

Conversion of Langbeinite and Kieserite in Schoenite With Mirabilite and Sylvite in Water and Schoenite Solution

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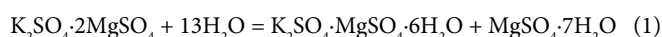
Abstract

The hydration of soluble Langbeinite and kieserite was investigated in the presence of potassium chloride and sodium sulfate. The addition of sodium sulfate affects water activity less than in the case of clean water. Therefore, we have conducted a research by adding water instead of schoenite solution. According to the results, hydration of Langbeinite by adding sodium sulfate in the first 240 hours occurs more intensively than without sodium sulfate with formation of a readily soluble schoenite and halite.

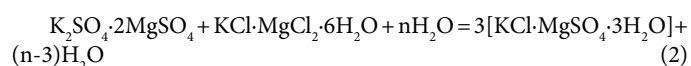
Keywords: Langbeinite; Kieserite; Conversion ; Sodium sulfate; Schoenite solution

Introduction

The polymineral potassium-magnesium ores contain both readily soluble minerals: kainite ($\text{KCl}\cdot\text{MgSO}_4\cdot 3\text{H}_2\text{O}$), sylvite (KCl), halite (NaCl) as well as hardly soluble: langbeinite ($\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$), polyhalite ($\text{K}_2\text{SO}_4\cdot \text{MgSO}_4\cdot 2\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4\cdot \text{H}_2\text{O}$). During their hot dissolution the readily soluble potassium minerals dissolve almost completely, and hardly soluble - only partially. So, during ore processing of Carpathians (Ukraine) the langbeinite dissolves only by 22-23% [1], kieserite - still less, and polyhalite is practically insoluble. Low degree of dissolution of sulfate mineral - langbeinite leads to saturation of the solution at the stage of ore dissolution by chloride salts. The mixture of chloride salts and schoenite crystallizes from the obtained solution at vacuum-crystallization, therefore, we received a low-quality potassium magnesium containing admixtures of chloride to 25% and an extract of potassium from the ore in potassium magnesium was no more than 50-60%. To increase the degree of dissolution of langbeinite from polymineral potassium-magnesium ore, the technology of complete dissolution has been developed [2], which consisted in additional dissolution of halite from solid residue with water with obtaining the halite solution as a raw material for the production of table salt, the next hot langbeinite dissolution, obtaining langbeinite solution and residue of polyhalite, by drying of which the low-grade potassium-magnesium sulfate fertilizer is obtained. However, the specified technology was complex, multistage, energy intensive and required significant capital costs. The technology of processing [3] of polymineral potassium-magnesium ore from previous hydration of hardly soluble langbeinite in the readily soluble schoenite has been developed by the reaction:



As a result of the processing of the hydrated ore of Carpathian, extract of potassium from ore in potassium-magnesium increased to 82%. The technology of processing of polymineral potash ores from the previous conversion of hardly soluble langbeinite with reversible carnallite in readily soluble kainite [4] has been developed by the reaction equation:



It is also known the technology that includes the dissolution of readily soluble minerals of polymineral ore, including halite, by means of water or dilute solutions with subsequent separation of the undissolved

residue of hardly soluble langbeinite, kieserite and polyhalite, its drying with obtaining potassium-magnesium concentrate, containing K_2O - 20,4%, MgO - 16,0% and Cl - less than 1%. The solution after the stage of dissolution of ore is illuminated, evaporated, separated at first sodium chloride and then schoenite [5].

During processing of kieserite hartzalts of Germany, containing 17-28% of kieserite, crushed ore is subjected to hot dissolution with the subsequent crystallization from the received solution of potassium chloride. Insoluble halite-kieserite residue is filtered and washed from halite. Kieserite residue is filtered and given on the more hotly dissolution by reversible epsomite solution with obtaining a concentrated solution of magnesium sulfate. This solution is cooled for crystallization of epsomite. The latter is filtered and given on the conversion of potassium chloride to receive potassium sulfate. The concentration of magnesium chloride increases in the process of conversion in reverse solutions, therefore, the part of the solution is evaporated with crystallization of kainite, and excess magnesium chloride solution is discarded [6].

Langbeinite ores of Carlsbad field (USA) [7], contain not only langbeinite, but also halite and sylvite. The breed, crushed to a size of 3.3 mm, is classified according to the class of 1.6 mm. The large class is washed with cold water, enriched on the hydrocyclones, filtered on centrifuges and dried. The fraction of 1.6 mm is washed and dried. The dried concentrate, containing 96-98% of langbeinite, is classified with obtaining a product that contains 22% of K_2O , 18% of MgO and no more than 2.5% of chlorine. Small fraction of dried langbeinite is used for the conversion of chloride potassium and by receiving potassium sulphate. The excess schoenite solution, received in the conversion, is evaporated to highlight potash salts, and the concentrated magnesium chloride solution is discarded. In all technologies through conversion of potassium chloride in schoenite, the excess magnesium chloride solution has been formed that should be evaporated to highlight salts

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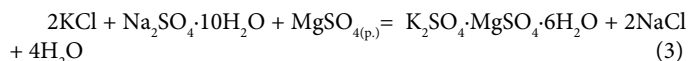
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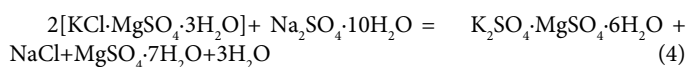
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of potassium, magnesium, sodium and sulfates that considerably increased capital costs. The final solution of chloride magnesium with a concentration of 25-32% had limited application and it was discarded. Conversion of hardly soluble and readily soluble minerals of polymineral potassium-magnesium ore with natural mirabilite is accompanied by formation of readily soluble schoenite and sodium of chloride without the formation of double salts with sodium sulfate by reaction equations:

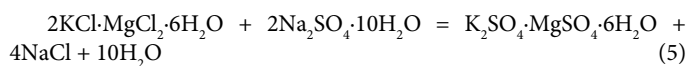
Sylvite:



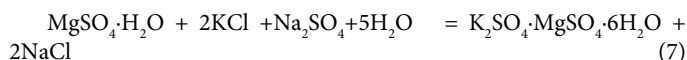
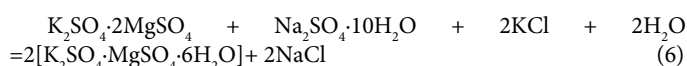
Kainite:



Carnallite:



Hydration of hardly soluble langbeinite and kieserite in the presence of potassium chloride and sodium sulfate occurs by the reaction equation:



Addition of mirabilite in the process makes it possible to regulate the ratio between MgSO_4 and MgCl_2 in the dissolving medium and set its optimum value at the stage of dissolution of convertible ore.

Experimental section

The monomineralic samples of natural langbeinite of the Dombrowskyi career of Kalush-Golyn fields of potassium salts were selected for the laboratory researched. Samples were crushed to size of 5 mm, the fraction of 3-5 mm was sifted on wire sieve, it was washed out from impurities with cold tap water, residual surface moisture was removed by initially 50% -, then 98% alcohol and dried at temperature of 50°C.

The chemical composition of the washed out and dried mineral, mas. %: K^+ - 18,31, Mg^{2+} - 11,35, Ca^{2+} - 0,11, Na^+ - 0,49, Cl^- - 0,66, SO_4^{2-} - 67,74, H_2O - 1,35. In terms of mineral composition it included, mas. %: langbeinite - 97,79; halite - 1,17; polyhalite - 1,13.

Kieserite was taken from samples of core material, received from exploratory drilling on the areas of occurrence of zechstein breeds. Core material was crushed to the size of less than 5 mm and washed from impurities of readily soluble minerals by means of limited amount of cold water, the residual moisture was removed by initially 50% then 98% ethanol. The chemical composition of the washed out and dried mineral, mas. %: K^+ - 4,37, Mg^{2+} - 6,08, Na^+ - 21,45, Cl^- - 39,49, SO_4^{2-} - 20,86, H_2O - 7,70. In terms of mineral composition it included, mas. %: kieserite - 30,09 halite - 54,71; karnalite - 9,32; sylvite - 5,89.

1020.4 g of washed Langbeinite, 352.2 g of waterless sodium sulfate, 369.7 g of potassium chloride and 267.8 g of water were taken for laboratory research. The amount of water was 50% from the stoichiometric on equation 6 of a condition of formation of the wet mixture. The mixture without sodium sulfate was also prepared.

Mixures were thoroughly stirred, filled up in tight polyethylene packs and placed in desiccator in an air thermostat, installed at the temperature of experiment. The experiments on hydration of Langbeinite with addition of waterless sodium sulfate and without it were conducted separately, a predetermined amount of water in which was added as a schoenite solution of structure, mas. %: K^+ - 2,50, Mg^{2+} - 3,19, Na^+ - 3,91, Cl^- - 14,19, SO_4^{2-} - 4,62, H_2O - 71,59.

The experiments with a sample of washed out kieserite were carried out separately. 360.4 g of washed out natural kieserite, 287.9 g of potassium chloride, 369.9 g of sodium sulfate and 257.8 g of water were taken according to the reaction equation (7). Water was taken 100% of stoichiometry, on the equation of reaction (7), while the mixture remained damp and solution from it did not drain. The researches were conducted at temperature of 40 °C, based on the exothermicity of the reactions of conversion and data given earlier [8].

The samples were taken in 1, 2, 3, 5, 7, 10, 15 and 20 days. For this purpose the contents of polyethylene pack was thoroughly mixed and 100 g 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 $20 \pm 0.5^\circ\text{C}$. The solution 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: method tetraphenylborate 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. The conversion degree of langbeinite was calculated using the results of liquid phases chemical analysis and Eq [9].

$$\alpha = \frac{(m_l \cdot C_{\text{Mg}^{2+}}) - (m_{l(b)} \cdot C_{\text{Mg}^{2+(b)}})}{m_l \cdot C_{\text{Mg}^{2+L}}} \cdot 100\% \quad (8)$$

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

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

$$m_l = \frac{400 + m_{\text{H}_2\text{O,mix}}}{C_{\text{H}_2\text{O}}} \quad (9)$$

where $m_{\text{H}_2\text{O,mix}}$ - weight of water in 100 g of the mixture withdrawn for dilution, g; $C_{\text{H}_2\text{O}}$ - concentration of water in the sample after dilution, %.

The experimental results are represented in (Figure 1).

Results and Discussion

As it is seen from the obtained data, Langbeinite hydration by water occurs intensively in the absence of sodium sulphate (curve 1). During the first 168 hours the degree of conversion increases to 39.4% and further practically does not change. In the presence of sodium sulfate the Langbeinite hydration slows down and for the same period makes 25.3%. The slower process of hydration in the presence of Langbeinite waterless sodium sulfate can be explained by decreased activity of water

in solution, which in addition to potassium and magnesium sulfates has sodium ions. In addition, sodium sulfate in the mixture is in crystalline form, therefore, the part of water is spent for its crystalline hydrate formation. So, for the Langbeinite hydration there is a smaller amount of free water.

Langbeinite is in mix with readily soluble minerals in polymineral ore. Therefore, the intercrystalline saline solution is formed, when it is mixed with water, and Langbeinite hydration occurs in saline solution. Addition of sodium sulfate affects the water activity less than in the case of pure water. Therefore, the research was conducted by adding the schoenite solution instead of water. According to the results, the hydration of Langbeinite by adding sodium sulfate during the first 240 h proceeds more intensively (curve 4) than without sodium sulfate (curve 3). This can be explained by the positive influence of sodium chloride on the Langbeinite dissolution process that is known from the literature [10,11]. Reacting mixture firmly grasps and becomes dry after 10 days. Moisture does not remain to continue hydration reaction. The mixture of sodium sulfate remains damp and the reaction continues throughout the research period.

Hydration of kieserite (Figure 1, curve 5) proceeds during the first 240 h and its degree reaches 73.0%. Reacting mixture hardens and becomes almost dry. Water, which had to be spent for the course of the reaction (7) contacted in crystalline sodium sulfate and due to lack of reaction medium the part of kieserite remained not reacted. After this its value remains practically constant for 480 h. So, we can expect that the hardly soluble kieserite of polymineral ore will convert to readily soluble shenity with a sufficient amount of water. We have executed X-ray analysis of the products of Langbeinite hydration with sodium sulfate in the schoenite solution medium. Radiograph is shown in (Figure 2), which shows that the Langbeinite hydration products are leonite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) and halite (NaCl) [12,13].

So, polymineral ores that contain hardly soluble minerals of Langbeinite and kieserite in the process of mixing with sodium sulfate in the presence of sylvite and saline solution convert into the readily soluble schoenite. The readily soluble minerals such as sylvite, kainite and carnallite also convert in these circumstances into schoenite. Convertible ore, which consists of conversion products - readily soluble schoenite and halite - are easily processed into schoenite and potassium sulphate by halurhynym method. This makes it possible to increase the extraction of potassium and magnesium in targeted products at

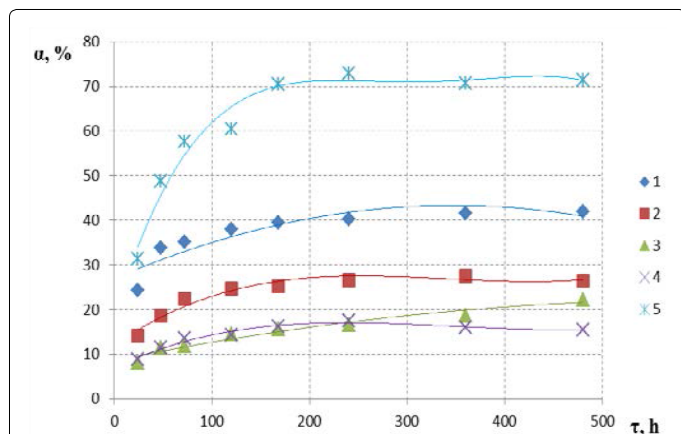


Figure 1: The dependence of the degree of hydration (α) of langbeinite by water (1) from the time (τ), water in the presence of sodium sulfate (2), langbeinite with sodium sulfate (4) and without it (3), kieserite hydration with sodium sulfate in schoenite solution (5).

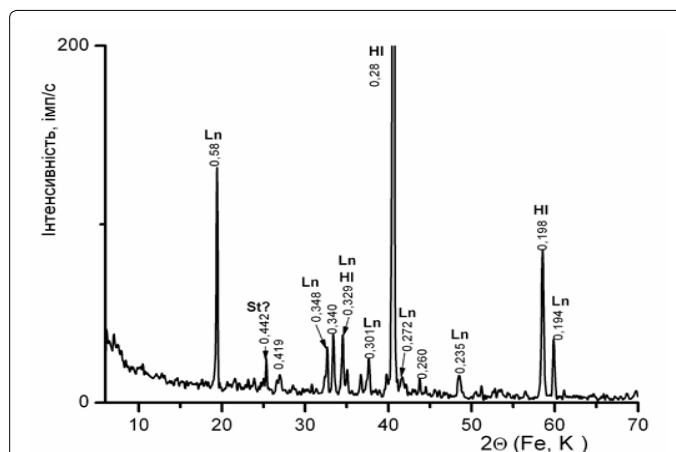


Figure 2: Radiograph of Langbeinite product hydration with sodium sulfate in schoenite solution medium.

reducing losses in comparison with known methods and to simplify processing technology of polymineral potassium-magnesium ore in magnesium and potassium sulphate.

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