid phase. Return them to the process of crystallization of kainite leads to the binding coarse grained potassium chloride in finely dispersed kainite. The result is a suspension of the solid phase, which can easily be cleaned of impurities coarse grained sodium chloride. Evaporation of sea system solutions of salts is accompanied by movement of figurative point of the system from one field to another crystallization. So for a solution with index x=20 ÷ 30 and above 368 K first crystallized mixture of NaCl+KCl. After reaching the limit saturation by sulfates crystallizing kainite, while previously separated KC1 dissolved [5]. With the concentration of Mg^{2+} 7.95 starts crystallization of kieserite and carnallite, accompanied dissolution of kainite reaction by the equation:

$$KCl \cdot MgSO_4 \cdot 3H_2O + MgCl_2 = KCl \cdot MgCl_2 \cdot 6H_2O + MgSO_4$$
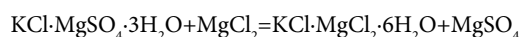
The above suggests that, being in the field of crystallization kainite, all other minerals are not stable. Similarly in other fields, crystallized mineral that corresponds this field, while the others are dissolved, increasing its output. This explains the fact that during the change of temperature changes border fields crystallization and system with constant composition of the liquid phase moves from one field to another crystallization. Therefore, during the temperature increasing chlorides salting sulfates, but with decreasing - sulfates salting chlorides [6]. Evaporation is carried out in vacuum evaporators, the temperature in corps which is 323 to 388 K. It is known [7] that the maximum size of the crystals kainite without impurities langbeinite is achieved by evaporation of the solution after separation sodium chloride from

the addition solid phase of kainite at a temperature of 363-368 K. The composition of the initial solution significantly affects the coefficient supersaturation of solution in the crystallization process at the rate of formation crystals and granulometric composition of sediment.

Experimental Section

Research of processes of evaporation and crystallization kainite was carried out on a laboratory vacuum evaporating installation and thermostatted glass reactor with paddle mixer. The first included throat round bottom flask with a capacity of 2500 cm^3, mechanical paddle mixer with electric meter and velocity, heater, glass refrigerator of vapors, calibrated collection of condensate, vacuum pump and system manually adjust the depth of vacuum, by which the temperature of evaporation supported in the temperature range 323-388 K with precision of ± 0.5 K. Thermostatted reactor includes a rubber cover closed double-walled glass vessel with a capacity of 1200 cm^3 elliptical bottom, glass paddle mixer with electric drive and electric thermostat which is supported temperature with a precision ± 0.1 K pumping water between the walls of the reactor.

Initial for researches was polymineral processing solution of potassium ores after evaporation and crystallization of sodium chloride composition by weight.%: 5.73 K^+, 4.33 Mg^{2+}, 2.82 Na^+, 16.76 Cl^-, 7.37 SO_4^{2-}, 63.00 H_2O, previously diluted with water to 30% to density of 1246 kg/m^3. In the flask for evaporation poured 2 dm^3 diluted solution. And added to change the composition of the solution different quantity of crystalline KCl, $MgSO_4 \cdot 7H_2O$, $MgCl_2 \cdot 6H_2O$, Na_2SO_4. This solution is heated to temperature of experiment and evaporated water, added earlier to dilution. Obtained initial solution. Thereafter evaporated the different quantity of water which corresponded to the specified degree of evaporation (α), which represented a ratio of the mass of condensate to initial solution. The temperature of evaporation supported constant and was 368 K. The intensity of evaporation in all experiments was constant and was equal to 0.45 h^{-1} (1 kg evaporated water with 1 kg of starting solution for 1 hour). After evaporation turned off heater and vacuum pump, open the flask and the sample of suspensions were selected for analysis by special sampler, and then again turn on the installation work. A sample of the suspension was filtered under vacuum in a heated crucible Schott № 16. The filtrate flow down in previously weighed test tube and solid phase after filtration were washed on the filter from intercrystalline solution first purified vegetable oil, and with organic solvent and dried at 323 K in an air thermostat for 30 min. The obtained liquid and solid phases were analyzed using tetraphenylborate weight method (for K^+ ions), complexometric method (for Mg^{2+} and Ca^{2+} ions), mercurimetry (for Cl^- ions), weight method (for SO_4^{2-} ions), as difference between the sum of equivalents of anions and cations (for Na^+ ions), H_2O – by difference. A result of analysis in a special program material balances were calculated and determined the degree of extracted components in the solid phase.

Results and Discussion

We have been studied the influence of composition and degree of evaporation to concentration in the solution evaporated SO_4^{2-} in solution. The results are shown in Figures 1 and 2. The composition of the solution given as equivalent indices $X=E\ SO_4^{2-} : (E\ 2K^+ + E\ 2Mg^{2+})$; $Y=E\ Mg^{2+}: (E\ 2K^+ + E\ 2Mg^{2+})$. Changing value X:Y of the initial solution and the ratio k=X:Y or, respectively, $k=E\ SO_4^{2-}:E\ Mg^{2+}$. The purpose of evaporating the solution at the stage of separating kainite is the maximum excretion of ions K^+ and SO_4^{2-} in the solid phase and obtaining a solution with a low concentration of SO_4^{2-}. The equivalent ratio $E\ SO_4^{2-}$ i $E\ Mg^{2+}$ corresponds to the ratio molar concentration of

magnesium sulfate to the sum molar concentrations of magnesium chloride and magnesium sulfate.

We investigated the value of the maximum concentration of SO_4^{2-} ion of evaporation process at a temperature of 368 K. The results are shown in Figure 1.

As follows from the data obtained (Figure 1), evaporation of the solution leads to a gradual supersaturation for its sulfate salts. In this time there is crystallization of potassium chloride and sodium [6]. In solutions with a high index value X before crystallization kainite SO_4^{2-} ion concentration is achieved 10% and above. This suggests that with increasing X index increasing quantity of kainite which crystallized. Due to this, the probability of formation of new crystals increases and the result of evaporation is the formation of a large number of finely dispersed crystals of kainite. After achieving a critical supersaturation begins intensive crystallization kainite and SO_4^{2-} concentration in the liquid phase decreases rapidly. Decreasing its intensity increases with increasing value of $k=E\ SO_4^{2-} : E\ Mg^{2+}$ the initial solution. During the dilution of initial solution by evaporated final solution is not enough crystallized material to increase the size of the crystals. Slowest decrease concentrations of SO_4^{2-} in the liquid phase is for
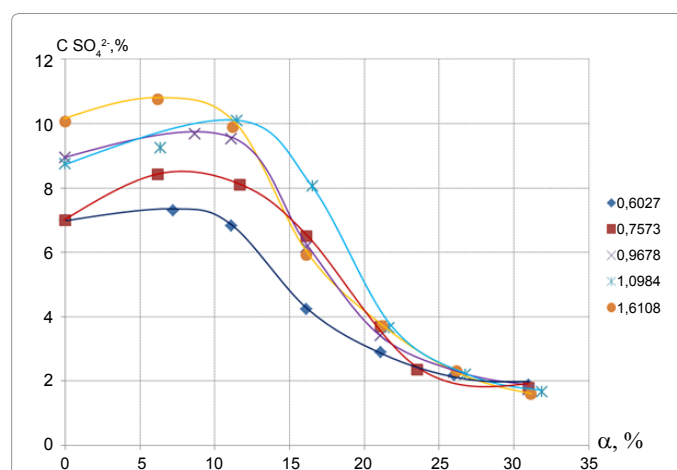

Figure 1: The dependence of the concentration (C) of sulfate ions in the solution *vs* the degree of evaporation (α) ratio for various equivalents $MgSO_4$ and $MgCl_2$ in the initial solution.
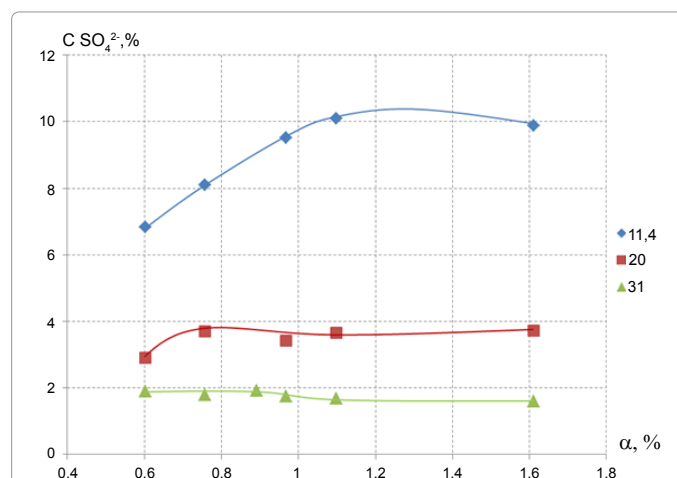

Figure 2: The dependence of the concentration (C) of sulfate ions in the evaporated liquid phase *vs* ratio of equivalents (k) $MgSO_4$ and $MgCl_2$ in the initial solution at different degrees of evaporation: 11.4; 20.0; 31.0%.

the value of k=0.6027, namely the highest concentration of magnesium chloride. This is caused by the lower number of ions SO_4^{2-} to form a solid phase kainite. Figure 2 shows the dependence of the concentration of SO_4^{2-} in evaporated solution under different degree of evaporation solution of the value k of initial solution. As can be seen from Figure 2, SO_4^{2-} concentration in solution evaporated at the degree of evaporation of a solution is 11.4% increasing with the value of k of initial solution to 1.09. For the degree of evaporation 20.0 and 31.0% SO_4^{2-} concentration in solution evaporated from the value of k does not change. So to achieve lowest value of concentrations of SO_4^{2-} in the evaporated solution can be by evaporation depth and addition part of evaporated solution to the original. Return part of the solution evaporated to evaporation causes reducing the intensity formation of crystals kainite and increase the size of its crystals. Figure 3 shows the results of calculation of the degree of extracted of K+ from the degree of evaporation and the initial value of k solution.

As seen from the above data, the most of potassium salts separated in the solid phase for the value k=0.7573 and achieves maximum value for the 82% degree of evaporation of 31%. With the increase in the value of k degree of extracted potassium in the solid phase decreases. Thus, the return of the evaporated solution on evaporation promotes the separation of potassium salts in the solid phase by salting action on $MgCl_2$ kainite. Figure 4 shows the results of calculation of the degree

Figure 3: The dependence of the degree of extracted ions K+ in the solid phase (β) *vs* the degree of evaporation (α) and the ratio E MgSO₄/E MgCl₂ in solution.

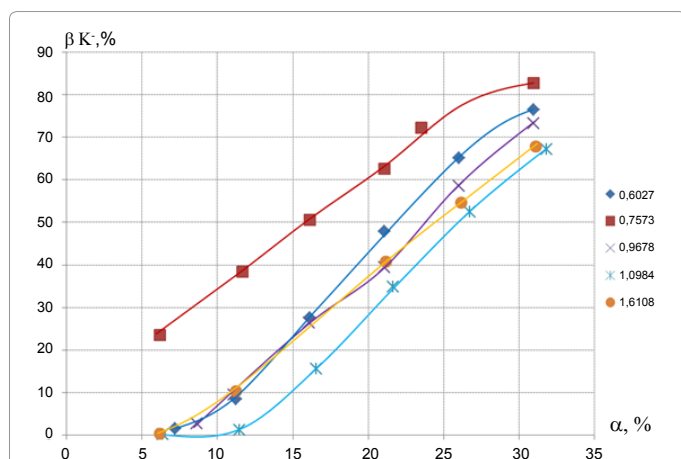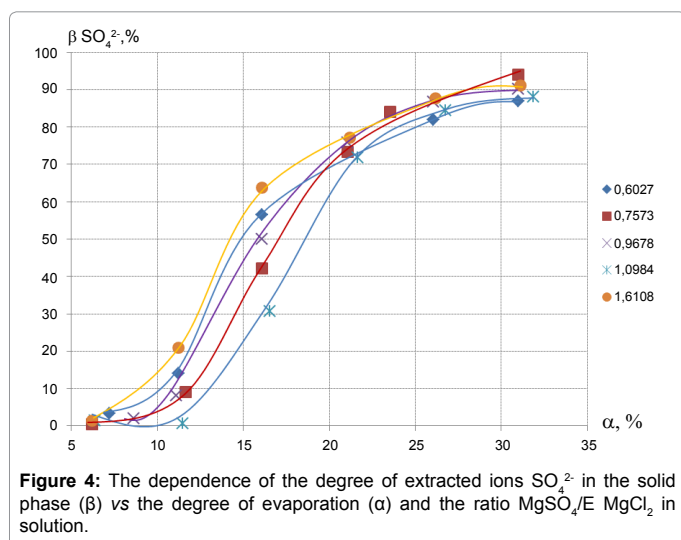**Figure 4:** The dependence of the degree of extracted ions SO₄²⁻ in the solid phase (β) *vs* the degree of evaporation (α) and the ratio MgSO₄/E MgCl₂ in solution.

of extracted SO_4^{2-} ions solid phase of the degree of evaporation for different values of k in the initial solution.

As can be seen from the data, with increasing degree of evaporation of the solution degree of extracted SO_4^{2-} in solid phase increased for all values of magnitude k. Most of the value is achieved by the degree of evaporation of the solution is 31% and about 90% for all values of k. This is explained by the increase concentration and salting action $MgCl_2$ liquid phase at kainite.

Conclusions

Consequently to achieve a high degree of excretion of salts K+ and SO_4^{2-} in the solid phase can be due to evaporation of a solution to the high concentration of $MgCl_2$. This increases the number of extraction of salts and content of solid phase in evaporated suspension, which limits the depth of evaporation. Return part of the evaporated solution contributes to increases salting action of $MgCl_2$ on potassium and sulfate, and also reduction of solid phase in suspension during evaporation. Results of laboratory researches have shown that for practical realization of the process of evaporation potassium chloride solutions which containing sulfate ions on stage of crystallization kainite rationally choose three stages vacuum evaporators with direct flow movement of the heating vapor and evaporation of the solution initially in the first corps at a temperature of 383-388 K, then in the third at a temperature 333-335 K for formation crystals of kainite and then pump over the suspension into a second corps for evaporation and crystallization kainite at a temperature of 363-368 K. Evaporated solution expedient partially to return in the third corps for formation of crystals kainite. Evaporation at a temperature of 363-368 K without a solid phase kainite leads to partial extraction except kainite and langbeinite, which complicates the subsequent conversion of selected minerals in schenite. Suspension of kainite which containing coarse grained sodium chloride crystals, which are separated by hydroseparation and clean suspension of kainite thickened and sent to the stage of crystallization schenite.

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