

**METHODS OF BENEFICIATION OF POTASH ORES AND POTASH MINES**

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**ABSTRACT**

Studies were conducted on the development of the technology of flotation concentration of potassium ores: sylvinite, kainite-halite, carnallite-kainite-halite. Optimum flotation conditions are developed for each ore: salt content, density and pH level of the dispersion medium, collector of the useful component, auxiliary reagents - blowing agents, dewatering agents, depressants, to obtain a high enriched potassium concentration. The density of 1235 kg/m provides amines. Kainite-halite ore is beneficiated by direct flotation in an aqueous saturated solution of magnesium chloride with a density of 1284 kg/m<sup>3</sup> and a pH of 6–7. In beneficiation of carnallite-kainite-halite ore, beneficiation is carried out by reverse flotation in aqueous solutions of magnesium chloride with a density of 1285–1295 kg/m<sup>3</sup> and a pH of 3–4, using alkylmorpholine hydrochloride salt as a halite collector.

**Keywords:** salt composition, density and pH of the dispersion medium, potassium chloride, Halite flotation of 5 g/t ore, technical and economic indicators of potassium chloride production, anhydrite, halopelites, study of potassium salts in thin slices, (-5, 0+3.0 mm, -3.0+2.0 mm), potash rocks.

**INTRODUCTION**

The development of the potash industry is related to the needs of agriculture, which uses about 90% of potash in the form of fertilizers. This element is also used in various industries - textiles, glass, chemistry, pharmaceuticals, pulp and paper, etc.

Properties of potassium ores and minerals

The development of the potash industry is related to the needs of agriculture, which uses about 90% of potash in the form of fertilizers. This element is also used in various industries - textile, glass, chemical, pharmaceutical, pulp and paper, etc. This is due to the rapid development of potash industry in Russia, USA, Canada, Germany, Great Britain and other countries[1,2,27] . In the beneficiation of water-soluble potassium salts, it is necessary to deal with many minerals that are contained in ores and appear in salt solutions during the beneficiation of these ores. Chloride ores contain sylvine and halite, and mixed ores contain sulfate minerals (langbeinite, polyhalite, kainite, kieserite). Minerals such as leonite and xenite are formed during the beneficiation processes.

In addition to these minerals, almost all ores contain small amounts of anhydrite and small silicate and carbonate clay admixtures that are insoluble in water.

The composition of the liquid phase strongly affects the interaction of reactants with minerals and the viscosity of the medium

Enrichment of potash ores largely depends on the composition and composition of clay mixtures in them[3,8].

There are two types of potassium ore deposits - sulfate-free and sulfated. Non-sulfate deposits are more common than sulfate deposits. The main reserves are collected in Canada, the Verkhnekamskoye field (Urals), Belarus and Ukraine. Sylvinite and carnallite occur as thick layers. The amount of KCl in mined sylvinite is from 23 to 30%, and the insoluble residue is from 0.5 to 3%. These rocks, especially carnallite, also contain bromine and some trace elements[4,26].

Methods of processing and beneficiation of potash ores

Potash ores are characterized by low hardness and significant brittleness, which allows them to be easily crushed.

Hammer and impact grinders are used for dry grinding. Wet grinding is done in rod mills. The use of self-grinding potash ores provides high productivity and selectivity with good joint opening and minimal overgrinding. The potash industry uses hydrocyclones and other sieves to classify the material by size[5,6].

The possibility of thermal grinding of sylvinite ores is shown. When coarse-grained sylvinite ore is heated to 300-400°C, the halite rock is destroyed up to 5-4 mm, while the pieces of sylvinite rich in potassium chloride remain intact. Further screening succeeds in isolating a product rich in potassium chloride. Superior grinding of halite during heating is due to the presence of microinclusions of salt water and gases in it. Thermal destruction of potassium ores can be promising in combination with their electrostatic beneficiation, which requires preheating the ore to 400-500°C[7,25].

Basically, there are two industrial methods of obtaining potassium salts: flotation and halurgic. The halurgic method consists of removing potassium chloride, for example from sylvinite, with a hot recycle liquid, removing the undissolved halite to a dump. The resulting hot strong liquid is settled to separate the salt and clay sludge. Potassium chloride is crystallized from the purified hot liquid. The resulting crystals are separated from the cooled mother liquor, dried, sometimes granulated and released as a finished product. After heating, the mother liquor is returned to the initial potassium chloride washing operation[9,10,24].

World experience shows that it is better to use flotation method with additional separation of potassium chloride from residue, mud and dust by galurgical method in processing sylvinites with low content of insoluble residues. Halurgic method is used for processing of ores with complex composition and sylvinite with high insoluble residue and salt water.

Most of the potassium salts are currently enriched by flotation, despite the progressive role of the halurgic method.

Pulp cleaning before flotation is a mandatory operation. Fine mud absorbs the cationic type of collector, disrupting the flotation of large particles. Careful initial degreasing of ores is more beneficial than subsequent sludge control (using peptization reagents and other methods).

Mechanical degreasing is carried out in classifiers, hydroseparators and hydrocyclones. After grinding the ore, additional grinding is sometimes used to completely transfer the clay mixtures to the clay. Mechanical desliming is usually done in several stages. Thickeners are also used for the second stage of desliming. It has been determined that it is expedient to use reagent-dispersants (peptizers) such as sodium hexametaphosphate or sodium trisodium phosphate, syntan, etc. in mechanical application[11,22,23].

Flotation desliming of ores prior to flotation ensures more complete removal of sludge. Organic flotation regulators (e.g. polyacrylamide) improve the flotation of silty sludges by exerting a flocculating effect on them. Amines are used as collectors. As the degree of oxyethylation of amines (as well as alcohols) increases, their collective effect on clay mud increases. Because there is always a residual amount of collectors in the recycled mother liquor, factories usually only add polyacrylate to the sludge flotation. Sludge flotation is best done in pneumatic flotation machines (columns and other machines).

Aliphatic amines are used for sylvite flotation in domestic refineries. Amines in salt flotation act as collectors and foaming agents. A 1:1 mixture of amines with C16 and C18 is more active. The flotation properties of cationic collectors can be significantly improved by the addition of other surfactants, particularly alcohols[12,13]. When flotation with cationic collectors, it is also important to maintain the optimum pH value of the solution. In an alkaline environment, the effect of amines weakens. Soluble salts can also be filtered with anion-type collectors. They are used in the flotation of potassium-magnesium minerals, not silvin, but sulfuric acid. Maximum buoyancy for all minerals is at pH 7. In the flotation of salts of fatty acids and their soaps, the flotation activity can be increased by adding other surfactants that ensure the dispersion of collector micelles, which leads to the activation of flotation.

Apolar collectors are used to increase the upper limit of the volume of floating minerals. They are also used to improve the flotation desliming of sylvinitic ores.

During flotation by cation collectors of sylvinitic-carnallite ores, sodium sulfide selectively suppresses carnallite flotation. Phosphoric acid salts (eg, sodium hexametaphosphate) inhibit the flotation of kainite without affecting sylvite[14,21].

The main subject of technological mineralogy is a comprehensive study of the technical and technological properties of minerals as a function of the composition and structure of a particular rock, as well as these same properties of the rock itself. At the same time, it is necessary to take into account the entire evolution of their formation and transformation. This makes it possible to establish the causes of different behavior in technical and technological processes of the same minerals not only from certain deposits, but also from their different areas. All works on technological mineralogy are based on studies of the mineralogical, chemical and physical properties of both productive and host rocks and their constituent minerals, since host rocks are always present in the resulting ore mass to one degree or another[15,16].

The whole complex of research works on the technical mineralogy of potassium salts can be subdivided into at least two stages. The first is the study of the technical and technological properties and characteristics of rocks and minerals of productive horizons and their host rocks. The second is preliminary mapping of the studied area (site) according to the selected properties and features.

The geotechnological extraction of potassium salts by dissolution or leaching is based on their ability to dissolve in water and water-containing solutions. The intensity, speed and kinetics of dissolution determine the possibility of obtaining one or another well productivity in terms of conditioned brine, as well as the ability to control the consequences of these processes. Thus, in order to plan a geotechnological method of extraction, it is necessary to study the values of the rate and kinetics of dissolution of salt mineral grains and pieces of the rocks they compose, as well as the density and viscosity of the resulting brines[17,20].

The need for a direction in the study of certain technological properties and features of potassium ore minerals is due not only to the presence of certain enrichment and processing methods that exist in the daily practice of Russian factories, but also the possibility of using methods used in certain countries of the world at these or other deposits.

The clay minerals that make up the halopelitic material, and especially their mixed-layer formations of the illite-montmorillonite type, are characterized by a significant exchange capacity and a large specific surface area.

The second, in terms of application, is the halurgical method of processing potash rocks. This method is understood as the production of potassium salts using successive processes of dissolution of the original rock and crystallization of the final product. For the processing of rocks of potassium salts by the halurgical method, their dissolution rates in a particular salt-dissolving solution are of great importance[18,19,24].

Along with the halurgical and flotation methods of enrichment, potash ores can be enriched under industrial conditions also by the methods of electrical and gravitational separation. Clay and some insoluble minerals during the separation of polymineral ores are separated by the crown separation method. Sylvine (KCl) and halite (NaCl) are separated by electrostatic separation. To predict the electrical methods of enrichment, it is necessary to study the electrical resistivity and dielectric constant of all minerals that make up potassium-bearing rocks.

Methods for the gravity separation of potash ores are based on the difference in the density values of the minerals that make up these ores. To predict gravity methods of enrichment, it is necessary to know the density values of all mineral components of various potassium-bearing rocks.

The study of the above properties of salt minerals of potassium-bearing rocks is the main set of works on the study of their technological properties and features. The first priority among them is the study of the material composition and mineralogical and petrographic features of the potash rock and its minerals. They are the basis for predicting their technological properties. The study of the material composition is carried out by chemical, spectral, X-ray phase, mineralogical methods and by the method of resonance and infrared spectroscopy [8].

The study of mineralogical characteristics includes the study of natural mineralogical and petrographic and structural features of rocks in order to identify their technological types and varieties. Two types of study of mineralogical and technological properties are distinguished - this is the study of the mineralogical, structural and technological features of potash rocks in thin section and the study of the properties of crushed potash rocks.

In thin sections, such quantitative parameters of the rock are determined as the natural size and shape of the grains of both the potassium minerals proper and the minerals containing them;

the shape of the contours and the nature of the intergrowth planes of grains of potash and non-metallic minerals (halite, anhydrite, halopelites), as well as the number and types of microinclusions in the grains of potassium minerals, which often determine not only the color of the mineral, but also its technological properties.

Determining the natural size makes it possible to predict the yield of one or another dimension of crushed mineral particles; determination of the shape of the contours and the nature of the intergrowth planes of grains of ore and non-metallic minerals makes it possible to predict their effect during crushing (grinding) on the formation of various types of technological intergrowths of potash minerals with non-metallic minerals and the content of a useful component in these intergrowths; determination of the amount and types of micro-inclusions in the grains of potassium minerals, which cause dilution of the potassium content in them, and also cause a change in their surface properties, which makes it possible to predict their behavior in enrichment processes. The presence of mutually perpendicular thin sections makes it possible to determine the natural shape of sylvite grains along three axes. If we build graphs of the dependence of the grain size along each axis on their number in a thin section, then it is easy to determine the volumetric shape of not only the grains of potassium salts and determine their predominant size, but also the grains of the minerals containing them. On fig. 1 shows such graphs for the red varieties of sylvite from the Kr-2 formation of the Ust-Yavinsky area of the Verkhnekamskoye field.

An analysis of these materials shows that already in the process of studying potassium salts in thin sections, one can see the difference between sylvite varieties in some technological properties, such as natural size, grain shape, nature of contacts, and the number of microinclusions. It follows from the above graphs that the natural form of the pink variety of sylvite of this formation is characterized by two grain shapes: isometric and less often flattened along the h axis (i.e., tablet-like); the red variety is characterized mainly by an isometric structure of grains, less often elongated, and the grains of wax-red sylvite have both flattened along the h axis (tablet-shaped) and elongated along the a axis (spindle-shaped) shape.

Thus, already in the process of studying potassium salts in thin sections, it is possible to establish the difference in the color varieties of sylvite according to some of their technological properties, such as natural size, grain shape, nature of contacts, and the number of microinclusions.

For this area of the Verkhnekamsk potash salt deposit, a clear dependence is established between the amount of certain size classes of crushed particles of potash rocks and the natural forms of sylvite grains. In particular, the isometric shape of grains in nature when crushed up to 5.0 mm gives the highest yield of the number of large classes (-5.0 + 3.0 mm, -3.0 + 2.0 mm). In addition, the isometric shape of sylvite grains in the rock apparently has a positive effect on the formation of sylvite particles presented as aggregates from their smaller grains.

The highest yield of the number of particles of classes -2.0 + 1.0 mm and -0.5 mm is observed for sylvites with a flattened (board-like) and elongated (fusiform) shape of sylvite grains. Thus, the study of mineralogical-structural-technological properties makes it possible to outline the dimension of crushing (grinding) of potash rock, and taking into account the mineralogical composition, to identify technological types or grades of ores and roughly plan the enrichment method.

However, it is difficult to predict the quantitative yield of classes of crushed sylvite particles based on the study of thin sections alone, because the process of factory crushing has a leveling effect, i.e. the predominant dimension of sylvite grains in the rock (in thin section) is (in most of it) fragmented to smaller classes (Fig. 2a).

The results of laboratory crushing with a jaw crusher compare well with the results of mechanical crushing of ores in a salt mill and concentrator. As follows from Fig.2b, histograms of the particle size distribution of sylvinites according to the analysis of samples subjected to crushing in the laboratory, and ore according to the analysis of samples crushed in a salt mill and a flotation plant, are similar in their configuration and close in percentage of particles of individual dimensions, except for the yield of large fractions.

Therefore, it is absolutely necessary to study the mineralogical and technological properties of potash rock crushed in the laboratory. Various types of potash rocks are crushed to those dimensions, the maximum parameters of which were revealed by the results of the study of grains in thin sections (in the example under consideration, in the Ust-Yavinsky area of the Verkhnekamsk potassium salt deposit, this is up to 5.0-0.0 mm, 3.0 -0.0 mm, 2.0-0.0 mm and 1.0-0.0 mm), which are then dispersed into standard size classes.

Based on the study of the granulometric composition of crushed rock (with the construction of histograms, cyclograms, differential partial distribution curves or cumulative total distribution curves, etc.) and the mineralogical and technological analysis of crushed particles for each size class of the sieve analysis of various crushings (with the determination of the number of free particles of potash and minerals containing them in crushed rock, the number and types of their technical intergrowths, as well as the quantitative (percentage) content of all other components), the degree of disclosure of potassium minerals is determined, the percentage of constituent mineral components of crushed rock, i.e. Graphs of the mineralogical composition and changes in the degree of disclosure of potassium minerals are plotted depending on the size class for all crushing dimensions. Such calculations make it possible to predict grinding parameters.



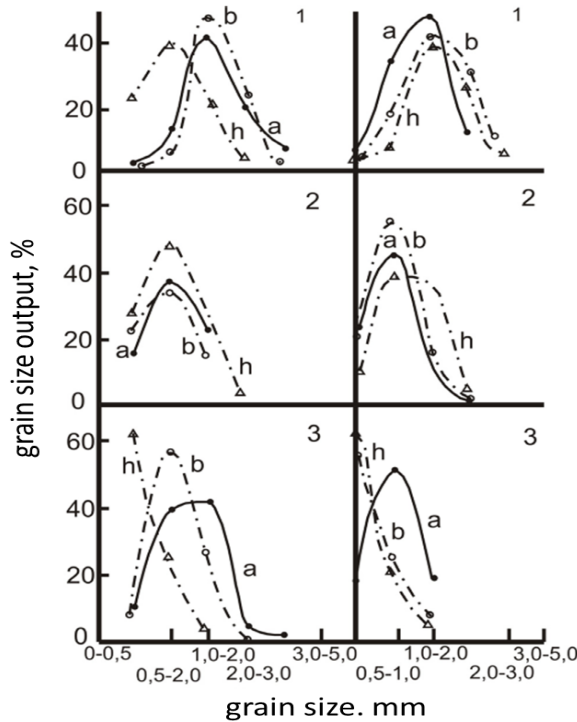


Fig. 1. Change in grain size in sylvin varieties in the Kr-2 formation of the Ust-Yayvinsky area of the Verkhnekamskoye field. 1 - pink sylvin; 2 - red sylvin; 3 – wax-red sylvin; a – grain length, b – grain width, h – grain height

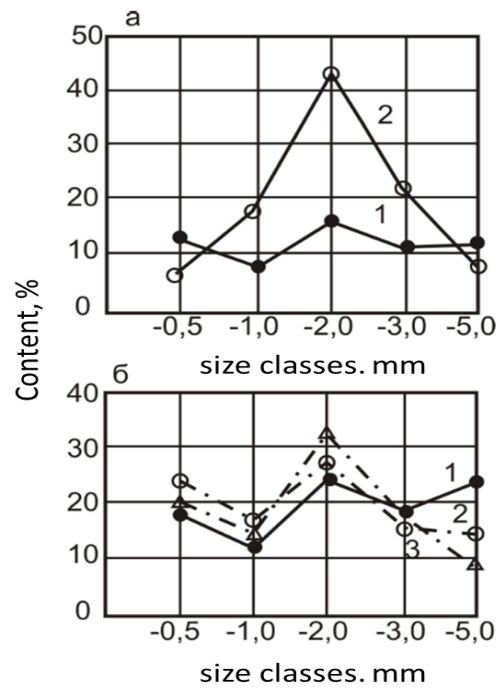


Fig. 2a. Comparison of the distribution of size classes of potash ore of the Kr-2 formation of the mine field of the Third Bereznykovsky ore occurrence of the Verkhnekamskoye deposit a – sylvite particles obtained by laboratory crushing (1) and sylvite grains in thin sections (2); b - particles of potash ore obtained during laboratory crushing (1) and after crushing in a salt mill (2) and grinding in a flotation factory (3)

Taking into account other data (for example, the content of solid micro-inclusions in potash minerals determined in thin sections, the content of magnesium chloride in the rock based on analytical studies, the content and types of clay minerals according to X-ray phase analysis, the disturbance of the crystal structure of grains of minerals composing the potash rock according to the materials of electron- paramagnetic resonance, X-ray diffraction analysis), all the above materials allow us to outline the method of enrichment.

Small classes (less than 0.1 mm) of various crushings, due to the fact that potash ores are processed both by flotation and galurgical methods, are studied in two versions: one half of the sample is studied as being part of the potash ore proper, characteristic of the flotation enrichment process, the other - as characterizing the possible composition of the non-salt component (N.O.) of potash ore after the halurgical enrichment process.

A special place in the direction of the study of crushed potash ore is occupied by the mineralogical study of the clay component of the water-insoluble residue. As is known, the basis of the flotation method for the enrichment of potash ores is a directed physical and

chemical change in the nature of the surface of salt minerals, which is achieved by treating them with selectively acting reagents-collectors and modifiers. The effectiveness of the reagents significantly depends on the composition of the clay components of the insoluble residue, because some of them (for example, montmorillonite), which have swelling interlayers, can significantly and even completely disrupt the course of the flotation process. For the developed formations of the Verkhnekamskoye field, trioctahedral chlorite and dioctahedral hydromica (illite) are common, often containing swelling montmorillonite interlayers.

It is known that the parameters of crystal lattices of mixed-layered swelling minerals noticeably change in an aqueous medium. Changes occur mainly due to an increase in interlayer distances, due to which flotation agent molecules can penetrate into these minerals. In connection with the above, it is especially important to have an idea of the area of the "inner" surface of clay minerals, which is defined as the difference between the "total" specific surface (including the "inner" surface) and the "outer" surface. The obtained data on the "inner" surface of minerals from the insoluble residue of potassium salts of the Verkhnekamsk deposit confirmed the presence of mixed-layered clay minerals in it and made it possible to establish for the southern part of the deposit an increase in the amount, firstly, of mixed-layered clay minerals up the section (in the "variegated" sylvinites, compared with the sylvinites of the underlying layer Kr-2, they are 2-5 times more) and, secondly, from west to southeast more than two times

Selected small size classes (less than 0.1 mm), where the overwhelming amount of halopelite material is concentrated, are analyzed by standard methods of optical microscopy, X-ray and infrared spectroscopy and thermal analysis; in addition, the values of their ("external", "total", "internal") specific surfaces are determined. Knowledge of the specific surface characteristics of the insoluble residue of potash ores is necessary not only to understand its behavior in the process of enrichment and to determine the nature of the relationship with surfactants, flotation reagents, but also to select a flotation enrichment scheme (with depression of clay sludge, with preliminary flotation or mechanical desliming).

Based on the results of studies to identify potash ores of different washability, the second stage of research is carried out - preliminary technological mapping, i.e. delineation on the plans and sections of the deposit for the placement of ore grades of various dressing grades or their individual features. For example, mapping of the working layer of the B. Verkhnekamskoye deposit, where it is represented over a large area by "variegated" sylvinites (composed mainly of a milky-white variety of sylvin), makes it possible to identify areas where this layer is represented by a pink-red or red variety of sylvin, and even with layers of carnallite. Ores from such a section of a given formation become difficult to be enriched or even very difficult to be enriched by those technological enrichment schemes that exist at the flotation plant at the present time. Working seams A and Kr-2 are composed of pink, red and wax-red varieties of sylvin, which differ somewhat in flotation properties. The study of the distribution of sylvinites, composed of certain varieties of sylvin, in a series of sections of the Kr-2 formation in the southern part of the Verkhnekamskoye field revealed an uneven distribution of these varieties in the formation, as well as the degree of openness of their grains over the formation area, which made it possible to predict the need for some change in the enrichment regime when mining various areas this layer. On fig. Figure 3 shows some schematic maps of the distribution



of such features for the Kr-2 formation for a part of the mine field of one of the sections of the Verkhnekamskoye deposit.

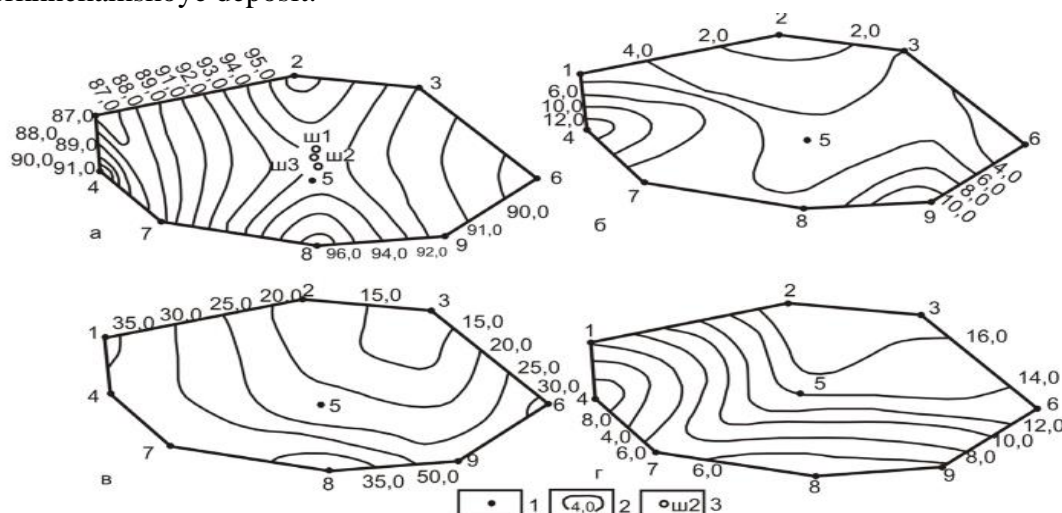


Fig. 3. Some technological maps-schemes of the Kr-2 formation of the mine field of the Third Berezniki Mining Administration of the Verkhnekamskoye deposit a - the distribution of the degree of opening of potash ore, the content as a percentage of the thickness of the formation; b – wax-red sylvinite, c – red sylvinite, d – pink sylvinite; 1 – sampling point; 2 - isolines; 3 - mine shaft

Conducting the above studies of the technical and technological properties of potash rock will not only increase the objectivity and reliability of assessing the possibility of using them for certain methods of extraction and processing, but will also allow timely focus on the most difficult problems of ore dressing and the complexity of their use, as well as significantly improve the technical, technological and economic efficiency of geological and industrial assessment of potassium salt deposits

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