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Potash Ore Processing: Technology Research and Physicochemical Properties

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ABSTRACT

The Republic of Kazakhstan is endowed with a distinctive endowment of potash ores, concentrated in the West Kazakhstan and Aktobe regions. These reserves are regarded as one of the largest in the world. The proven reserves are estimated at approximately 6 billion tons and are distributed across four major deposits: These are the Zhilyanskoye, Satimola, Inderskoye and Chelkar deposits. The article provides a concise overview of the major potassium salt deposits and the chemical composition of the associated minerals. Notwithstanding the existence of these deposits, the production of potash salts in the country, for which there is an ever-increasing demand, is yet to be established, resulting in a high level of demand. In light of this, it is imperative to conduct a comprehensive investigation into the mineralogical and chemical composition of these promising potash ores, to identify viable methods for processing natural salt systems into products that meet the high demand both within the domestic fertiliser and salt market and abroad. The Satimola deposit represents one of the largest silvinite basins yet to be sufficiently studied, and its industrial development has yet to commence. The analysis of raw materials and products was conducted using a combination of spectral microscopy, X-ray analysis, and differential thermal analysis. A comprehensive study of the composition of the silvinite ore from the Satimola deposit has been conducted. The elemental composition and the ratio of potassium and sodium salts in the mineral were established. The ore was found to have a heterogeneous composition, with sodium chloride representing the dominant component.

Keywords: potassium chloride, potassium, halurgic method, silvinite, Satimola deposite.

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Introduction

Potassium salts represent a significant and highly sought-after resource in the contemporary economic landscape. The principal product resulting from the processing of potash salts is potash fertilisers. Since the middle of the 20th century, the global population has continued to grow at a steady rate, which has increased food shortages. In the contemporary era, the intensification of food production, including the introduction of fertilisers, is a prerequisite for global agricultural practices. Consequently, at the beginning of the 21st century, there was a notable surge in demand for potash fertilisers. For the first time since the 1970s, projects for the expansion of existing production facilities, as well as the study of new fields, and the design and construction of new enterprises, have commenced. In addition to the well-known potassium basins of Western Europe, Canada, Russia and Belarus, new deposits of potassium salts are currently being explored in Central and Southeast Asia, South America, West and East Africa, as well as previously undeveloped euporite deposits in North America (Rauche, 2015; Cocker, 2016). The global total of potash salt reserves is estimated at 40 billion tons. According to reference [1], the leading producers of potassium are Canada, Russia, Belarus, and Germany (Figure 1).

Nevertheless, the intensification of production inevitably conflicts with the objective of preserving and developing the natural environment of the regions in which it is situated, while simultaneously minimising anthropogenic impact. The potash industry represents a complex economic sector, encompassing both mining and chemical production [2].

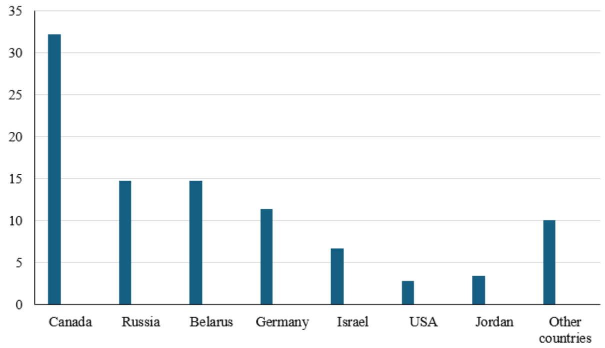

Figure 1 - Distribution of potash production by country, % [1]

Potassium is a relatively common chemical element. In terms of its concentration in the Earth's crust (approximately 2%), potassium is the second most abundant element after oxygen, with silicon, aluminium, iron, calcium and sodium also present in significant quantities [3]. Potassium is present in several naturally occurring minerals, including feldspar, granites, leucites, gneiss, and solid fossil salt deposits. It is also found in salt waters of marine and continental origin. The most common minerals containing potassium are as follows: sylvine KCl, carnallite $KCl•MgCl_2•6H2O$, langbeinite $K_2SO_4•2MgSO_4$, cainite KCl- $MgSO_4•3H_2O$, shenite $K_2SO_4•MgSO_4•6H_2O$, glazerite $K_2SO_4•XNa_2SO_4$, polygalite $K_2SO_4•MgSO_4•2CaSO4•2H_2O$, and alunite $K_2SO_4•A1_2(SO_4)_3•4Al(OH)_3$. The potassium-containing aluminosilicates are as follows: $K_2O•Al_2O_3•6SiO_2$; muscovite $K_2O•3Al_2O_3•4SiO_2•2H_2O$; nepheline $(K, Na)_2O • Al_2O_3 • 2SiO_2$; leucite $K_2O • Al_2O_3 • 4SiO_2$ [4].

The main sources of potassium compounds are soluble potassium salts such as sylvinite, carnallite, langbeinite and kainite [[5], [6]]. In Kazakhstan, the main potassium salt reserves are located near the North Caspian Sea (potassium chloride salts) and the Ural Mountains in Aktobe (potassium sulphate salts). In the North Caspian region, the balance reserves are 8 million tonnes, with inferred resources of about 500 million tonnes. In the vicinity of the Ural Mountains (Aktobe), balance reserves are estimated at 100 million tonnes and inferred reserves at 300 million tonnes. The inferred potash resource in Western Kazakhstan in the 1980s was 1 billion tonnes, including 217 million tonnes of sulphate salts.

The Inder salt dome deposit has proven reserves of 709 million tonnes, of which 40 million tonnes are in commercial categories. Lake Inder in Inder district contains about 1.5 billion tonnes of salt, of which 647 million tonnes have been explored since 1993 [7].

Potassium salts are an important commercial product of Kazakhstan. Studies of their raw material base began in the 1950s [8]. The availability of reserves and the demand for potash fertilisers require the development of new processing technologies. The potash industry development strategy includes increasing explored reserves and introducing innovative technologies [[9], [10]]. It is also important to develop resource-saving potash processing technologies and improve the qualifications of labour resources for the efficient operation of the mining and processing complex [11].

The high demand for potassium salts in Kazakhstan emphasises the relevance of developing technologies for the production of chlorides, sulphates, phosphates, and other products from local chloride salts [12].

The Republic has significant reserves of natural salts containing sodium and potassium chloride. These salts are found in different regions of the country, including Atyrau (deposits of Inder, Chelkar, Satimola), and Zhambyl regions [[13], [14]].

The Satimola, Inder, Shalkar and Zhylandy deposits have some of the largest potash reserves. A mining and processing complex is currently under construction at the Satimola deposit to produce potassium chloride. The mine is expected to have a capacity of 25 million tonnes of potash ore per year and the reserves will take more than 50 years to develop. Geological studies began as early as the 1960s, and in 2010 a potash fertiliser production technology was developed [15].

The Satimola deposit, located in the West Kazakhstan region, contains potassium and boron salts. The potassium content of the ore characterises ores for medium, high and priority recovery. The salt and mineral composition of the samples Satimola deposit is shown in Table 1,2 [[16], [17]].

Table 1- Salt content of the ore [16]

№	Mass fraction, %					
	KCl	NaCl	$CaSO_4$	$MgSO_4$	K_2SO_4	i/r
1	27.2	65.1	14.4	1.44	1.13	0.48
2	42.8	52.44	1.83	1.47	0.96	0.33
3	32.9	60.78	2.65	2.33	0.86	0.48

Table 2 - Mineral composition of the ore [16]

№	Mass fraction, %					
	Sylvin	Halite	Anhydrite	Polyhalite	Kieserite	i\r
1	27.21	65.1	2.63	3.91	0.76	0.48
2	42.76	52.4	0.33	3.32	0.93	0.33
3	32.86	60.8	1.31	2.98	2	0.48

When studying the mineralogy of halide deposits of the Satimola structure, it is important to consider the minerals of the salt beds. The salt beds contain more than 30 minerals including halogens, sulphates, borates and carbonates due to the presence of clayey material and differences in their quantities and textures.

Lake Inder is a large salt lake in the northern part of the Atyrau region of Kazakhstan. Since 1932, potash salts have been prospected in the pre-Caspian lowland. From 1939 to 1945, drilling operations on the Inder Upland revealed deposits of polyhalite rocks and sylvinites, and further research was carried out by the Inder Geological Exploration Expedition and the Research Institute of Galurgy [13].

The Zhylandy deposit in the Ural region, 5-10 km from Aktobe, has potash reserves of 500 to 600 million tonnes of crude ore [18]. The rocks of the deposit contain polyhalite (65%) and sylvinite with anhydrite and calcite. Polyhalite deposits are located at a depth of 235-770 metres and are separated by layers of rock salt. The Shalkarskoye potash deposit is a salt dome with commercial layers of potassium-magnesium salts at a depth of 300-1000 metres [[20], [21]].

From the analytical review, it can be concluded that potash processing is of high relevance due to the significant resources and long-term development prospects. The Satimola deposit, with more than 50 years of reserves, is of strategic importance for agriculture, as potash is an important fertiliser. The development of efficient processing technologies will support the region's economic growth, creating jobs and improving the environmental situation. The introduction of resource-saving technologies will ensure sustainable development of the industry and meet the growing demand for potash fertilisers.

Experimental part

Methods of analysis. The analysis of raw materials and products was conducted using a combination of spectral microscopy, X-ray analysis, and differential thermal studies. X-ray identification was conducted on a stationary installation, designated DRON-4, which employs a tube with a cobalt anode. The voltage applied to the tube was 40 kV, and the current was 40 mA. The decoding of samples and the search for phases were conducted using the Search/Match program with the 2003-2023 CRYSTAL IMPACT powder diffractometric database, Bonn, Germany. A raster electron microscope (REM) JSM 6490l V (Jeol, Japan) was employed for the microscopic spectral analysis of raw materials. The REM is based on scanning the surface of the sample with an electronic probe, whereby a wide range of radiation is recognised during this process. The ore was subjected to differential thermal analysis using a Q-1500D derivatograph. A derivatograph is a device for complex thermal analysis that allows for the simultaneous measurement of changes in temperature and mass, the rate of temperature change and the change in enthalpy of the substance under study.

Experimental methodology. A pre-prepared solution containing 12.5% potassium chloride (KCl) and 18.5% sodium chloride (NaCl) is placed in the reactor, which corresponds to the composition of the mother liquor obtained after crystallization of potassium chloride (KCl). This solution serves as the basis for further leaching and separation of the components. The reactor is placed in a thermostat, where it is heated to a temperature of 100 °C. After reaching the set temperature, a set amount of sylvinite is added to the reactor. Leaching of potassium chloride (KCl) is carried out within 1- 1.5 hours. During this period, it is important to maintain a stable temperature (100°C) and continue mixing the solution to speed up the dissolution process and ensure complete potassium extraction. At the end of the leaching time, the process is interrupted, and the mass from the reactor is transferred to the filter for hot filtration. For this purpose, a cylinder and a funnel are used, which are pre-weighed, which allows you to accurately take into account the mass of the filtrate. The filtrate is collected in pre-weighed vessels (cylinder or glass), after which the solution and the wet NaCl precipitate remaining after filtration are weighed. After collecting the filtrate, the solution is cooled under running water to 25 ° C. As a result of cooling, a precipitate of CL precipitates on the surface of the solution. This precipitate is further filtered and then weighed to determine the mass of the extracted potassium. After all operations, the data obtained is analyzed, calculating the effectiveness of leaching of potassium oxide and determining the potassium content in the sediment.

The discussion of the results

The objective of this research was to obtain a natural mineral potassium from the Satimola ore. The resulting mineral sample is illustrated in Figure 2.

Figure 2 - Natural Potassium Mineral from Satimola Ore

In order to fully study the mineral composition, a series of physicochemical analysis methods were employed, including raster electron microscopy, differential thermal analysis and X-ray phase analysis. The results of the XRF (Fig.3) indicated that the mineral is composed of 81.2% NaCl and 13.1% KCl, with a further 5.7% constituted by okenite mineral.

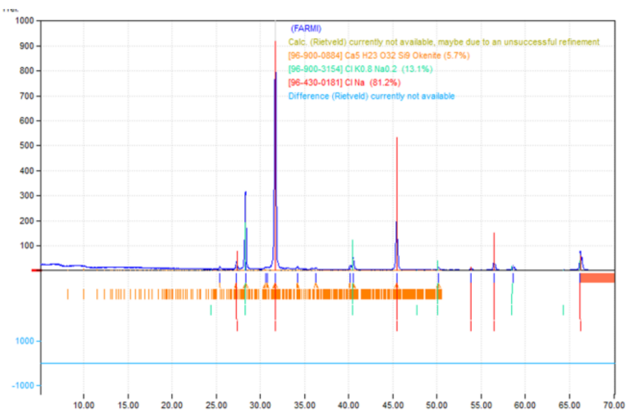

Figure 3 – XRF of potassium mineral from Satimola ore

The results of the REM analysis (Fig.4., Tab.3.) indicate that the ore contains significant quantities of sodium, potassium and chlorine elements. Upon calculation of the elemental composition of the salts, it was determined that the mineral comprises 68% NaCl and 32% KCl.

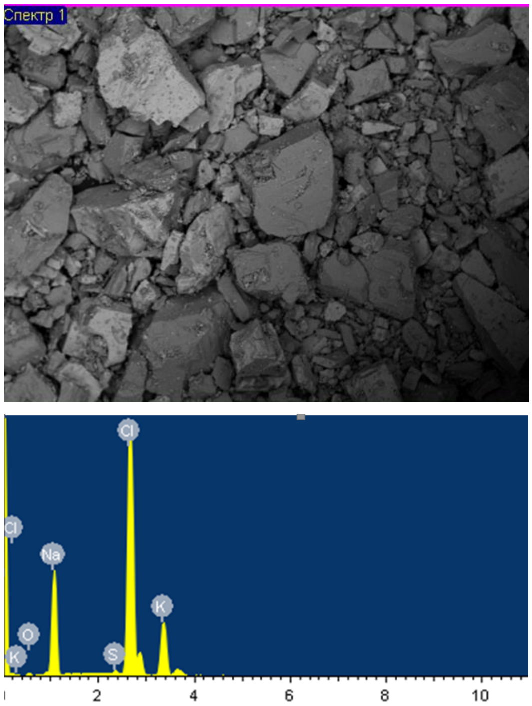

Figure 4 – Microstructure image and spectrogram of potassium mineral from Satimola ore

Table 3 - Elemental composition of potassium mineral from Satimola ore

Element	O	Na	Cl	S	K	Total
Mass. %	3.39	26.78	52.29	0.33	17.21	100.0

The DTA curve (Fig.5) of the natural salt of potassium chloride and sodium with a twofold predominance exhibits four stepwise exothermic effects and two intense endothermic effects.

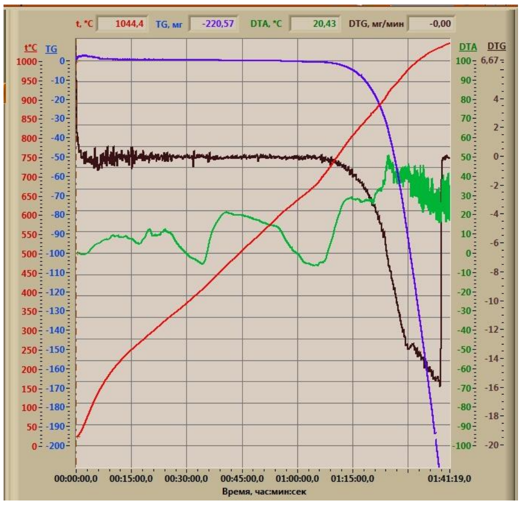

Figure 5 - Differential-thermal analysis of potassium mineral from Satimola ore

The stepwise exoeffects observed in the region of 230-330°C are indicative of the molecular-bound moisture. At 470°C, the exothermic effect indicates the removal of crystallohydrate moisture. An intensified endoeffect at 670°C is linked to the decomposition of potassium chloride salt. The stepwise curve of the endoeffect in the region of 950°C is indicative of the decomposition of the complex of inorganic salts.

The discrepancy in salt content between the REM and XRF results can be attributed to the unequal distribution of elements in the resulting sample. As illustrated in Figure 2, the sample comprises a mixture of pink, white-yellow, and maroon crystals. To comprehensively examine the mineral's composition, a detailed physical and chemical analysis was conducted on each individual crystal. The elemental analysis revealed that the red-coloured composition of the mineral (Fig.6., Tab.4.) is predominantly composed of potassium chloride, with a range of 90-98%.

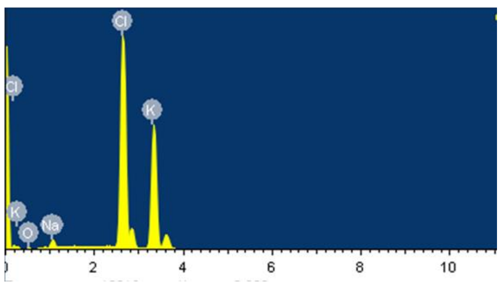

Figure 6 - Spectrogram of red crystals of potassium mineral from Satimola ore

Table 4 - Elemental composition of red crystals of potassium mineral from Satimola ore

Element	O	Na	Cl	K	Total
Mass. %	3.01	3.21	48.52	45.26	100.0

The results of the elemental analysis of the white crystals (Fig.7., Tab.5.) of the natural mineral from the Satimola deposit demonstrated that the sample contains 97-99% sodium chloride, which is distinguished by markedly intense picts of sodium and chlorine elements.

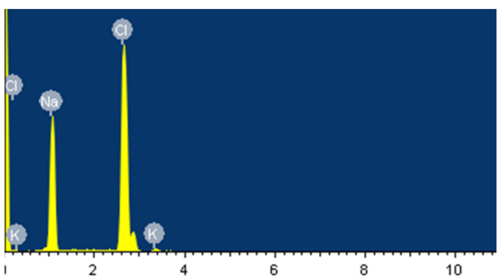

Figure 7 - Spectrogram of white crystals of potassium mineral from Satimola ore

Table 5 - Elemental composition of white crystals of potassium mineral from Satimola ore

Element	Na	Cl	K	Total
Mass. %	39.15	59.75	1.10	100.0

According to the results of physico-chemical analyses, the sample contains 81.2% sodium chloride (NaCl) and 13.1% potassium chloride (KCl), which indicates the presence of two main components in the mineral — halite (NaCl) and sylvinite (KCl). A high level of sodium chloride indicates the predominance of halite, which is typical for minerals formed under conditions of evaporation of water, such as in salt deposits. The sample also contains 5.7% okenite, a calcium silicate mineral that is an insoluble residual. This indicates that calcium compounds could be involved in the formation of the mineral, forming okenite as a by-product. Okenite is insoluble in water and is part of the insoluble residue, which indicates its role as a mineral that cannot be dissolved during processing. The sample is a mixture of halite and silvinite with the presence of okenite. This composition is typical for potash deposits or evaporative deposits, where sodium and potassium chlorides, as well as insoluble minerals such as okenite, can coexist. This confirms that the sample is potentially promising for the extraction of potassium and sodium salts, as well as for further research for possible processing.

The halurgical method was chosen for processing the potassium salt of the Satimol deposit. The halurgic method of mineral processing has several key advantages over flotation, including higher separation efficiency, less dependence on chemical reagents, a high degree of extraction of target components, and the ability to process complex mineral compositions. These aspects make the halurgy method preferable in several cases, especially in the processing of potassium and sodium salts, where the accuracy and purity of the final product play an important role. The processing of this sample by halurgy involves the effective extraction of sodium chloride (NaCl) and potassium chloride (KCl) by dissolution and crystallization, as well as the processing of the insoluble mineral okenite to obtain additional products. This approach will make it possible to obtain high—quality products - potassium and sodium salts, which can be used in industry, as well as calcium compounds, if necessary.

By the method of metallurgy described earlier, the technological scheme is shown in Figure 8.

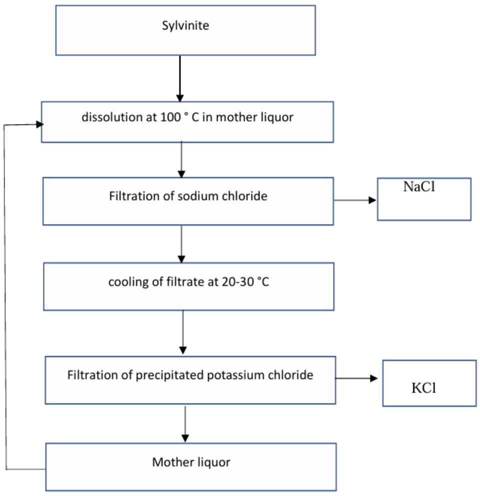

Figure 8 - Technological scheme of potassium chloride processing by the halurgic method

Processing of potash ore allowed to obtain high—quality products - potassium chloride (KCl) and sodium chloride (NaCl). According to the experimental results, the yield of the potassium chloride product was 95-98% of the theoretically possible, which indicates a high efficiency of leaching and separation of components during processing.

Elemental analyses of the obtained potassium and sodium chlorides, carried out using spectroscopy methods, showed that the products have a high degree of purity and meet the standards for further industrial use. The spectrograms obtained during the analysis, as well as the results of the elemental analysis, are shown in Figures 9,10 and Tables 6,7, which reflect the content of potassium and sodium in the obtained substances.

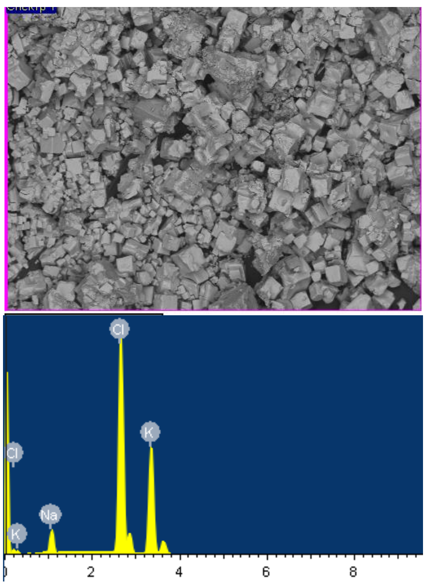

Figure 9 – Microstructure image and spectrogram of potassium chloride obtained by the halurgic method

Table 6 - The elemental composition of potassium chloride obtained by the halurgic method

Element	Na	Cl	K	Total
Mass. %	3.17	50.66	46.17	100.0

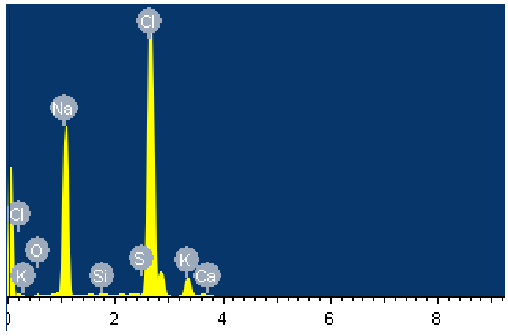

Figure 10 – Spectrogram of sodium chloride obtained by the halurgic method

Table 7 - The elemental composition of sodium chloride obtained by the halurgic method

Element	Na	Cl	O	S	Total
Mass. %	3.49	55.47	1.98	0.16	100,0
Element	Ca	K	Si		
Mass. %	0.30	2.95	0.18		

These data confirm the success of the applied technology of halurgy for the separation of potassium and sodium salts, and also demonstrate the stability and high degree of extraction of useful components from the source ore.

The elemental analysis of the obtained products, including potassium and sodium chloride, confirmed the high degree of purity of these compounds, which makes them suitable for further use in agriculture and the chemical industry. The spectrograms obtained during the analysis showed compliance of the potassium and sodium content with the established standards, which confirms the success of the chosen technology. Thus, the results of the study confirm the prospects of the halurgy method for processing potash ores, ensuring effective separation of components and obtaining high-quality products. This technology has potential for industrial applications, especially in the context of the need to increase the efficiency of processing potassium and sodium salts, as well as improve the environmental safety of the process.

Conclusions

The article offers a concise overview of the occurrence of large deposits of potassium salts, as well as an analysis of the chemical composition of minerals.

A comprehensive study of the chemical composition of the silvinite ore from the Satimola deposit has been conducted. The elemental composition and the ratio of potassium and sodium salts in the mineral were established. Additionally, it was established that the naturally occurring mineral potassium in the Satimola deposit exhibits a minor insoluble residue. The ore was found to have a heterogeneous composition, with sodium chloride representing the dominant component.

According to the results of physico-chemical analyses, the sample contains 81.2% sodium chloride (NaCl) and 13.1% potassium chloride (KCl), which indicates the presence of two main components in the mineral — halite (NaCl) and sylvinite (KCl). A high level of sodium chloride indicates the predominance of halite, which is typical for minerals formed under conditions of evaporation of water, such as in salt deposits. The sample also contains 5.7% okenite, a calcium silicate mineral that is an insoluble residual.

In the course of the study, the technology of processing potash ore by the method of halurgy was considered, which demonstrated high efficiency in the extraction of potassium oxide and sodium chloride. The technique, including leaching in solution followed by filtration and precipitation, made it possible to obtain potassium chloride with a yield of 95 to 98%, which indicates the high productivity of the process.

CRediT author statement: D.Urazkeldiyeva : Methodology, formal analysis, investigation, Data writing, Original draft preparation, writing– review and editing; **A.Kadirbayeva:** Data curation, Reviewing and Editing; **Sh.Koshkarbayeva:** Investigation.

Conflicts of Interest. On behalf of all authors, the correspondent author declares that there is no conflict of interest.

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Калий кенін өңдеу: технологиялары мен физика-химиялық қасиеттерін зерттеу

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ТҮЙІНДЕМЕ

Қазақстан Республикасының Батыс Қазақстан және Ақтөбе облыстарында калий кендерінің бірегей қорлары шоғырланған. Бұл қорлар әлемдегі ең ірі қорлардың бірі болып саналады. Дәлелденген қорлар шамамен 6 миллиард тоннаға бағаланады және төрт ірі кен орындарына бөлінеді: олар Жилянское, Сатимола, Индер және Челкар кен орындары. Мақалада калий тұздарының негізгі кен орындары мен онымен байланысты минералдардың химиялық құрамы туралы қысқаша шолу берілген. Бұл кен орындарының болуына қарамастан, елімізде сұраныс үнемі өсіп келе жатқан калий тұздарын өндіру әлі жолға қойылмаған. Осыны ескере отырып, табиғи тұз жүйелерін тыңайтқыштар мен тұздардың ішкі нарығында да, шетелде де жоғары сұранысты қанағаттандыратын өнімдерге айналдырудың өміршең әдістерін анықтау мақсатында осы перспективалы калий кендерінің минералогиялық және химиялық құрамын жан-жақты зерттеу өте маңызды. Сатимола кен орны әлі жеткілікті зерттелмеген ең ірі сильвинит бассейндерінің бірі болып табылады және оның өнеркәсіптік дамуы әлі басталған жоқ. Шикізат пен өнімге талдау спектрлік микроскопия, рентгендік талдау және дифференциалды термиялық талдаудың көмегімен жүргізілді. Сатимола кен орнындағы сильвинит кенінің құрамына жан-жақты кешенді зерттеу жүргізілді. Элементтік құрамы және минералдағы калий мен натрий тұздарының қатынасы анықталды. Сонымен қатар, Сатимола кен орнының табиғи калий минералында ерімейтін қалдықтардың аздаған мөлшері болатыны анықталды. Кеннің құрамы әртекті екені және оның құрамында натрий хлориді басым екендігі дәлелденді.

Түйін сөздер: калий хлориді, калий, галургиялық әдіс, сильвинит, Сатимола кен орны.

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Переработка калийной руды: исследование технологий и физико-химических свойств

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АННОТАЦИЯ

Республика Казахстан обладает уникальными запасами калийных руд, сосредоточенных в Западно-Казахстанской и Актюбинской областях. Эти запасы считаются одними из крупнейших в мире. Доказанные запасы оцениваются примерно в 6 миллиардов тонн и распределены по четырем крупным месторождениям: Жилянскому, Сатимольскому, Индерскому и Челкарскому. В статье представлен краткий обзор основных месторождений калийных солей и химического состава сопутствующих минералов. Несмотря на наличие этих месторождений, производство калийных солей в стране, спрос на которые постоянно растет, еще предстоит наладить. В свете этого крайне важно провести всестороннее исследование минералогического и химического состава этих перспективных калийных руд с целью определения эффективных методов переработки природных солевых систем в продукты, которые удовлетворяют высокому спросу как на внутреннем рынке удобрений и соли, так и за рубежом. Месторождение Сатимола представляет собой один из крупнейших сильвинитовых бассейнов, который еще недостаточно изучен, и его промышленное освоение только начинается. Анализ сырья и продуктов был проведен с использованием комбинации методов спектральной микроскопии, рентгеноструктурного анализа и дифференциального термического анализа. Проведено комплексное исследование состава сильвинитовой руды месторождения Сатимола. Установлен элементный состав и соотношение солей калия и натрия в минерале. Кроме того, было установлено, что природный минерал калия месторождения Сатимола содержит незначительное количество нерастворимых остатков. Было установлено, что руда имеет неоднородный состав, при этом преобладающим компонентом является хлорид натрия.

Ключевые слова: хлорид калия, калий, галургический метод, сильвинит, месторождение Сатимола.

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