

ABSTRACT

of the thesis completed by **Assylkhankyzy Aigerim** on the topic «Development of technology of obtaining potassium fertilizer from carnallite ores of Chelkar deposit», submitted for the degree of Doctor of Philosophy (PhD) on the specialty 6D072000 – Chemical Technology of Inorganic Substances

The relevance of the topic under study. In the world market of inorganic compounds, consumption of potassium salts, unlike most others, has been steadily increasing for several decades. One of the main areas of application of potassium salts is their use as mineral fertilizers, the consumption of which is also continuously growing with insufficient production capacities. The rapid growth of interest in potash fertilizers is caused by increased requirements for the quality of agricultural products.

There is no potash fertilizer production in Kazakhstan, which causes an extremely high demand for potassium salts. Potassium salts are raw materials for production of chloride and sulfate potassium fertilizers. Demand for potassium and complex fertilizers is growing annually both in the domestic and global markets. Potassium sulfate is of particular interest as chlorine-free one-component fertilizer and as a part of complex fertilizers, which is well combined with microelements and used to increase the yield of crops, especially those that cannot tolerate chlorine excess, on all types of soils. High content of chlorine in many potash fertilizers adversely affects the growth and development of plants, and sodium presence worsens composition of soils, especially black soil, chestnut and white alkali soils. Another advantage of potassium sulfate is sulfur presence in its composition as the fourth “macroelement”, which is necessary in significant quantities for most crops. In addition, for saline soils, which are a threat to agriculture, potassium sulfate is very useful due to low salt index.

At present, there is a need for potash fertilizers and salts production in Kazakhstan, the basis of which is a unique raw material base. Salts are embedded close enough to the surface in domestic deposits. According to published data, country's bowels store more than 6.6 billion tons of potassium salts, represented by potassium chloride in the form of sylvinite, carnallite-sylvinite and polyhalite. Large deposits of potassium salts are located in Aktobe (Zhilyan), Atyrau (Inder) and West Kazakhstan (Satimola and Chelkar) regions, the reserves of which are among the largest in the world. The explored field Chelkar has not yet moved to the stage of production and is not sufficiently studied. This is a rather complex deposit, representing a layered salt dome containing several minerals: sylvinite, carnallite, bischofite, halite, borate, etc. Carnallite is main component of the ore. Currently, “Batys Kaliy” LLP, together with “Batys” JSC, is working on the commercial development of the Chelkar deposit.

The results of studies of Kazakhstan's scientists indicate high responsiveness to potassium of feed and vegetable crops, cotton, sugar beet, fruit and berry crops. An analysis of trends in the consumption of mineral fertilizers in Kazakhstan shows that nitrogen and phosphorus fertilizers occupy a predominant position in terms of supply and use, while potash fertilizers are used much less. This is due to the lack of operating production of potash fertilizers in Kazakhstan, which is a

deterrent to the use of potassium-containing fertilizers. The testing of potash fertilizers directly under potassium-responsive crops on the irrigated zone is of scientific and practical interest. Therefore, the need to create a domestic production of potash chlorine-free fertilizers based on natural salts of Western Kazakhstan is obvious.

A review of domestic and foreign scientific publications indicates the absence of works related to the study of composition and methods of processing the potash ores from the Chelkar deposit. In this regard, a detailed study of the mineralogical and chemical composition of these promising potash ores and search for rational ways to process natural salt systems into products that are in high demand both on the domestic market of fertilizers and salts and abroad is an urgent task.

Goal and objectives of the study.

The goal of the study is to develop a technology for obtaining ballast-free potassium fertilizers by processing carnallite ores of the Chelkar deposit.

To achieve the goal, the following **tasks** were set:

- analysis of known methods for potash fertilizers production, the choice of a method for processing natural potash ore of the Chelkar deposit;
- study of chemical and mineralogical compositions of natural potash ore;
- study of processes of potassium salts' dissolution and crystallization on the basis of solubility diagrams in K_2SO_4 - $MgSO_4$ - H_2O and KCl - $NaCl$ - H_2O systems;
- investigation of the processes of natural ore enrichment and enriched ore processing into potash and complex mineral fertilizers;
- development of a technological scheme and technological mode for obtaining potash and complex chlorine-free fertilizers from carnallite ore of the Chelkar deposit.

Object of the study. Potassium ore of the Chelkar deposit.

Research methods. To complete main tasks set in the research, chemical and instrumental methods of research and analysis were used. Washing of potash ore from sodium salts was carried out by the method of incomplete dissolution. Determining the optimal conditions for the ore washing was studied by double and triple washing with mother liquor. The content of potassium and sodium in the systems under study was determined using Kvant-2 atomic absorption spectrometer and PFA-378 flame photometric analyzer. The analysis of raw materials and products was carried out by the methods of spectral microscopic, X-ray, differential thermal and IR spectroscopic research. X-ray semi-quantitative analysis of solid phase samples was carried out on D8 Advance (Bruker) apparatus, processing of the obtained diffraction pattern data and calculation of interplanar distances were carried out with the use of EVA software. Sedimentation analysis of the insoluble residue was performed with the use FSK-6 photosedimentometer. Total standard uncertainty of measurement of K_2O and Na_2O content in liquid and solid phases was calculated from two parallel measurements of the sample, taking into account the uncertainty of sample weighing, calibration and measurement on a flame photometer and a spectrometer. Statistical processing of experimental data was carried out in the program Statistica 10, significance of the regression coefficients was determined by calculating the Student's *t*-test.

Relationship with the research plan. The work was carried out in accordance with the plan of research work of the department “Chemical Technology of Inorganic Substances” of the M.Auezov South Kazakhstan University on state budget research for 2016-2020 as number B-16-02-03 “Research on creation of alternative innovative technologies for raw material enrichment and production of products of inorganic compounds synthesis from natural ore and mineral resources and technogenic waste from various industries” and for 2021-2025 as number B-21-03-02 “Development of new promising technologies and improvement of traditional technologies for obtaining inorganic products, environmentally friendly fertilizers and plant growth stimulants based on mineral raw materials and technogenic waste”.

Scientific novelty of the research:

- chemical and mineralogical composition of the studied natural salt from Chelkar deposit was determined, on the basis of which it was established that potash minerals predominate in the composition, namely carnallite and glaserite, there are also insoluble gypsum and impurity halite;

- optimal mode for washing potash ore from sodium salts for 20 minutes at water/salt mass ratio of 1/2 was established, at which the maximum ore enrichment degree is achieved with minimal losses of potassium with washing water and with minimal water input into the process;

- statistical processing of experimental data of ore enrichment for potassium was carried out, based on which the statistical significance of coefficients of the regression equation describing the process was determined by calculating the Student's t-test for equations with a correlation coefficient close to 1. The equations can be used to operate the process of potassium ore enrichment and predict these dependencies in various process conditions.

- the kinetics of nitric acid decomposition of enriched carnallite ore was researched; it has been established that equilibrium on potassium and magnesium in liquid and solid phases of the nitric acid suspension reaches to 30-th minute of decomposition. Values of Gibbs energy close to zero for reaction of potassium sulfate with nitric acid were determined by thermodynamic analysis. It characterizes the state of the system as close to equilibrium and does not indicate reaction thermodynamic prohibition. For magnesium sulfate, the possibility of reaction proceeding with dissolution of a small part of ϕ magnesium salt is substantiated up to establishment of equilibrium in the system with respect to magnesium.

- the order of proceeding reactions was determined by the Van't Hoff method. The calculated value of activation energy of the reaction of potassium sulfate interaction with nitric acid, equal to 41.37 kJ/mole, characterizes the internal kinetic region of the process, on the basis of which decomposition temperature of the enriched ore was chosen as 50°C; optimal decomposition parameters were established: the process time is 30 minutes, concentration of nitric acid is 20%.

Main provisions for the defense:

- chemical and mineralogical composition of carnallite ore from the Chelkar deposit; enrichment of natural ore on potassium by the method of incomplete dissolution;

- mathematical processing of experimental data on washing of raw materials from sodium chloride, determination of significant coefficients of regression equations;

- kinetics of nitric acid decomposition of enriched carnallite ore from the Chelkar deposit; calculation of the Gibbs energy of potassium and magnesium sulfates interaction with nitric acid;

- filtration properties of the insoluble residue and the mode of gypsum washing in the process of washed potash ore decomposition with nitric acid solution; tests of gypsum for compliance with its normally hardening gypsum binder;

- processes of dissolution and crystallization of potassium and potassium-magnesium salts to obtain water-soluble chlorine-free ballast-free fertilizer;

- technology for processing carnallite ore from the Chelkar deposit into potash and potash-nitrogen-magnesium fertilizers.

Practical significance of the work:

- based on the research results, a technology was developed for processing carnallite ore of the Chelkar deposit into potash and potassium-nitrogen-magnesium water-soluble chlorine-free fertilizers: the optimal mode for potash ore enrichment, nitric acid decomposition of the enriched ore, ensuring the complete potassium extraction into the liquid phase, and crystallization of salts from nitric acid solution;

- an effective mode is proposed for filtering a suspension obtained by washed potash ore decomposition with nitric acid to obtain large, well-filtering gypsum crystals and to input minimal amount of water into its washing; Obtained gypsum has successfully passed tests for compliance with its normally hardening gypsum binder (index B) of grade G-2 B, which can be used as a binder in the construction industry. The advantage of the gypsum is its environmental safety due to the absence of impurities in its composition.

- a technological scheme for production of potash and potassium-magnesium fertilizers was developed and consumption coefficients for raw materials were determined; for the proposed technology, a utility patent “Method of processing potassium ores to obtain potassium sulfate” was received;

- the advantage of the developed technology is absence of solid and liquid production waste, possibility of complex use of all components of natural potassium salt. The scheme is flexible and can be modified to produce only one type of nitrogen-potassium water-soluble fertilizer. The developed technology can serve as a basis for creating a project for production of potassium and potassium-magnesium fertilizers from carnallite ore from Chelkar deposit, which is absent in Kazakhstan.

The degree of reliability and approbation of results. Reliability of new scientific data obtained is ensured by calculation of total standard uncertainty of

measurement of potassium and magnesium components content in natural salt composition, in its processed products and target products, as well as by the use of instrumental research and analysis methods and modern analytical devices for research.

The proposed technology for processing the carnallite ore was tested in the process of laboratory testing in Testing Regional Laboratory of Engineering Profile “Constructional and Biochemical Materials” at M. Auezov South Kazakhstan University. The results showed reproducibility of experimental scientific data. Based on the established optimal parameters, developed technological scheme for processing and determined consumption coefficients for raw materials, the mass balance of enriched potassium ore decomposition was calculated. The research results were reported at the international scientific and practical conferences “International Conference of Industrial Technologies and Engineering” and “Auezov Readings”.

Personal contribution of the doctoral student consists in analysis and generalization of the literary data on thesis research topic, choice of research and analysis methods, conducting the theoretical and experimental research, mathematical and statistical processing and interpretation of the research results.

Publications on the thesis topic. 10 works were published on the thesis topic, 3 of which were published in journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan; 1 paper was published in the journal included in the international database Scopus; 3 - in proceedings of international scientific and practical conferences; 3 - in other scientific editions; 1 utility patent was received.

The structure and scope of the thesis. The work is presented on 105 pages of typewritten text, consists of an introduction, 5 sections, a conclusion and 7 annexes. It contains 43 figures, 27 tables and a list of references including 104 titles.