

# An Innovative Environmentally Friendly Processing Method of Promising Carnallite Ores

**Aigerim Assylkhankyzy**

Mukhtar Auezov South Kazakhstan University, 160012 Shymkent, Kazakhstan  
asykhankyzy092@mail.ru (corresponding author)

**Galina Seitmagzimova**

Mukhtar Auezov South Kazakhstan University, 160012 Shymkent, Kazakhstan  
galinaseit@mail.ru

Received: 27 March 2025 | Revised: 2 May 2025 and 11 May 2025 | Accepted: 15 May 2025

Licensed under a CC-BY 4.0 license | Copyright (c) by the authors | DOI: <https://doi.org/10.48084/etasr.11159>

## ABSTRACT

This paper investigated a reagent-free approach for processing carnallite raw materials from the Zhilyan deposit in Kazakhstan to produce high-quality potassium fertilizers. A new method was developed based on the principle of fractional isothermal crystallization of mineral salts according to the temperature-dependent solubility differences of potassium and sodium chloride in the KCl-NaCl-H<sub>2</sub>O system between 100 °C and 25 °C. The process analysis revealed high efficiency capable of achieving a minimum water consumption, with verification by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The proposed technique could create an inexpensive and sustainable solution with no wastes for processing carnallite ores while also supporting the domestic fertilizer industry development in Kazakhstan and Central Asia.

*Keywords-potash fertilizer; carnallite; crystallization; mother liquor; halite; fractional separation*

## I. INTRODUCTION

Potash plays an important role in the global economy, particularly in ensuring food security. These natural minerals are widely utilized across various sectors, with almost 95% used in the fertilizing production to enhance the agricultural industry. Potassium salts have recently gained attention due to global climate change and the need for sustainable agricultural practices. According to preliminary data, in 2022, 41 million tons of K<sub>2</sub>O were produced worldwide [1].

Potash ores deposits are found in the subsoil of 20 countries, with recoverable reserves of about 3.7 billion tons of K<sub>2</sub>O and resources of 250 billion tons. Four of the largest producers include Canada, Russia, China, and Belarus, which provide approximately 75-80% of the global production. Additionally, Germany, Israel, and Jordan contribute to the global production by about 17% [1]. Besides these countries, the Central Asian region of the CIS countries has gained significant reserves of potassium-containing ores. In order to provide the domestic and foreign markets with potassium fertilizers, a number of countries in this region (Kazakhstan, Turkmenistan, Uzbekistan) have intensified their efforts to create their own production industry. The interest of these countries in potassium fertilizer production is also due to the proximity of large distribution markets (China, India, etc.) [2].

Natural minerals, such as kainite and sylvinit -products of industrial processing of minerals, mixed potassium salts, and electrolyte solutions- are chloride-type potassium fertilizers. In contrast, non-chloride potassium fertilizers include potassium sulfate and potassium magnesium sulfate. Both types of potassium fertilizers are water-soluble, easily assimilated, and provide the necessary nutrients for plant growth [3, 4].

The processing of sylvinit (NaCl·KCl) and carnallite (KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O) ores into potassium chloride is typically performed using flotation or the mineral-salt method, where potassium chloride is leached from sylvinit with hot recycled liquor, followed by the removal of the halite sediment to the dump [5]. To enrich ore for potassium, the incomplete dissolution method is often deployed in which the crushed ore is treated with an amount of water, insufficient to dissolve all potassium chloride [6].

There is limited information about the processes/processing of carnallite ores, as the majority of research focuses on the production of artificial carnallite and final liquors, which are then processed into bischofite and metallic magnesium [7]. The potassium chloride production from carnallite through flotation enrichment and subsequent carnallite decomposition is considered less cost-effective compared to its extraction from sylvinit [8-14].

The Republic of Kazakhstan possesses some of the largest reserves of potash ores, with major deposits located in the Aktobe, Atyrau, and West Kazakhstan regions. Especially, the Zhilyan deposit placed in Aktobe region, is characterized by a large territory, sharp fluctuations in conditions of occurrence, thickness of the ore bodies, and content of useful components. The upper layer of potassium salts includes sylvinites and sylvinite-carnallites, and a rock salt layer with a thickness of 30-120 m separates it from the polybasite layer. Sylvinites and sylvinite-carnallites occur in the form of sheet-like lenses, 1-6 km in length and 150-500 m in width, at depths ranging from 318 to 670 m and the thickness varying from 1-70 m [15-16]. The Zhilyan deposit contains over 1 billion tons of potassium salts with potassium oxide ( $K_2O$ ) content ranging from 8% to 18.6%, which makes it an important national resource. Although geological exploration and reserve assessment have been conducted, subsoil users have not yet moved to the production stage [17, 18].

Previous research has investigated the composition and processing of carnallite salt from the Chelkar deposit, revealing complex mineralogical content and the need for preliminary purification of raw materials from sodium chloride impurities to obtain potassium sulfate, as well as the need to remove the insoluble residue from composition using nitric acid decomposition of the enriched ore [18]. The utilization of the nitric acid solution resulted in high water consumption for washing out the insoluble calcium sulfate precipitates, leading to toxic emissions of nitrogen oxides and corrosion of the used equipment. Zhilyan salts also contain carnallite as the main component, but until now no study has examined its mineral composition and processing potential.

Within the framework of global efforts to reduce environmental impact from agricultural and industrial activities, the development of sustainable techniques for potash ore processing, including those that result in ballast-free potash fertilizers is of great importance [19]. For Zhilyan type carnallite ores, acid decomposition can be excluded due to the absence of insoluble components. Therefore, a promising approach is the reagent-free mineral-salt method, which reduces both reagent and water consumption while mitigating negative environmental impacts.

## II. MATERIALS AND METHODS

The carnallite ore from the lower layer of the Zhilyan deposit contains (by weight): 77.4% carnallite ( $KCl \cdot MgCl_2 \cdot 6H_2O$ ), 8.0% halite ( $NaCl$ ), 10.9% periclase ( $MgO$ ), and a mixture of carnallite and brucite of 3.7% [20]. This composition reveals that the Zhilyan salt does not contain insoluble impurities in the form of gypsum or anhydrite. This means that it is a raw, completely water-soluble material, which may simplify the process of removing impurity sodium chloride from it.

The contents of  $K_2O$ ,  $Na_2O$ , and chloride ions in the liquid and solid phases were determined using the pH meter/ion meter ITAN. The combined standard uncertainty of these measurements was calculated based on two parallel sample measurements, accounting for uncertainties in sample weighing, calibration, and ion meter readings. Quantitative

XRD analysis of solid phase samples was carried out using the D8 Advance Bruker apparatus (Germany). For microscopic spectral analysis of raw materials and products, a SEM JEOL JSM-6490LV (Japan) was applied.

The separation process of Zhilyan salt was studied using an isothermal fractional evaporation method and separate polythermal crystallization. This technique consisted of gradual evaporation of the saturated solution at 100 °C during which crystallization of different compositions occurred depending on their crystallization field indicated in the solubility diagram in the  $KCl-NaCl-H_2O$  system. Potassium and sodium chlorides were further split through the mineral-salt method, based on different solubility of salts in the same system with a temperature change [7, 21].

During the subsequent cooling of the partially evaporated solution, the crystallization of an additional amount of salt took place, which was then removed by filtration. Further evaporation of the resulting eutonic solution led to the formation of additional crystals, again dependent on their specific crystallization zones. A schematic representation of the fractional separation of Zhilyan salt is provided in Figure 1.

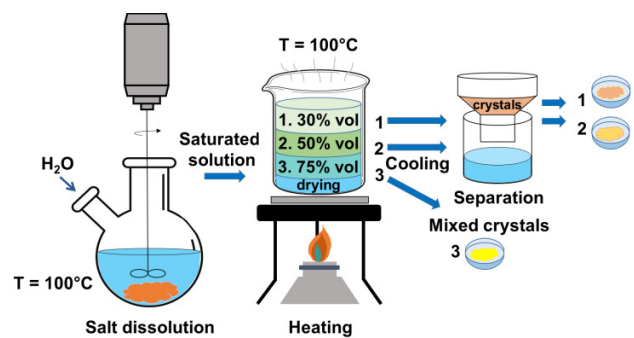


Fig. 1. The process of fractional separation of Zhilyan salt.

## III. RESULTS AND DISCUSSION

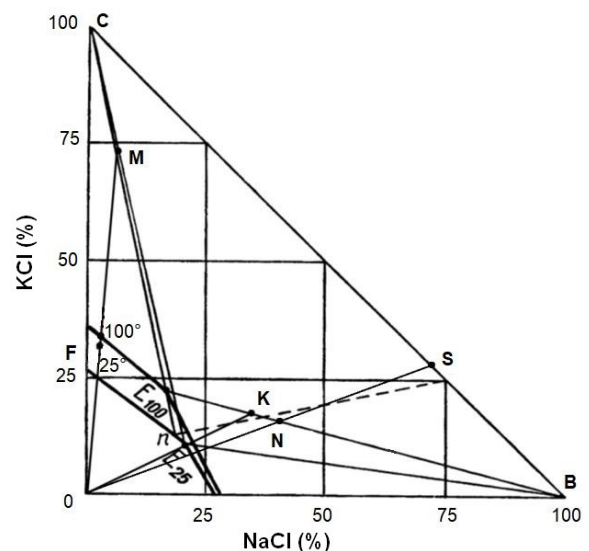


Fig. 2. Solubility diagram in the  $KCl-NaCl-H_2O$  system.

For fractional crystallization of salts, the required water consumption for a saturated solution at 100 °C was experimentally determined to be 1.67 weight parts of H<sub>2</sub>O per 1 weight part of salt. This value was validated based on calculations according to the solubility diagram in the KCl-NaCl-H<sub>2</sub>O system (Figure 2).

The effect of evaporation degree on the composition of the forming liquid and solid phases was investigated across the range of 0-75% and up to complete drying of the solution. The composition of the crystallized phases and mother liquors, as well as the intermediate cooling of the filtrates with crystallization of salts are presented in Table I.

During the evaporation of a water portion, registered by a 30% reduction in solution volume, potassium chloride crystals started to form as the solution became more concentrated. According to Table I and the salt spectrograms (Figure 3), at

the first evaporation stage (No. 1 in Table I), the solid phase contained 47.49% K<sup>+</sup>, 50.21% Cl<sup>-</sup>, and minor impurities of 2.3% Na<sup>+</sup>, with no magnesium ions (Figure 3(a)). The subsequent cooling of the solution to 25 °C, shifted the system composition into the KCl crystallization field, resulting in further crystallization of pure potassium chloride with a content of 45.57% K<sup>+</sup> and 48.97% chloride ions in the complete absence of sodium ions (Figure 3(b)).

Columnar octahedral well-faceted crystals were detected in Figure 3(a), while homogeneous transparent crystals of layered texture of cuboctahedral shape were observed in Figure 3(b). These crystals are easily separated from the liquid phase through centrifugation and then dried. The maximum number of crystals that can be separated in the solid phase, occurred at equilibrium with the eutonic solution (point E<sub>100</sub> in Figure 2), which had a composition of 16.85% NaCl and 21.75% KCl.

TABLE I. COMPOSITION OF PHASES DURING THE FRACTIONAL PROCESSING OF ZHILYAN ORES

Step	Process conditions	Evaporation degree (%)	Phase	Content			
				Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>
-	Saturated solution	0	-	2.83	13.00	1.18	15.02
1	Evaporation of saturated solution	30	Liquid	3.98	15.88	1.34	16.91
			Solid	0	47.49	2.30	50.21
	Cooling	30	Solid	0.28	45.57	0	48.97
2	Evaporation of solution	50	Liquid	5.61	17.67	3.23	18.60
			Solid	0.38	11.73	27.42	54.71
	Cooling	50	Solid	0.68	35.32	9.86	49.69
3	Evaporation of solution	75	Liquid	9.80	14.74	4.34	23.10
			Solid	8.46	28.77	1.01	54.85
	Drying the remaining solution	100	Liquid	6.82	11.12	2.20	23.30
4	Evaporation of mother liquid	30	Liquid	6.82	11.12	2.20	23.30
			Solid	1.40	37.75	5.45	53.50

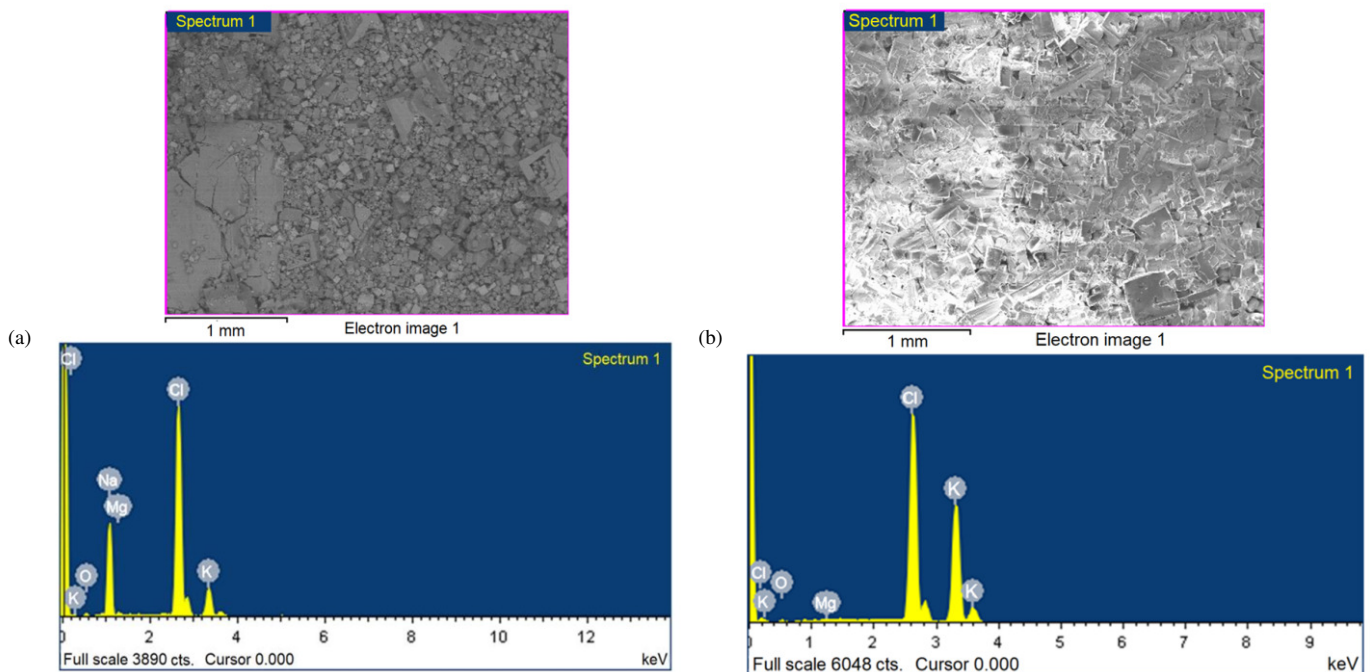


Fig. 3. Micrographs and spectrograms of salts crystallizing at 30% evaporation: (a) after evaporation, (b) after cooling.

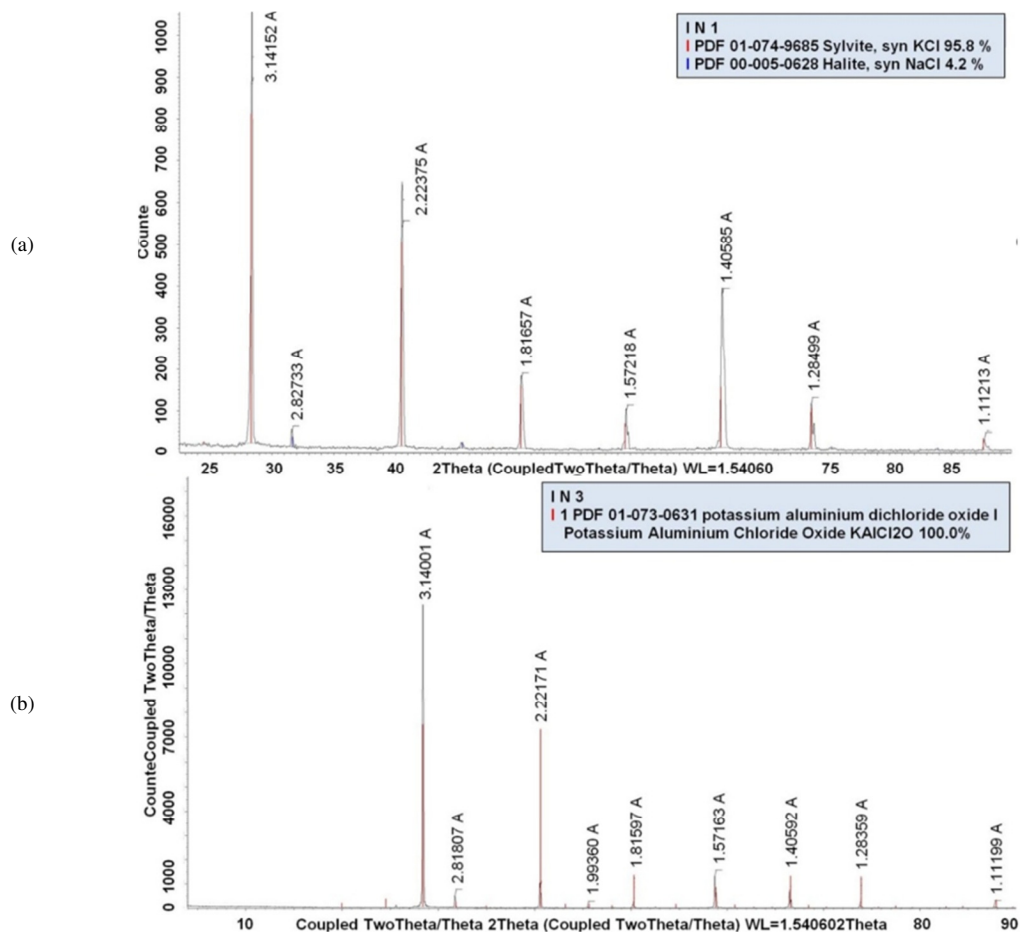


Fig. 4. XRD patterns of crystallized salts: (a) after evaporation, (b) after cooling.

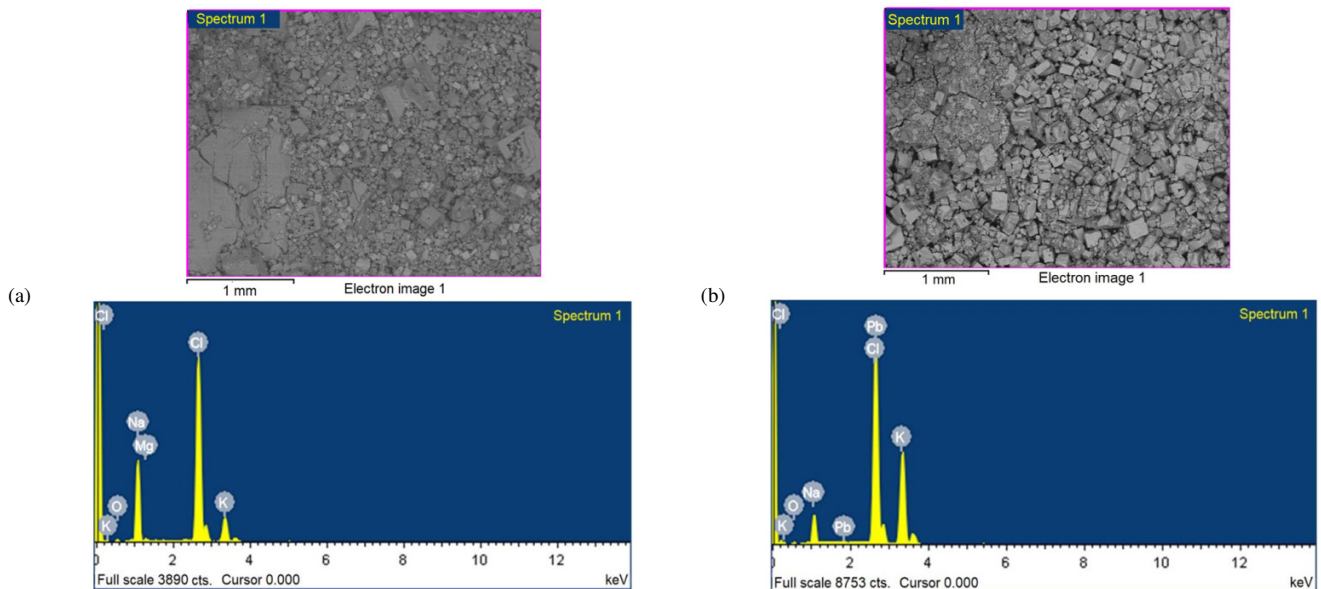


Fig. 5. Micrographs and spectrograms of salts crystallizing at 50% evaporation: (a) after evaporation, (b) after cooling.

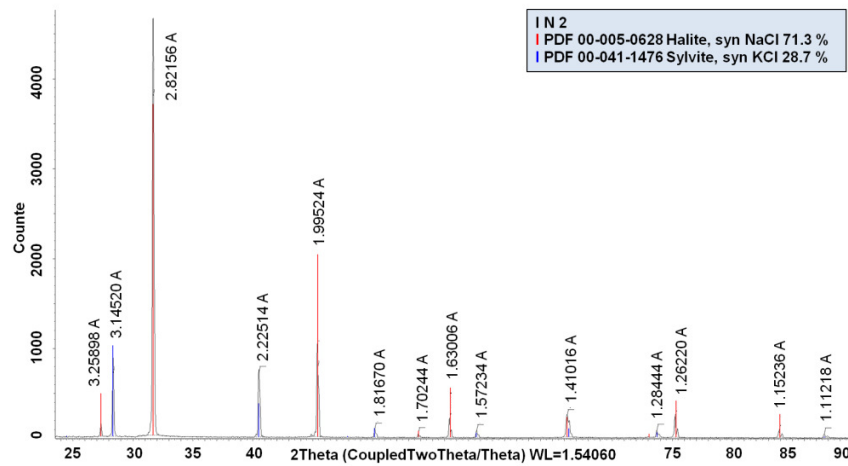


Fig. 6. XRD pattern of potassium-sodium salt obtained at the 2<sup>nd</sup> stage of separation.

The XRD analysis of the solid phase at 30% evaporation confirmed the formation of pure KCl, as shown in Figures 4(a) and 4(b) (stage 1 separation results). After separating KCl crystals at stage 2, the remaining liquor was further evaporated to 50% of its initial volume, obtaining a crystallization of 11.73% K<sup>+</sup>, 27.42% Na<sup>+</sup>, 54.71% Cl<sup>-</sup>, and 0.38% Mg<sup>2+</sup> (Figure 5(a)). In this case, mainly sodium chloride crystallized in accordance with the OK dissolution curve as the system composition point is in the NaCl crystallization field (Figure 2). As a result of the subsequent cooling, an additional amount of salt was crystallized (Table I), which also exhibited a mixed composition of predominantly halite in nature (Figure 5(b)). The crystallized salts were separated from the mother liquor by filtration. The micrographs clearly demonstrated isometric crystals with a cubic habit, which corresponds to halite.

In Figure 6, the XRD analysis of crystallized salts during the second stage of separation displayed a mixed salt of sylvinite composition, containing 71.3% NaCl and 28.7% KCl. Its composition corresponded to the point S on the KCl-NaCl-H<sub>2</sub>O solubility diagram (Figure 2).

The resulted crystallizate was divided into pure salts using the mineral-salt method. To reach the maximum NaCl output into the solid phase, the salt-to-water mass ratio was calculated using the rule of segments based on Figure 2, where ON:NS = 42:35 = 1:0.83. Under these conditions, 24 weight parts of NaCl per 64 weight parts of the mother liquor remained in the solid phase. The mother liquor, which is a diluted KCl solution, can be recycled for leaching the initial ore.

Regarding the liquid phase composition, the content of all ions increased as the solution became more concentrated. Figure 7 illustrates the dependence of ion content in the liquid phase on the evaporation degree. It was observed that the content of K<sup>+</sup> ions decreased significantly as more than half of the solution volume evaporated. This can be attributed to the crystallization of a significant portion of potassium in stages 1 and 2 of salt separation.

It should also be noted that the content of Mg<sup>2+</sup> ions in the solid phase remained practically unchanged in the range of 0-0.68% during all crystallization stages (Table I). Consequently,

only potassium and sodium chlorides were crystallized from the solution during evaporation and subsequent cooling.

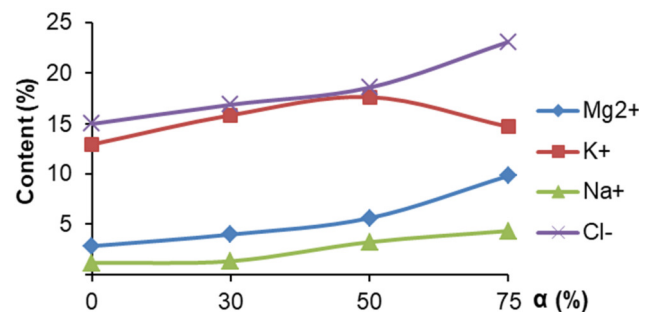


Fig. 7. Dependence of ion content in the liquid phase on the evaporation degree.

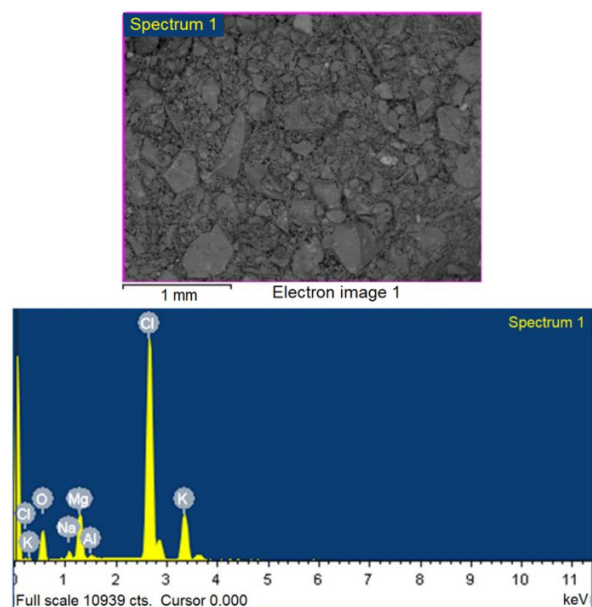


Fig. 8. Micrograph and spectrogram of salt crystallizing upon complete solution drying.

At the last stage of salt separation, the mother liquor was evaporated to 75% of the original volume and the solution was then dried. From Table I (stage No. 3) and the spectrogram (Figure 8), a mixed salt of 8.46%  $Mg^{2+}$ , 28.77%  $K^+$ , 1.01%  $Na^+$ , and 54.85%  $Cl^-$  was crystallized. A micrograph of the sample indicated heterogeneity of the crystal size and surface texture. The obtained product was a double salt  $KCl \cdot MgCl_2$ , with a chemical composition of 34.7%  $K_2O$  and 14.1%  $MgO$ , which is close to the mineral fertilizer Kalimag.

TABLE II. CHEMICAL COMPOSITION OF CRYSTALLINE PRODUCTS

Step	Components	Content in the product (%)			
		$K_2O$	$Na_2O$	$MgO$	$Cl^-$
1	KCl	45.60	-	-	48.91
2	NaCl	-	42.1	0.22	53.70
3	$KCl \cdot MgCl_2$	34.70	1.18	14.10	54.85

The composition of all crystallized salts is presented in Table II. The obtained products from fractional separation were pure salts of NaCl, KCl, and  $KCl \cdot MgCl_2$ , with the last two being water-soluble potassium fertilizers that do not contain sodium chloride.

The possibility of using recycled mother liquor was evaluated in order to minimize the amount of inserted water in the technological process. A comparative analysis of the stage 4 results (Table I) demonstrated that the evaporation of the

mother liquor led to the formation of a more concentrated solution with higher content of sodium and magnesium ions in the solid phase (5.45%  $Na^+$  and 1.40%  $Mg^{2+}$ ). Therefore, to achieve better separation and obtain pure components, it is more appropriate to conduct the process using water without the addition of recycled mother liquor.

Based on the research findings, a flow chart for processing carnallite ore to produce ballast-free potash and potassium-magnesium fertilizers was proposed in Figure 9.

In this process, crushed natural carnallite salt was mixed with wash water at 100 °C to form a solution saturated with potassium. This solution was then evaporated to separate crystals and subjected to additional crystallization upon cooling to 25 °C in a vacuum crystallization unit. The resulting crystal suspension was separated into a crystalline product, potassium chloride, and mother liquor. The separated liquor was subjected to further evaporation according to a similar scheme, followed by cooling and crystallization of the mixed product. The crystallizate was separated using a belt vacuum filter and then processed based on the standard sylvinite separation scheme, deploying the mineral-salt method with crystallization of pure sodium chloride and separation by filtration. The mother liquor underwent further evaporation and drying into a spray dryer to form a mixed salt consisting of potassium and magnesium chlorides.

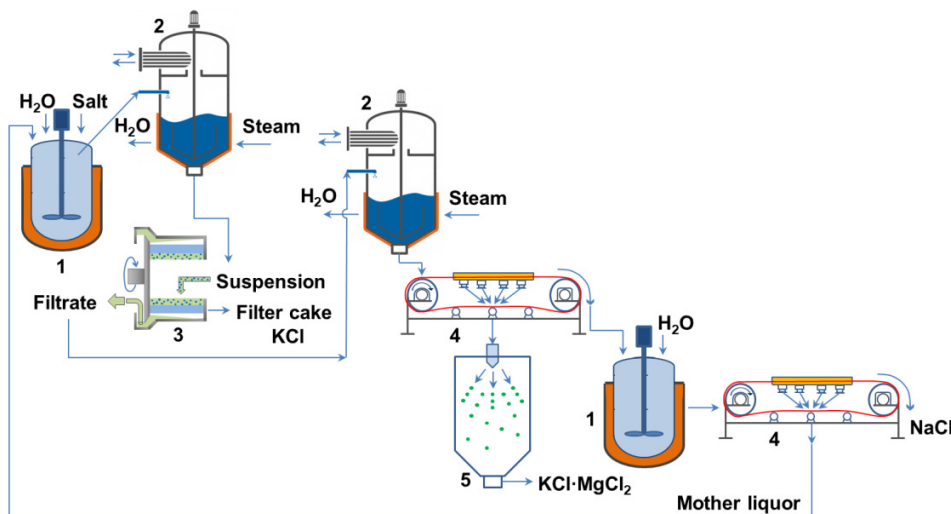


Fig. 9. Potash ore processing flow chart: (1) reactor, (2) crystallization evaporator, (3) centrifuge, (4) vacuum filter, (5) drying chamber.

#### IV. CONCLUSION

The process of fractional separation of carnallite ore from the Zhilyan deposit through gradual evaporation and polythermal crystallization was investigated to produce high-grade potassium mineral fertilizers that do not contain sodium chloride impurities. The proposed method was based on the temperature-dependent solubility differences between potassium and sodium chlorides in water (from 100 °C to 25 °C) with intermediate evaporation of solutions. From the experimental results, the method proved to be quite efficient in separating the individual pure salts KCl and NaCl and in precipitating the double salt  $KCl \cdot MgCl_2$ . X-Ray Diffraction

(XRD) and spectroscopic analysis was utilized for further validation. Based on these findings, a new, sustainable, and cost-effective method for processing potash ores to ballast-free mineral fertilizers has been proposed, allowing the simultaneous recovery of potassium, sodium, and magnesium chlorides in pure form.

#### FUNDING

This research is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP19175404).

## REFERENCES

- [1] "Potassium Salts. World Ranking of Countries." Nedradv. <https://nedradv.ru/nedradv/ru/msr?mp=1&obj=ca79a46078f5785d6a24f2c3830d650f>.
- [2] M. P. Turko, T. I. Kasehob, A. S. Stromskiy, E. M. Miskov, and K. V. Sivtsov, "Development of potash ore enrichment technology Satimola deposit (Republic of Kazakhstan)," *Gornyy Zhurnal*, no. 2, pp. 87–89, 2014.
- [3] W. Chen, Y. Geng, J. Hong, D. Yang, and X. Ma, "Life cycle assessment of potash fertilizer production in China," *Resources, Conservation and Recycling*, vol. 138, pp. 238–245, Nov. 2018, <https://doi.org/10.1016/j.resconrec.2018.07.028>.
- [4] M. M. E. Ali *et al.*, "Plant Growth, Yield and Quality of Potato Crop in Relation to Potassium Fertilization," *Agronomy*, vol. 11, no. 4, Apr. 2021, Art. no. 675, <https://doi.org/10.3390/agronomy11040675>.
- [5] "Enrichment of potash ores," Metallolome.ru. <https://metallolome.ru/obogashhenie-kalijnyh-rud/>.
- [6] I. Petropavlovsky, B. Dmitrevsky, B. Levin, and I. Pochitalkina, *Mineral Fertilizer Technology*, Saint Petersburg, Russia: Prospekt Nauki Press, 2018.
- [7] A. Paskina, S. Aliferova, S. Titkov, and N. Yakovleva, "Method of Obtaining Enriched Carnallite," RU Patent 2701609, Sep. 30, 2019.
- [8] V. Marakov and A. Zarubin, "Systems and Methods for Processing Sylvinit and Carnallite Ores," RU Patent 9227849, Jan. 5, 2016.
- [9] N. P. Krutko, V. V. Shevchuk, A. D. Smychnik, and T. N. Potkina, "Cold Decomposition of Carnallite Ores," *Proceedings of the National Academy of Sciences of Belarus, Chemical Series*, vol. 54, no. 2, pp. 231–237, Jun. 2018, <https://doi.org/10.29235/1561-8331-2018-54-2-231-237>.
- [10] T. Shakirov, "Research of leaching processes in the technology of producing potassium fertilizers from carnallite rocks," *Bulletin of the Technological University*, vol. 25, no. 6, pp. 54–57, 2022.
- [11] H. D. Cheng *et al.*, "Implications for the origin of secondary sylvite from a simulation of carnallite dissolution," *Journal of Geochemical Exploration*, vol. 165, pp. 189–198, Jun. 2016, <https://doi.org/10.1016/j.gexplo.2016.03.016>.
- [12] David, "Carnallite & Sylvinit Ore - Potash Flotation," *911Metallurgist*, Aug. 16, 2017. <https://www.911metallurgist.com/blog/carnallite-sylvinit-ore-potash-flotation/>.
- [13] X. Yu, Z. Fu, Y. Ma, C. Li, S. Zhang, and Z. Zhang, "Polyethylene glycol regulated carnallite decomposition-crystallization: Experimental and theoretical analysis," *Minerals Engineering*, vol. 195, Apr. 2023, Art. no. 108021, <https://doi.org/10.1016/j.mineng.2023.108021>.
- [14] J. A. Tavares, L. F. Moura, A. Bernardo, and M. Giulietti, "Crystallization and separation of KCl from carnallite ore: Process development, simulation, and economic feasibility," *Chemical Industry and Chemical Engineering Quarterly*, vol. 24, no. 3, pp. 239–249, 2018, <https://doi.org/10.2298/CICEQ170119036T>.
- [15] G. A. Fortunatov, N. F. Krasiuk, A. N. Zemskov, and O. V. Ivanov, "Gas Content of Saliferous Rocks of Potassium Deposits Zhilianskoe and Satimola (Kazakhstan)," *Perm Journal of Petroleum and Mining Engineering*, no. 11, pp. 88–98, Dec. 2014.
- [16] A. Konoplev, R. Iblaminov and I. Kopylov, "Engineering-geological conditions of the Zhilyanskoe potassium deposit (Kazakhstan)," *Modern Problems of Science and Education*, no. 5, 2014.
- [17] "Kazakhstan Potash Company Begins Exploration of Potash Deposits in Western Kazakhstan," *Qazgeology*. <https://qazgeology.kz/kazakhstan-potash-company-%D0%BF%D1%80%D0%B8%D1%81%D1%82%D1%83%D0%BF%D0%B0%D0%B5%D1%82-%D0%BA-%D1%80%D0%B0%D0%B7%D0%B2%D0%B5%D0%B4%D0%BA%D0%B5-%D0%BA%D0%B0%D0%BB%D0%B8%D0%B9%D0%BD%D1%8B%D1%85-%D0%BC/>.
- [18] G. Seitmagzimova, A. Assylkhankyzy, A. Kadyrbaeva, and R. Abisheva, "Analysis of the enrichment process of natural potassium salts," *Rasayan Journal of Chemistry*, vol. 15, no. 1, pp. 586–592, 2022.
- [19] Y. Kassem, H. Camur, and E. G. Ghoshouni, "Assessment of a Hybrid (Wind-Solar) System at High-Altitude Agriculture Regions for achieving Sustainable Development Goals," *Engineering, Technology & Applied Science Research*, vol. 14, no. 1, pp. 12595–12607, Feb. 2024, <https://doi.org/10.48084/etasr.6494>.
- [20] A. Assylkhankyzy and G. Seitmagzimova, "Advanced technologies of potash fertiliser production from promising raw materials," *The Open Chemical Engineering Journal*, vol. 18, Sep. 2024, <http://doi.org/10.2174/0118741231330310240906080722>.
- [21] M. Pozin, *Technology of Mineral Fertilizers*, Leningrad, Russia: Chemistry, 1989.