

MISTI 52.13.19.

DEVELOPMENT OF TECHNOLOGY FOR PROCESSING THE CHELKAR DEPOSIT ORE INTO POTASSIUM FERTILIZERS

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ABSTRACT

Kazakhstan possesses significant reserves of potash ores located in the Caspian lowland. Chelkar deposit is one of the largest deposits. It is characterized by carnallite mineral content in the composition, which can serve as raw materials for potash fertilizer production. However, nowadays such production is absent, and the technology for obtaining potassium salts from domestic raw materials has not been also developed. At the same time, the agricultural demand for potash fertilizers is extremely high, which are still imported from Russia and Belarus. In this regard, we carried out a set of studies of Chelkar ore composition and methods of enrichment and processing this raw material to obtain chlorine-free water-soluble potassium and complex mineral fertilizers. The article presents the research results of processing washed potash ore. Optimal enrichment mode was determined using the mother liquor to achieve natural salt maximum washing degree from sodium. The process of nitric acid decomposition of concentrated ore at a temperature of 50°C has been studied. Kinetics of ore decomposition has been preliminary studied. The optimal time for reaching equilibrium equal to 30 minutes and nitric acid concentration equal to 20% was established. To ensure high suspension filtration rate the washed non-calcined ore should be used. Mineral potassium-magnesium sulfate fertilizers were obtained by crystallization from nitric acid solution by a isothermal method and by drying the ammoniated solution. The developed technology is patented by a useful model "Method for processing potash ores to obtain potassium sulfate".

Keywords: potash ore, mineral fertilizer, potassium sulfate, sodium salts, Chelkar deposit, mother liquor, decomposition, evaporation, crystallization.

INTRODUCTION

Due to the growing demand in the market and the consumption growth, the mineral fertilizer production is scaled up all over the world. Modern factories are being built everywhere and automation of technological processes is being introduced to obtain products of a high quality [1]. Any crop needs potassium more than any other nutrient. The value of potash fertilizer can hardly be overestimated. If there is no enough potassium in the soil, then flowers and fruits of a plant are not formed; it can lead to a complete yield loss. More than half of world's reserves of potash salts are concentrated in the Saskatchewan (Canada) and Verkhnekamsky (Russia) potassium-bearing basins. Belarus, Germany, Brazil, Israel and Jordan are also large reserves holders. Mining and processing of potash salts is mainly performed in Canada, Belarus, Russia, China and Germany, which account for almost 81% of

the world production of potash fertilizers. There are about ten mines in Canada, providing about 30% of world potash salts production [2].

The mineral fertilizer industry in Kazakhstan is represented by simple nitric and phosphoric and complex NP fertilizers. The availability of potash fertilizers on the market, despite their effective contribution to the development of agriculture, is still minimal [3]. Potassium sulfate is of particular interest as a chlorine-free one-component fertilizer and as a part of complex fertilizers, which is well combined with microelements and used to increase the agricultural crop yield.

It is known that natural deposits of potassium salts are used to obtain potash fertilizers; they are sylvin, kainite, sylvinit, carnallite, alunite, polyhalite, langbeinite. According to academic data, in Kazakhstan, potash salts are abundant in the Caspian Basin. Composition of the salts is predominantly chloride, their beds are found in the arched parts of many salt domes practically throughout the entire territory of the lowland. The most studied domes are "Satimola", "Chelkar", "Inder", and "Zhilyanskoe" [4]. According to Kazakh Potash website, the company registered in Australia, the Zhilyansk potash deposit in Aktobe region and Chelkar deposit in West-Kazakhstan region belong to it through the local subsidiary "Batys Kaliy" [5]. At the Chelkar field, geological exploration and assessment of reserves were conducted, however, subsoil users did not proceed to the production stage for an unknown reason [6]. In addition, foreign companies changed their minds to invest in the production of potash fertilizers [7]. However, Kazakhstani businessmen intend to build two plants for potash fertilizers production in West-Kazakhstan region, at Satimola and Chelkar deposits [8].

The main ore component of the Chelkar deposit is carnallite, which is a 6-aqueous crystalline hydrate of a double salt, potassium-and-magnesium chloride. In terms of mineral composition, carnallite ore contains up to 65% carnallite, 5-15% sylvite and 15-25% halite. As you can see, in its composition, carnallite ore compares favorably with sylvinit ore in that it contains a wider range of salts. The lack of a developed technology for processing Chelkar deposit ore is an urgent problem in development of the domestic industry of potash fertilizers based on these raw materials. To solve these problems, we carried out a set of studies on processing the potash ore to obtain potassium sulfate.

MATERIALS AND METHODS

An object of the study is the Chelkar deposit ore. A preliminary study, carried out by us earlier, showed that natural salt has a complex heterogeneous composition, contains, in addition to the main carnallite component, large amount of halite and an insoluble residue in the form of calcium sulfate dihydrate [9]. For the study, X-ray, IR spectroscopic, differential thermal, flame photometric and spectrophotometric methods of analysis were used to determine qualitative and quantitative composition of raw materials, intermediates and products. X-ray analysis of solid phase samples was performed using a DRON-3 stationary installation with Cu-K α radiation. Differential thermal analysis of the ore was conducted using Q-1500D derivatograph. Composition of liquid and solid phases was analyzed for K $_2$ O and Na $_2$ O content using PFA-378 flame photometer, the content of CaO, MgO, Cl $^-$, SO $_4^{2-}$ and N was determined by a chemical titrimetric method according to standard methods. For microscopic spectral analysis of salts, a JSM-6490I V scanning electron microscope (Jeol, Japan) was used. Semi-quantitative X-ray analysis of samples of the target product and insoluble residue was carried out on D8 Advance apparatus (Bruker), Cu-K α , tube voltage 40 kV, current 40 mA. Processing of the data obtained of diffraction patterns and calculation of interplanar distances were carried out using the EVA software. Sample decoding and phase

search were carried out using the Search/match program with the use of 2020 PDF-2 powder diffractometric data base of the International Center for Diffraction Data (ICDD), USA.

RESULTS AND DISCUSSION

Sodium chloride is an impurity component in composition of potash ore under studying, because it reduces the obtained fertilizer quality. This caused need to study the process of preliminary sodium removal from ore composition. Based on the analysis of known enrichment methods of carnallite ore for potassium to remove sodium chloride as a salt with greater solubility from the multicomponent system, the method of incomplete dissolution was chosen, consisting in treatment of an averaged sample of crushed carnallite ore with water taken in an amount insufficient to dissolve the whole potassium chloride [10, 11].

The experimental results showed effectiveness of this method for sodium salts removal from raw material composition. The obtained data on ore washing degree from sodium chloride made it possible to propose a washing mode that ensures minimal losses of valuable potassium with washing water: temperature 20°C, washing time 20 minutes, water consumption - 0.5 mass parts per 1 mass part of raw materials [12].

Further, the optimal enrichment mode was worked out using the mother liquor for two-fold washing of the original ore to achieve maximum washing from sodium with a solution saturated with potassium and with a minimum water introduction into a process. The process was studied under the established optimal conditions for ore enriching by potassium component - with a ratio of water:salt = 1:2 at 20°C for 20 minutes. As a result of washing, almost all sodium chloride was removed from the ore with preservation of potassium and magnesium sulfates, as evidenced by the results of X-ray phase analysis. For further ore processing into fertilizers, the ore dried after washing was calcined in a muffle furnace at a temperature of 550°C for 1 hour, since it was revealed by DTA method that this ore contains calcium sulfate crystalline hydrate.

The calcined washed ore was dissolved in water at temperatures of 50 and 90°C. But this led to only a partial transition to the solution of potassium and magnesium salts with complete dissolution of residual amounts of sodium salts, therefore, this method of separating the insoluble residue is not acceptable for obtaining a water-soluble fertilizer [13].

To achieve complete dissolution of potassium and magnesium salts, in particular, sulfates, which are the target components for obtaining mineral fertilizers, a method of ore decomposition with nitric acid was used [14]. The prepared raw materials were decomposed with nitric acid solution of various concentrations in a time interval of 10-40 minutes with a salt: acid ratio equal to 1:1.5. The suspension was separated by filtration on a vacuum filter. As a result of studying the process, the time to reach equilibrium equal to 30 minutes and optimal concentration of nitric acid 20% were determined. By calculating kinetic parameters of decomposition, the reaction order and reaction activation energy, equal to 92.22 kJ/mole, were determined, on the basis of which the kinetic region of the process was established. The optimum decomposition temperature of 50°C was determined for this area.

Crystallization of potassium-and-magnesium salts was carried out by mineral-salt method taking into account initial solution composition and crystallization fields on the solubility diagram in the K_2SO_4 - $MgSO_4$ - H_2O system. The solution was evaporated in a UT-4302E laboratory water bath at a constant temperature of 75°C. The precipitated crystals were separated by filtration, washed with ethanol, and examined by X-ray diffraction. The mother liquor was ammoniated to pH = 6 and dried in an oven at 60°C. Semi-quantitative X-ray analysis of a product sample obtained by isothermal evaporation of the filtrate (Figure 1)

identified a pure double acidic salt of potassium-magnesium sulfate $\text{KMgH}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. This indicates that, upon evaporation at a temperature of 75°C , the system composition point was in the field of joint crystallization of potassium sulfate and this double salt. The obtained crystalline product contains 18.0% K_2O and 10.3% MgO in the form of sulfates, does not contain chloride ions and insoluble impurities.

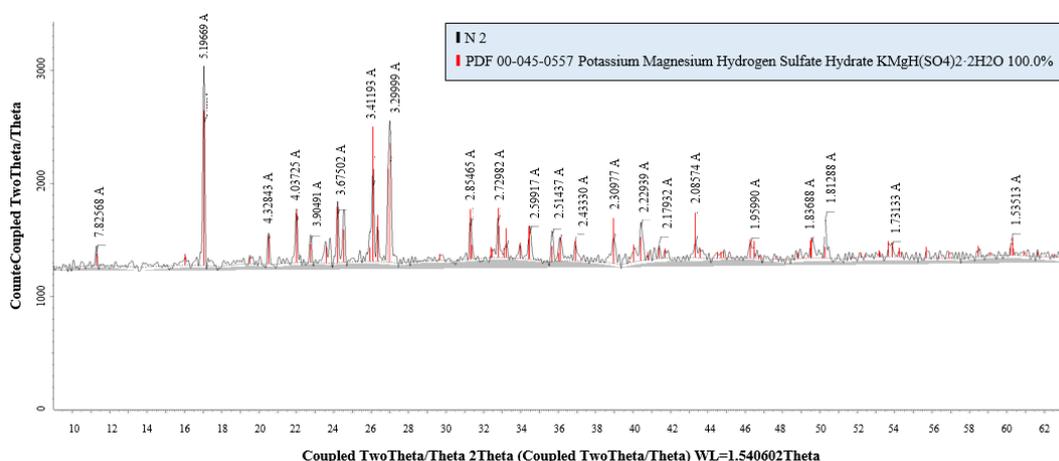


Fig.1. X-ray diffraction pattern of the salt obtained by isothermal crystallization from the filtrate

After drying the ammoniated solution, a crystalline product was obtained that does not contain insoluble impurities and chlorine. It is completely water-soluble salt and consists of three salts: 39.8% of potassium-ammonium nitrate, 31.8% of magnesium-ammonium sulfate and 10, 2% of ammonium nitrate (Figure 2).

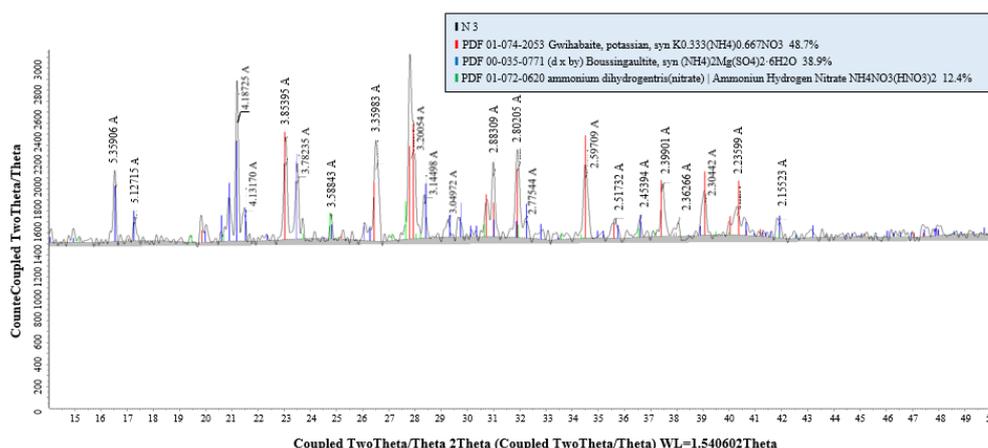


Fig.2. X-ray diffraction pattern of the salt obtained by drying the ammoniated production solution

Experimental and laboratory testing of the technology of processing the potash ore under study, performed in the Testing Regional Laboratory of the Engineering Profile "Constructional and Biochemical Materials", confirmed the experimental results and made it possible to establish the optimal parameters of all the stages of processing. Based on the

results obtained, a principal flow scheme was developed for obtaining potash and complex potassium-nitrogen-magnesium fertilizers from the Chelkar ore. The proposed technology is patented by a useful model "Method for processing potash ores to obtain potassium sulfate" [15].

CONCLUSION

The results of studying are presented on the process of enrichment of potash ore from the Chelkar deposit by incomplete washing with the use of mother liquor to achieve maximum washing degree of natural salt from impurity sodium chloride. The optimal enrichment mode with two-fold washing of the original ore for the minimum water input into the process has been determined. Nitric acid decomposition of enriched ore at a temperature of 50°C was investigated. Kinetics of ore decomposition has been preliminary studied. The optimal time for reaching equilibrium equal to 30 minutes and nitric acid concentration equal to 20% have been determined. To ensure suspension good filterability, the washed, non-calcined ore should be used. Salts which are chlorine-free potassium-magnesium sulfate fertilizers were obtained as a result of crystallization from nitric acid solution by the isothermal method and by drying the ammoniated solution. Based on the results obtained, a principal flow scheme was developed for obtaining potash and complex potassium-nitrogen-magnesium fertilizers from the ore of Chelkar deposit.

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